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PREFACE

The gasification of carbon has been the subject of numerous investigations over a long period of time. The first part of this thesis deals with the kinetics of the reaction of thin films of pyrolytic carbon with oxygen with particular emphasis on the role of the surface oxygen complex in the mechanism. In the second part, a new technique is described for quantitative measurement of the conditions of reactant concentration at ignition in mixtures of carbon monoxide and oxygen. The third part is concerned with the effect of water vapour and of inert gas on the kinetics of the carbon-oxygen reaction.

Some of the work described in this thesis has been published as follows:

1. The Role of the Surface Complex in the Kinetics of the Reaction of Oxygen with Carbon, S. Ahmed and M.H. Back, Carbon 23, 513-524 (1985).
2. Kinetics and Mechanism of the Explosive Reaction of Carbon Monoxide and Oxygen, S. Ahmed and M.H. Back, Int. J. Chem. Kinet. 18, 181-203 (1986).
3. The Explosive Reaction of Carbon Monoxide and Oxygen at 973 and 1048 K, S. Ahmed and M.H. Back, Int. J. Chem. Kinet., in press.

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With deep respect and gratitude I wish to thank my parents for their support and good wishes during my stay in Ottawa.

Last but not least, I would like to thank my wife Yasmin for her encouragement, patience and understanding during the course of my studies.

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ABSTRACT

The kinetics of the reaction of molecular oxygen with carbon was studied in a static system over the temperature range 748-1173 K at pressures in the neighbourhood of 1 Torr. Carbon was obtained as a thin film on the surface of a quartz reactor by pyrolyzing methane at 1223 K. The active surface area of the carbon film was measured by saturating the active sites with the surface oxygen complex by chemisorption of oxygen at 673 K, followed by temperature-programmed desorption to 1223 K for recovery of the complex as carbon monoxide and carbon dioxide. The activation energy for desorption of the complex was about 65 kcal mol^{-1}. The amount of carbon on the surface was monitored during the course of the reaction from the attenuation of the light beam from a He-Ne laser. The rates of formation of carbon monoxide and carbon dioxide were obtained from the measurement of the total pressure in the reaction system.

At temperatures below 900 K an induction period was observed in the formation of carbon dioxide, the only product of the reaction in this region of temperature, but no induction period was observed in the formation of adsorbed oxygen and the surface complex. The rate of oxidation of the carbon film was measured in the presence and absence of the complex on the surface before the commencement of the reaction. The presence of the complex shortened the induction period and increased slightly the rate of gasification. It was concluded that the surface complex was an intermediate in the oxidation process.

ABSTRACT (Continued)

At higher temperatures carbon monoxide became an important product and the activation energy for its formation, about 70 kcal mol^{-1}, was in agreement with that obtained for the desorption of the surface complex as carbon monoxide. The activation energy for the formation of carbon dioxide, about 40 kcal mol^{-1}, was considerably lower.

A mechanism for the reaction was proposed, involving secondary interaction of oxygen with the complex, which accounted qualitatively for the kinetics of the reaction. A turnover number defined as,

$$\frac{\text{rate of gasification of carbon}}{\text{number of active carbon atoms}}$$

was calculated from the present measurements and from measurements reported by other authors. This method of comparison gave better agreement among data reported in the literature.

At temperatures above 900 K and pressures in the range 15-150 Torr, an explosive reaction between oxygen and the product carbon monoxide occurred under certain conditions. It was shown that traces of hydrogen in the carbon film, which continuously formed a small yield of water during the gasification, played a key role in the development of explosive conditions. Explosions occurred with ratios of CO/O_2 as low as 5×10^{-3} far below those hitherto explored. Explosion was promoted by the addition of hydrogen, methane and water to the reactants. The addition of inert gas inhibited explosion at temperatures below 935 K but promoted explosion above about 1000 K. A simple mechanism accounted quantitatively for the occurrence of explosions over a wide range of

ABSTRACT (Continued)

temperature, total pressure and composition of reactants. Because the film of carbon provided a reproducible surface for termination of radicals, a quantitative description of the conditions at explosion in the region of the first limit was obtained. The results also showed that during the oxidation water vapour can have an important effect through gas-phase reactions; the results of previous studies on the effect of water vapour had been interpreted entirely in terms of processes occurring on the carbon surface.

PART I

KINETICS OF THE REACTION OF OXYGEN WITH CARBON AND THE ROLE OF THE SURFACE COMPLEX

CHAPTER 1

INTRODUCTION

The reaction of carbon with molecular oxygen has been of great interest to chemists for many decades [1-3]. The reaction is of considerable significance to many industrial processes, such as combustion reactions, reactions occurring in flames and corrosion of the graphite components in the High-Temperature Gas-Cooled Reactor (HTGR). It is also important from a fundamental point of view, since it provides an example of a gas-solid reaction where the products are entirely gaseous. Despite numerous studies, however, it must be acknowledged that the mechanism of the reaction, in terms of elementary surface processes of adsorption, migration, rearrangement, dissociation and desorption, is not understood in detail.

The term 'carbon' covers a wide variety of carbonaceous materials ranging from carbon black (soot like materials) to single-crystal graphite. It may be assumed that in all carbonaceous substances (excluding diamond), carbon atoms are arranged in hexagonal rings with Π-bonds and these rings are linked together to form what Marsh [1] called the lamellar constituent molecules of carbon. Thus a carbon surface consists of basal planes terminating in "zig-zag" and "arm-chair" edge sites (Figure 1.1). Hennig [4,5], Thomas [6] and Evans, Griffiths and Thomas [7], using optical and electron microscopies, have shown that during the oxidation of single-crystals of graphite with oxygen, edge or peripheral carbon atoms (possessing unpaired sp^2 electrons) are more readily attacked than the basal surface, which reacts only from lattice defects such as atomic vacancies and screw dislocations.

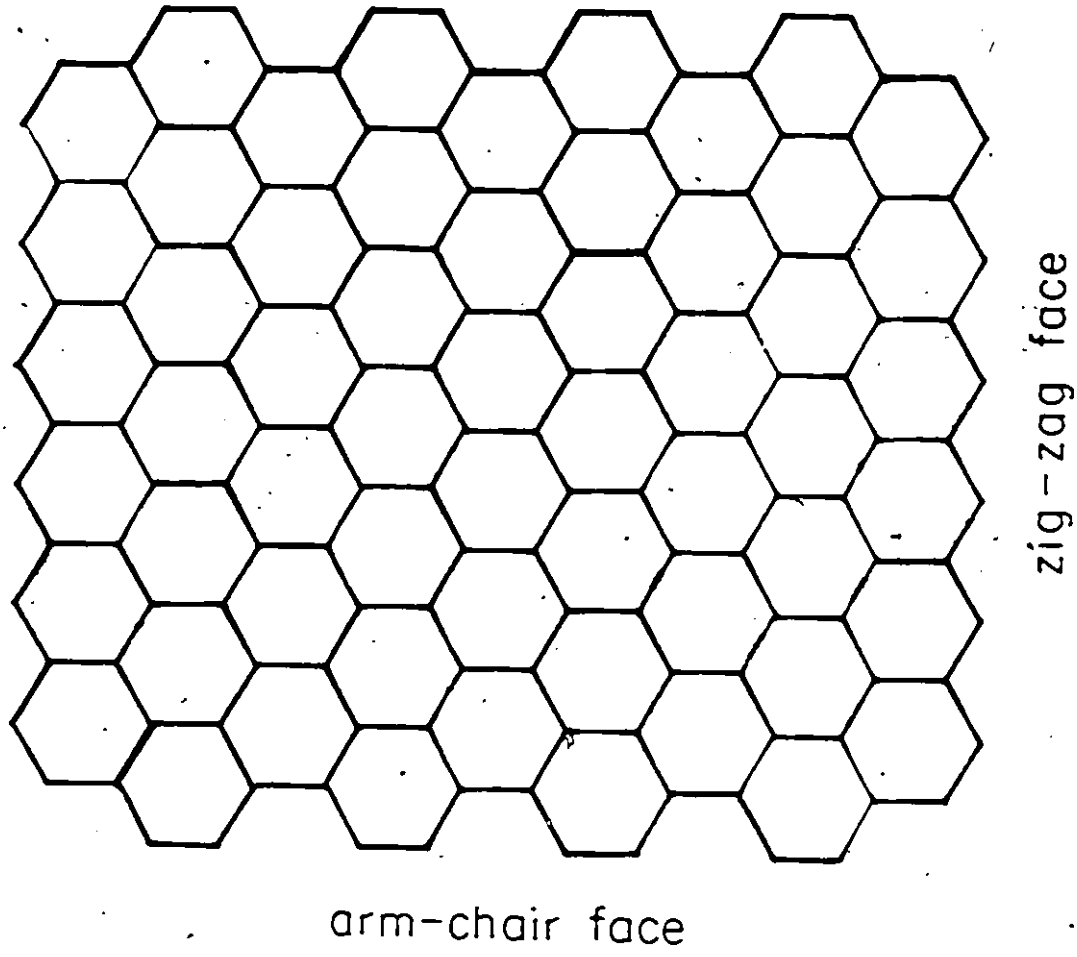


Figure 1.1. Illustration of the "arm-chair" and "zig-zag" configurations of the carbon layer edge.

Chemisorption of oxygen on carbon forms a strongly-bound complex or surface oxide at the reactive edges of the basal planes [8], and may form various functional groups, for example, carboxyl, carbonyl, lactone and phenol [9-14]. These complexes also form during the gasification reaction and one of the main concerns of chemists engaged in studies of carbon is to establish the role of these complexes in the over-all gasification process.

The properties of surface oxides have been investigated by various techniques. Hennig [4] and Thomas [6] have found that the two types of edge sites undergo oxidation at different rates. Thus, the same functional group attached to a "zig-zag" and an "arm-chair" carbon atom is energetically different. Therefore, variations in the binding energies of surface complexes on a carbon surface may arise both from the differences in the nature of functional groups and in the surface energy characteristics of the parent carbon. Each class of the energetically dissimilar surface species may be regarded as a kinetic species [15].

The characteristics of these surface complexes have often been explored by chemisorption-desorption studies [15-23]. During the process of thermal desorption, the oxygen is released directly from the surface as carbon monoxide and carbon dioxide [24-26]. Tremblay, Vastola and Walker [15] have critically examined the results of these studies. When the desorption was performed in a series of isothermal stages at successively higher temperatures (step-TPD) [16-19], the results indicated the existence of one kinetic species with the energy of desorption being a continuous function (either linear or Gaussian) of the surface coverage. This behaviour is consistent with Elovich-type

desorption. On the other hand, when the desorption of products was monitored by linear temperature-programmed desorption (linear-TPD) [15,20-23], the existence of multiple kinetic species was indicated. In an attempt to rationalize this discrepancy between the results of the two techniques, these authors suggested that the differences in energy among the various kinetic species may not be sufficiently large (perhaps 0-10 kcal mol^{-1}) to be resolved by step-TPD with its relatively large temperature increments.

Attempts to characterize the surface oxygen complexes were also made by spectroscopic measurements [27-33] and by chemical analysis [11,34,35]. Infrared spectroscopic techniques [27-30] have been used to examine the chemical structure of the surface functional groups on carbons. These studies have indicated the presence of carboxylates, lactones, phenols and quinone type carbonyls on oxidized carbon. X-ray photoelectron spectroscopy, which permits the measurement of binding energies of core electrons, was employed to determine the binding energies of the oxygen 1s electrons of the surface complex [31,32]. It was possible to identify more than a single oxygen 1s peak on oxidized carbon surface indicating the existence of more than one species of complex, in agreement with thermal desorption studies.

A method to measure the extent of carbon edge surface, which is widely used today, was developed by Laine, Vastola and Walker [36,37], based on the conclusion that the complex forms at the edge carbon atoms. The method involves saturation of these edge sites with oxygen complexes by exposure to oxygen at about 673 K for a prolonged period. The amount of complex formed is measured by its recovery as carbon monoxide and

carbon dioxide by thermal desorption to 1223 K. Each oxygen atom in the desorbed product was assumed to have come from one surface complex. By further assuming that the complex consists of one oxygen atom per edge carbon atom and that each edge carbon atom occupies an area of 0.083 nm^2, the amount of complex formed on the surface can be converted to an area, called the Active Surface Area, and designated ASA. This description of the number of active sites as an area allowed comparison with the total surface area of the carbon.

Laine et al. [36,37] have stressed the importance of the active surface area of the carbon surface in the kinetics of the gasification process. From studies of the reaction of oxygen with thin films of carbon Tong, Pareja and Back [38] have demonstrated the dependence of the rate of oxidation of a carbon surface on its ASA. They observed that, with changes in the amount of carbon in the film, the ASA also changed and this was accompanied by a corresponding change in the reactivity of the carbon. Interestingly, they observed a maximum in the ASA with increasing thickness of the carbon film and this maximum correlated closely with the maximum in reactivity.

One major area of experimental investigation into the kinetics of the carbon-oxygen reaction involves the measurement of total rates of oxidation, individual rates of formation of products, carbon monoxide and carbon dioxide, the temperature coefficient of these rates to obtain the apparent activation energies and the order of the rate of the reaction with respect to oxygen pressure. Unfortunately, wide variations in each of these kinetic parameters have been reported. Several authors, including Moorman, Anhalt, Ashworth, Hinseen and Katscher [39], Tyler,

Wouterlood and Mulcahy [40], and Ong [41] have summarized the existing data and attempted to account for the observed variations. The wide disagreement among the reported values can be largely accounted for by differences in the impurity content (particularly metallic impurities), surface area, method of preparation and pre-treatment procedure of the carbon, in gaseous impurites (particularly hydrogeneous substances) in oxygen, in the techniques employed and in the conditions of reaction, including temperature and pressure.

A key question in understanding the complexities of this reaction is the effect of the surface complex on the mechanism of the reaction. While it has been realized that the mechanism should be related to the formation and decomposition of the complex, its precise role has been difficult to define. Some results on this aspect of the carbon-oxygen reaction have been reviewed by Boehm and Bewer [42]. Without doubt, most of the studies on this question have been done by Walker and his associates [11,36,37,43-48] and yet their investigations were limited mainly to one form of carbon, Graphon, which is a graphitized carbon black. They interpreted their kinetic data to indicate that the formation of the stable surface oxygen complex actually inhibits the gasification process by blocking a portion of the ASA. They suggested that the gasification occurred through what they called a 'reactive surface oxygen complex' intermediate. Bonnetain and co-workers [49-52], however, from their experiments on synthetic graphites concluded that the gasification with oxygen proceeds by continuous formation and decomposition of a surface oxide intermediate.

The effect of the complex on the reaction is difficult to test experimentally. As the gasification proceeds the carbon atoms from the surface of carbon are removed thus altering the physical and electronic features of the carbon surface. This would, in turn, affect the binding energies of surface complexes. Thus during the oxidation reaction complexes with a range of binding energies and different degrees of mobility are present on the carbon surface [53,54]. Furthermore, reaction conditions such as temperature and pressure would affect the amount of complex on the surface through their effects on the rates of formation and desorption of the complex. On the whole, the interaction of the complex with the surface and with the oxidizing gas represents a complex system, which has led to many apparently contradictory results and interpretations.

1.1 Outline of the present study

Recently, a technique suited to the kinetic study of reactions of carbon with gaseous reactants has been developed in this laboratory [55]. Carbon is produced as a thin film covering the surface of a reaction vessel by pyrolysis of a hydrocarbon under suitable conditions of temperature and pressure. The kinetics of the reaction of the carbon with the gaseous reactant is followed by continuous monitoring of the optical density of the film using a He-Ne laser as light source.

This part of the thesis describes a study of the kinetics of the reaction of carbon, obtained by the procedure indicated above, with molecular oxygen, with particular attention to the role played by the surface oxygen complex in the mechanism. Measurements of the time course

of the reaction under a variety of carefully defined conditions, in conjunction with measurements of the ASA of the carbon and the amount of strongly-bound complex retained on the surface at various stages of the reaction, constitute important parts of the present work. The reaction was studied in a static system in which pyrolytic carbon was obtained by decomposition of methane as a thin film of high purity. From the results of the present investigation, the complex has been shown to play an important role in the oxidation process through participation in several concurrent and consecutive surface processes. The relative significances of these processes depend on several factors but most importantly on the pressure of oxygen. A mechanism for these processes is suggested which accounts for some of the differences in interpretation of previous results. The results obtained with this pyrolytic carbon will be compared with those obtained with other types of carbon.

CHAPTER 2

EXPERIMENTAL

2.1 Apparatus

The kinetics of the reaction was studied in a conventional static vacuum system. The main features of the apparatus are shown schematically in Figures 2.1A and 2.1B. The gas storage and measuring system, and the gas burette and Töpler pump assembly for collection and sampling of products for gas chromatographic analysis are included in Figure 2.1A. The section of the apparatus incorporating the reaction vessel and pressure transducers is shown in Figure 2.1B, which also includes the optical arrangement for measuring the amount of carbon on the surface of the reaction vessel. The entire system could be evacuated to about 10^{-6} Torr using mercury diffusion pumps in conjunction with standard mechanical pumps.

The reaction vessel was a quartz cylinder with plane windows sealed at a small angle to the axis. The dimensions were: internal diameter, 4.35 cm; lengths, 10.8 and 9.3 cm. The volume was 149 cm^3 and the surface area 167 cm^2. The vessel was cleaned ultrasonically and was positioned in the centre of a horizontal tubular furnace equipped with a power supply and a temperature controller unit. The temperature was maintained within $\pm$ 1 K along with the length of the vessel and was measured by a chromel-alumel thermocouple in conjunction with a digital thermometer.

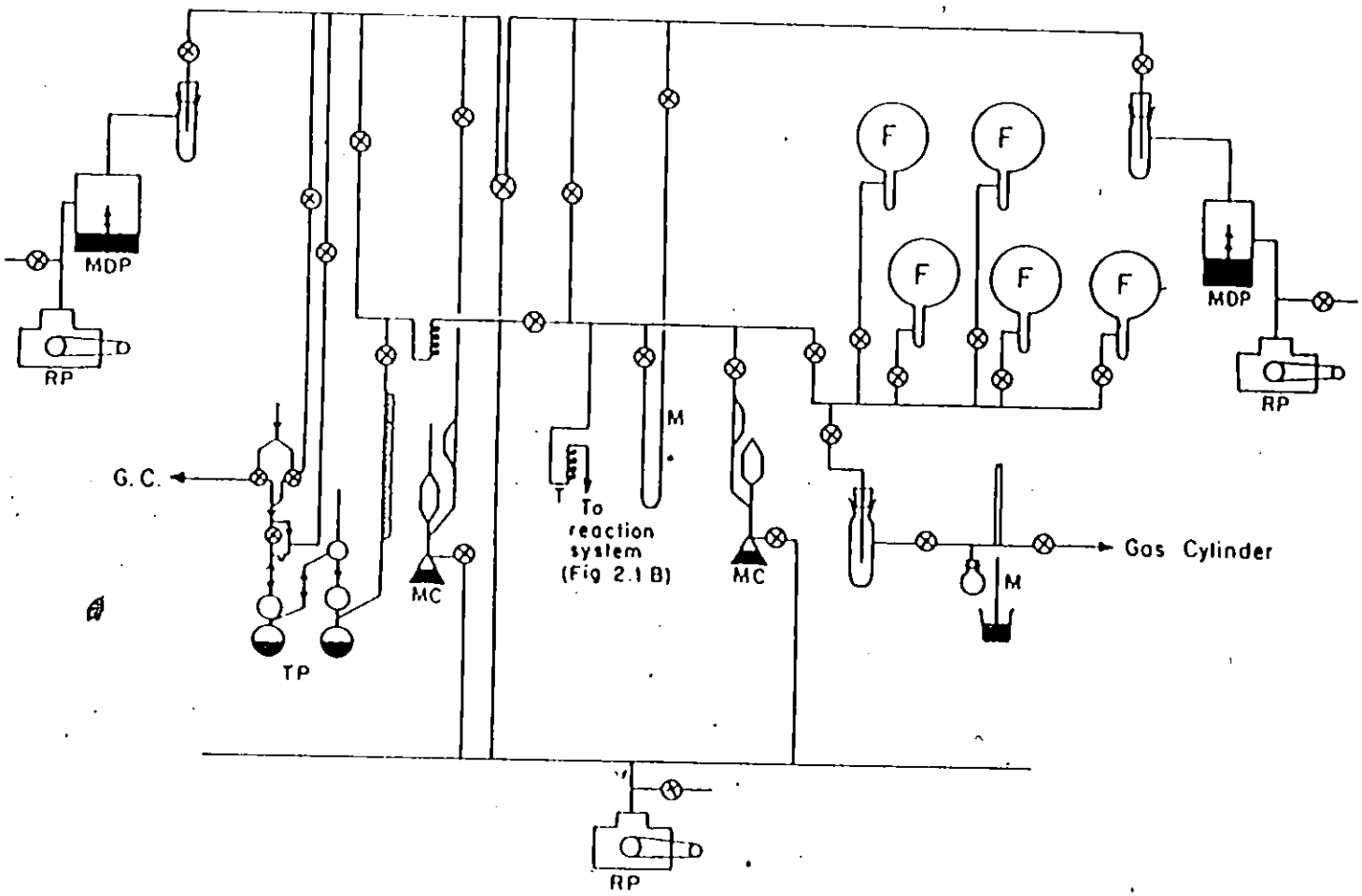


Figure 2.1A. Schematic diagram of the apparatus.

R.P: Rotary pump; MDP: Mercury diffusion pump;
M.C: McLeod gauge; F: Flask; T: Spiral trap;
G.C: Gas chromatography (Carle Microdetector, Model 100);
T.P: Töpler pump assembly.

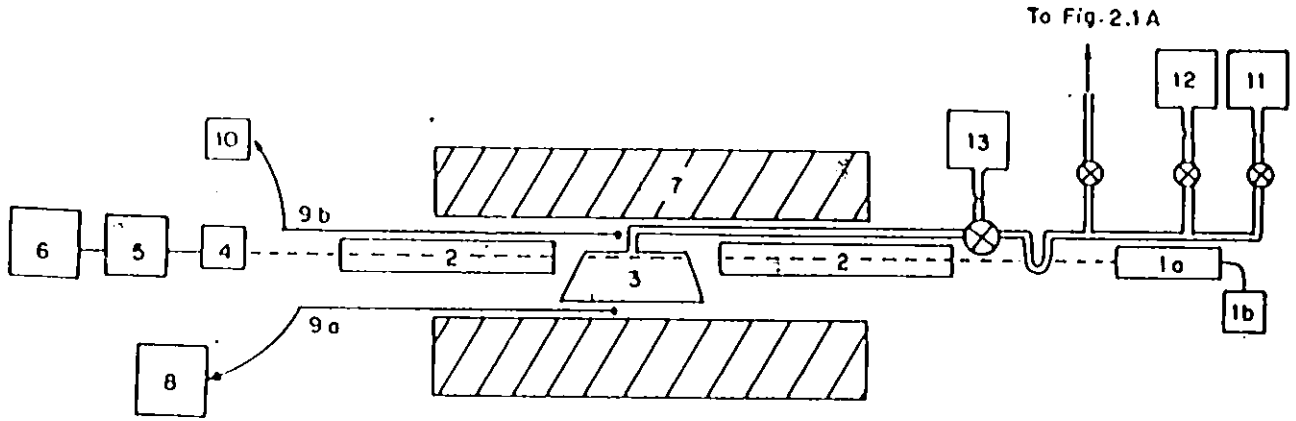


Figure 2.1B. Schematic diagram of the reaction vessel, the manifold with pressure transducers and the arrangement for measuring optical absorbance of the carbon film.

1a: 1 mW He-Ne laser head (Melles Griot 05-LHP-111 model);
1b: He-Ne laser power supply unit (Melles Griot 05-LPL-340 model);
2: Evacuated cylinder; 3: Quartz reaction vessel;
4: Photodiode; 5: Keithley Electrometer (600 A);
6: Recorder (Sargent model SRLG); 7: Furnace (Autoclave Engineers Inc.);
8: Furnace power supply and Temperature controller unit (Autoclave Engineers Inc.); 9a: Regulating thermocouple;
9b: Measuring thermocouple; 10: Digital thermometer (Wahl);
11: Pressure transducer (1 Torr maximum, MKS Baratron 227A);
12: Pressure transducer (10 Torr maximum, MKS Baratron 222A);
13: Pressure transducer (1000 Torr maximum, MKS Baratron 223B).

The reactor was connected to a manifold containing two pressure transducers with full scale ranges of 1 Torr and 10 Torr. The gauges were capable of measuring four decades of pressures. The volume of the manifold was about 70 cm^3.

2.2 Materials

Research grade methane, with a stated minimum purity of 99.99% was obtained from Matheson Gas Products Canada, Whitby, Ontario. Industrial high purity grade oxygen (purity 99.6%) was supplied by Air Products and Chemicals, Inc. Carbon monoxide (C.P. grade, purity 99.5%+) and carbon dioxide (purity 99.99%+) used for calibrations were obtained from Matheson Gas Products Canada, Whitby, Ontario and Union Carbide Canada Limited, Toronto respectively.

2.3 Preparation and analysis of the carbon film

Thin films of high purity carbon were deposited on the surface of the reaction vessel by pyrolysis of 45 Torr of methane at 1223 K. Before admission to the vessel the gas was passed through a spiral trap at 195 K to remove mercury or water vapour. The amount of carbon in the film was measured by the attenuation of the beam of a 1 mW He-Ne laser passed axially through the vessel. The signal was detected with a photodiode and Keithley Electrometer. In order to suppress convection currents caused by temperature gradients, which could distort the beam, each end of the furnace was plugged with an evacuated cylinder. The attenuation of the beam was correlated with the amount of carbon in the film by complete combustion of carbon to carbon dioxide at 1100 K with pressures

of oxygen in the range 80-300 Torr. The carbon film acted as a neutral density filter and the absorbance, $\log(I_0/I_t)$ was a linear function of the total amount of carbon in the film. From this relation an apparent extinction coefficient of 2.2×10^6 cm^2 mol^{-1} or 1.8×10^5 cm^2 g^{-1} was calculated. Note that this extinction coefficient correlates with an amount of carbon per unit area of surface and does not include a path length for absorption [55]. Most of the experiments described in this part of the thesis were performed with films with a concentration of carbon of about 2×10^{-7} mol cm^{-2}. This corresponds to an average thickness of 13 nm assuming a uniform deposit and a density of carbon of 1.9 g cm^{-3} [56,57].

After formation the films were outgassed at 1223 K for 1½ hours to a residual pressure of 10^{-5} Torr. This treatment was found to reduce evolution of hydrogen from the film to a negligible amount. Prolonged heat treatment slowly reduced the activity of the film. The carbon films produced in this manner were free of metallic or inorganic impurities and were not exposed to air or water vapour. Previous studies in this laboratory on the measurement of the surface area of the film relative to that of the quartz vessel showed that the ratio of the areas was close to unity for films less than about 50 nm in thickness [38]. It may therefore be assumed that these films are practically free of pores of appreciable sizes. Indeed, other studies [3,58] also suggest that pyrolytic carbons obtained by decomposition of hydrocarbons are usually of very low porosity. Examination of these films by electron microscopy (at the magnification of 10K) indicated no details or features at concentrations used in the present study [59].

2.4 Temperature-programmed desorption of the surface complex

After the deposition and treatment as described above, the carbon film was cooled under vacuum to 673 K. Oxygen was dried by passage through a trap at 195 K (dry ice and acetone) and was allowed to chemisorb on the carbon film at a specified temperature and pressure. The system was then evacuated to a pressure of about 10^{-6} Torr. Adsorption with an oxygen pressure of 300 Torr at 625-673 K for about 15 hours was found to saturate the active sites with oxygen complexes. Equilibration with oxygen for longer periods did not change the extent of chemisorption appreciably but a slow gasification occurred. For measurement of the total ASA, the experimental conditions, in terms of temperature, pressure of oxygen and time, were always chosen to adsorb the maximum quantity of oxygen without causing gasification since the latter process may change the total number of active sites [36,37].

After adsorption and evacuation, the temperature of the furnace was allowed to fall to 473 K. The temperature was then raised to about 1223 K at a rate of 5^{o} min^{-1}. Linear programming of the furnace temperature was accomplished using the control unit of a Differential Thermal Analyser (Fisher Scientific Inc., Model 260 P). The purpose of the drop in temperature to 473 K was to achieve a steady rate of increase in temperature before appreciable desorption began. As mentioned earlier, the surface oxygen complexes desorb to give carbon monoxide and carbon dioxide. In the present investigation, carbon dioxide was condensed in a liquid nitrogen trap and the desorption of carbon monoxide was followed by measuring the increase in pressure in the system. The Baratron pressure transducer with full scale range of 1 Torr was used to monitor

the pressure. In most of the experiments the final pressure of carbon monoxide was in the range 0.01-0.1 Torr. These pressures were measured with the Baratron gauge on the range where a pressure of 0.01 Torr corresponded to a reading of .100 ± .001 volt and could therefore be measured with an accuracy of ± 1%. Because of other factors, however, such as non-uniformity in temperatures during TPD and zero adjustment of the gauge, the uncertainty in the measurement of pressure was probably much greater than ± 1%.

At the end of the desorption, the total amount of both desorption products was obtained by gas chromatographic analysis (described in the following section). The agreement between the pressure measurement and the analysis of carbon monoxide was within ± 5%. The ASA of each film used in subsequent measurements was measured in this manner. The ASA was a reproducible quantity for films prepared as described.

2.5 Kinetic measurements

The course of the reaction with oxygen was monitored continuously as the loss of carbon, from the absorbance of the film, and as the formation of carbon monoxide from the change in total pressure in the system. At the end of the reaction, an aliquot of the reactant and products was transferred to the gas sampler by the Töpler pump assembly and analyzed with a Carle Microdetector consisting of a thermistor detector and a bridge circuit. Carbon monoxide and oxygen were analyzed using a molecular sieve column (250 x 6 mm) at 273 K and carbon dioxide using a Porapak T column (230 x 6 mm) at 295 K. The carbon and oxygen balance as

well as the yields of carbon monoxide and carbon dioxide measured by optical absorbance and pressure change were thus verified. Agreement was within 5%.

Since the reaction volume consisted of considerable dead space, it was desirable to confirm that the mixing of the reactant and products between the dead volume and the reaction vessel was rapid compared to the rate of the reaction under the conditions of the present study. Reaction was allowed to proceed at 923 K where carbon dioxide was the only product of the reaction (Chapter 3). The composition of the mixture in the dead space, as a function of time, was determined by gas chromatographic analysis, using a sample small enough not to alter the total pressure appreciably. At the same time the rate of production of carbon dioxide was measured by the loss of carbon from the surface. The composition of the product mixture, calculated assuming rapid mixing of the reactant and product, agreed well with the analysis of the aliquot samples. That good mixing was achieved was further verified after installation of the 1000 Torr Baratron pressure transducer in the system which reduced the dead volume to 10 cm^3 (described in Part II). The reaction at 1048 K with 1 Torr of initial pressure of oxygen, where both carbon monoxide and carbon dioxide were produced in significant amounts, was repeated with this reduced dead volume. The time course of the reaction with respect to the consumption of carbon as well as the formation of products was, except towards the latter stages, in excellent agreement in two cases.

CHAPTER 3

RESULTS

The present chapter describes the results of three types of experiments:

1. Measurements of the decomposition of the complex on the surface by temperature-programmed desorption.
2. Measurements of the rate of removal of carbon from the surface and of the rate of formation of products from the reaction with oxygen at pressures in the neighbourhood of 1 Torr.
3. Comparison of the kinetics of the reaction in the presence and absence of the strongly-bound complex on the carbon surface at the beginning of the reaction.

3.1 Decomposition of the surface oxygen complex by temperature-programmed desorption (TPD)

Three series of experiments were done using films containing approximately the same amount of carbon (2×10^{-7} mol cm^{-2}).

In the first series, the surface was covered with different amounts of oxygen complex. This was achieved by adjusting the time for adsorption and the pressure of oxygen over the range 15-60 hour and 30-300 Torr respectively, keeping the temperature of adsorption constant at 673 K. For each experiment a new film was used and conditions were so chosen that no gasification (loss of carbon) occurred during adsorption. For example, with 300 Torr of oxygen periods of adsorption were kept below 15 hours, whereas longer times were allowed with lower pressures.

The recovery of the complex as carbon monoxide and carbon dioxide was followed by linear temperature-programmed desorption, as described earlier in Section 2.4. In all experiments, the rate of evolution of carbon monoxide gave one well-defined peak. A typical example is given in Figure 3.1.

If S-CO represents a surface species which would give carbon monoxide on thermal desorption then, d[CO]/dt, the rate of appearance of carbon monoxide may be expressed using the Arrhenius relation as follows,

$$d[CO]/dt = A[S\text{-}CO]^n \exp(-E_d/RT) \qquad (3.1)$$

where A is the frequency factor for the dissociation, n the reaction order, E_d the activation energy for desorption, R the universal gas constant and T the absolute temperature. The decomposition of adsorbed species is usually considered as a first-order unimolecular fission [60,61]. For such a first-order desorption process (n=1), when E_d and A are independent of the adsorbate concentration, equation (3.1) reduces to [62]

$$E_d/RT_m = \ln(A/b) + \ln[T_m/\ln(A/b)] \qquad (3.2)$$

where T_m is the temperature at the maximum rate of desorption and b the heating rate. Therefore, when A is known, E_d may be obtained from experimental determination of T_m. Previous workers [63] have assumed a value of 5×10^{12} s^{-1} for A, as a reasonable value for a bond-fission process involving an adsorbed species.

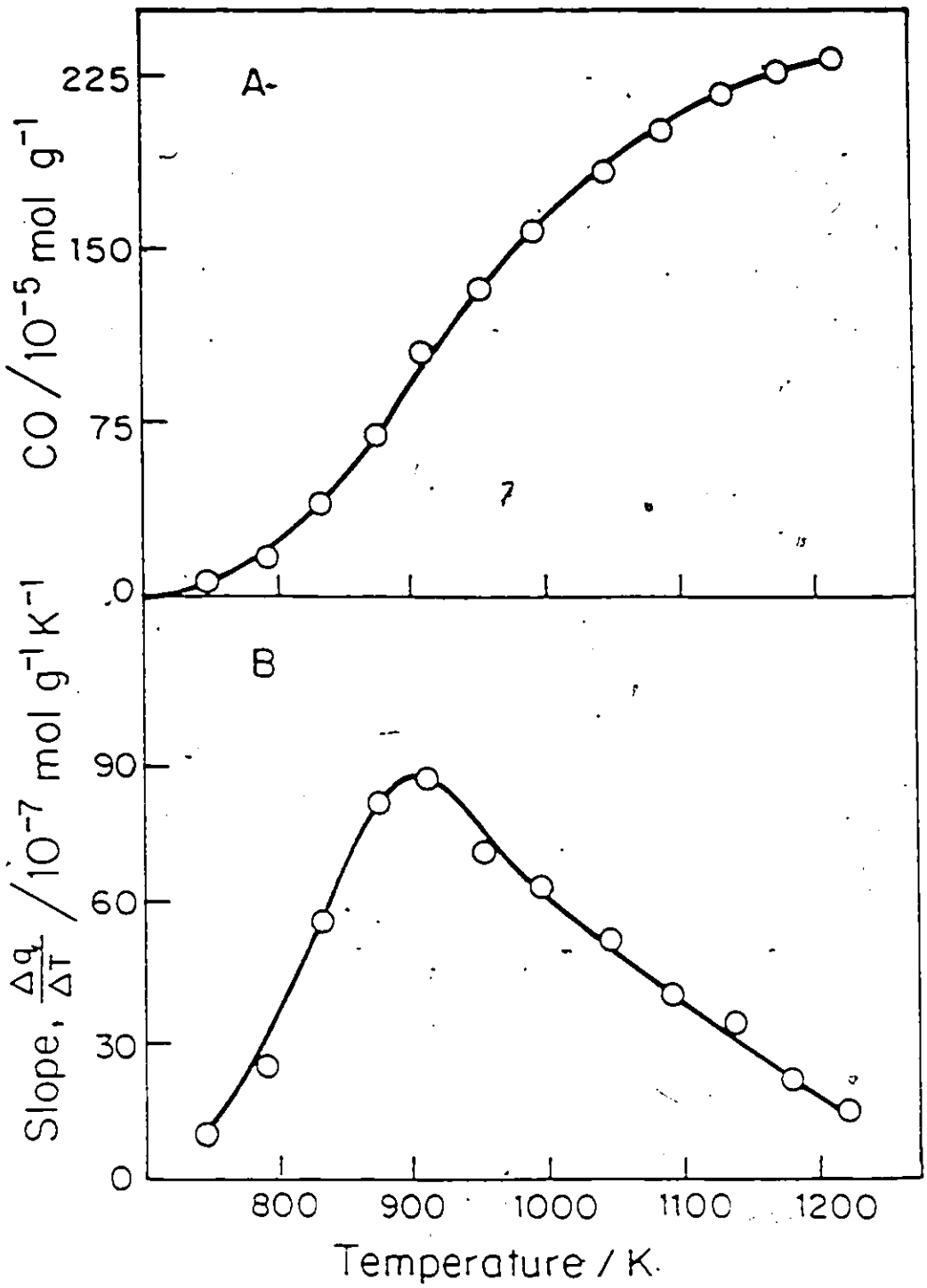


Figure 3.1. Recovery of the complex by TPD. Complex formed at 673 K with 300 Torr oxygen. In this experiment prolonged exposure gasified 35% of the initial amount of carbon (series 2, Table 3.2).

A. Cumulative amount of CO produced as a function of temperature.

B. Slope of A as a function of temperature.

The results of the first series of experiments are summarized in Table 3.1. These results show that the temperature at the maximum rate of desorption and therefore the calculated activation energy of desorption are a function of the amount of complex present initially on the surface. In fact most of the studies [15-23] on the desorption of the complex suggest an even stronger dependence of the energy of desorption on the coverage.

It was mentioned in Chapter 1 that when the desorption of the complex from a carbon surface is performed by linear-TPD, the presence of more than a single species of chemisorbed oxygen may be indicated [15,20-23]. Nevertheless, Tremblay et al. [15] stressed that on a carbon surface, multiple functional groups and/or sites may be energetically so similar that the resolution would depend critically on the heating rate, the relative amount of each (kinetic) species and the spread of the activation energy of desorption. By extensive computer-assisted mathematical modelling of an apparently continuous integrated linear-TPD desorption curve of carbon monoxide from Graphon, these authors deduced the existence of two types of functional groups and/or sites with energies of activation of 64.6 and 70.6 kcal mol^{-1}. Feates and Keep [22] reported even closer activation energies (62.7, 65.8 and 67.7 kcal mol^{-1}) for the three kinetic species responsible for carbon monoxide evolution from graphite. In differential curves such as shown in Figure 3.1, where the rate of desorption is estimated from the amount desorbed during a certain temperature interval, these subtle changes in the cumulative desorption curve may not be revealed. The possibility that the carbon films used in the present investigation may, unlike graphon (spheron-6)

Table 3.1. Temperature-programmed desorption of the surface oxygen complex (Series 1)

Temperature of adsorption: 673 K; $[C]^{\circ} = 2 \times 10^{-7}$ mol cm^{-2}

Product desorbed			
$CO/10^{-7}$ mol	$CO_2/10^{-7}$ mol	T_m/K	E_d/kcal mol^{-1}
0.41	0.12*	1003	70
0.59	0.18*	943	66
0.97	0.29*	933	66
1.02	0.30*	953	67
1.51	0.44	923	65
2.96	0.89*	913	64
3.17	1.02	913	64

* Quantity of CO_2 calculated from the ratio $CO_2/CO = 0.3$.

[15,20,21], natural graphite (SP-1) [23] used in previous studies, have a relatively large population of a particular type of site or functional group should not, however, be excluded. Hughes, Williams and Thomas [64] have shown that indeed by pre-oxidation of graphite below or above 1223 K a preferential "arm-chair" or "zig-zag" configuration of the layer edge can be produced. In any rate, the magnitude of the activation energy measured in the present experiments indicates that the complexes formed on these carbon films are similar to those formed on other types of carbon.

The second and third series of experiments dealt with the measurement of active sites according to the method suggested by Laine et al. [36,37]. In the second series of experiments, the carbon surface was allowed to remain in contact with 300 Torr of oxygen at 673 K for periods longer than 15 hours so that varying amounts of carbon were gasified while the stable complex formed on the surface. This procedure allowed the determination of the ASA for various degrees of burn-off. It was recognized at an early stage that the number of active sites on a carbon surface may be significantly changed by partial oxidation. For this reason, kinetic studies usually refer to the degree of oxidation, or "burn-off" of a carbon surface prior to kinetic measurements.

In the third series, after the measurement of the ASA of the film in the usual way, the temperature of the furnace was lowered to 1048 K. The carbon film was oxidized to about 25% burn-off at this temperature with an initial pressure of oxygen of 1 Torr. The temperature was again raised to 1223 K to remove any complex formed during the reaction and then the temperature was reduced to 673 K and the ASA again measured.

The entire procedure was performed a few times to about 70% burn-off. In some cases, the measurement of the ASA was repeated without intermediate oxidation of carbon to examine the possibility of annealing of active sites during thermal desorption to 1223 K. The ASA did not alter significantly between these successive measurements showing that annealing was not important in TPD treatment.

The results of both series are shown in Table 3.2 where besides the customary units ($m^2\ g^{-1}$), the ASA is also expressed in units of mol cm^{-2} utilizing the geometric area of the reaction vessel. As discussed in the Introduction, the BET area of the carbon film (of thickness used in these experiments) is close to the BET area of the quartz vessel, which is comparable to the geometric area [38]. The fraction of the total carbon which constitutes active sites and the manner in which this fraction changes with burn-off depends upon the structural properties of the specific carbon under examination [37]. With the carbon films used in the present study, both the second and third series of experiments showed a modest increase in the ASA, by a factor of 2 to 3, after 50% burn-off. Laine et al. [37] observed an 18-fold increase in the ASA of Graphon (a graphitised carbon black, microcrystalline but without microporosity) after 35% burn-off, but with a saran char (a pure microcrystalline, microporous carbon), Taylor and Walker [65] noted that the ASA remained essentially constant with burn-off. It is interesting to note that the unoxidized graphon [37] had a relatively low ASA (0.2 $m^2\ g^{-1}$) while the saran char [65] had an ASA of 50 $m^2\ g^{-1}$ comparable to that found for the thin films used in the present study.

Table 3.2. Temperature-programmed desorption of the surface oxygen complex (Series 2 and 3)

Temperature of adsorption: 673 K; Pressure of O_2: 300 Torr; $[C]^\circ = 2 \times 10^{-7}$ mol cm^{-2}

Percent burn-off	Time of adsorption/ hours	Product desorbed		Active Surface Area/	
		CO/	CO_2/		
		10^{-7} mol	10^{-7} mol	10^{-10} mol cm^{-2}	m^2 g^{-1}
Series 2					
0	16	3.28	1.02	31.9	70
12.5	23	3.92	1.33	39.4	100
34	35	5.94	1.78	56.9	193
80	46	4.88	1.46	46.7	494
Series 3					
0	15	2.07	0.77	21.6	45
27.5	15	3.70	0.95	33.5	96
57.2	15	3.25	0.70	27.8	135
67.5	15	1.87	0.60	18.4	118

The ASA of the carbon films was a reproducible quantity for films deposited and treated by similar procedures, as were all films of a particular series. It may be noted, however, that the films listed in series 3 have a lower ASA than those listed in series 2. This difference is the result of a minor variation in the procedure for preparation of the films and is reflected in a slightly larger rate of oxidation for the films prepared as in series 2. The films with lower ASA were, in general, used for the experiments in the high-temperature region, 948-1173 K, while the films with higher ASA were used for the experiments in the lower temperature region, 748-923 K.

3.2 Time course of the reaction

The time course of the reaction of thin films of carbon with oxygen at initial pressures in the vicinity of 1 Torr was measured over the temperature 748-1173 K. This pressure was selected to bridge the gap between experiments at pressures below 10^{-2} Torr [11,36,37,43-49,66] and those with pressures exceeding 100 Torr [39,40,67,71]. The reaction was followed by monitoring the concentration of carbon on the reactor surface and the total pressure in the reaction system. The measurements can be conveniently divided into two temperature ranges, 748-923 K and 923-1173 K.

3.2.1 748-923 K

Below about 898 K carbon monoxide was produced in amounts less than 1% of carbon dioxide. Under these conditions, the yield of carbon dioxide may be equated to the loss of carbon from the surface. The total

pressure in the system is the sum of pressures of oxygen and carbon dioxide and a fall in pressure from its initial value will indicate loss of oxygen due to adsorption. These processes may be expressed as follows:

$$\Delta n_C = n_{CO_2} \tag{3.3}$$

$$P_T = P_{O_2} + P_{CO_2} \tag{3.4}$$

$$P_{O_2} = P_o - P_{CO_2} - O_2 \text{ (adsorbed)} \tag{3.5}$$

$$\Delta P = P_o - P_T = O_2 \text{ (adsorbed)} \tag{3.6}$$

where Δn_C and n_{CO_2} are the molar loss of carbon and the number of moles of carbon dioxide produced respectively, P_T, P_{O_2} and P_{CO_2} are the total pressure and the pressures of oxygen and carbon dioxide respectively, and P_o is the initial pressure of oxygen. In these expressions, the 'O_2 (adsorbed)' indicates only removal of oxygen from the gas phase. That this adsorbed oxygen forms the strongly-bound complex will be shown in a subsequent series of experiments. The processes of reorganization on the surface which may occur during the formation of the complex will be discussed later.

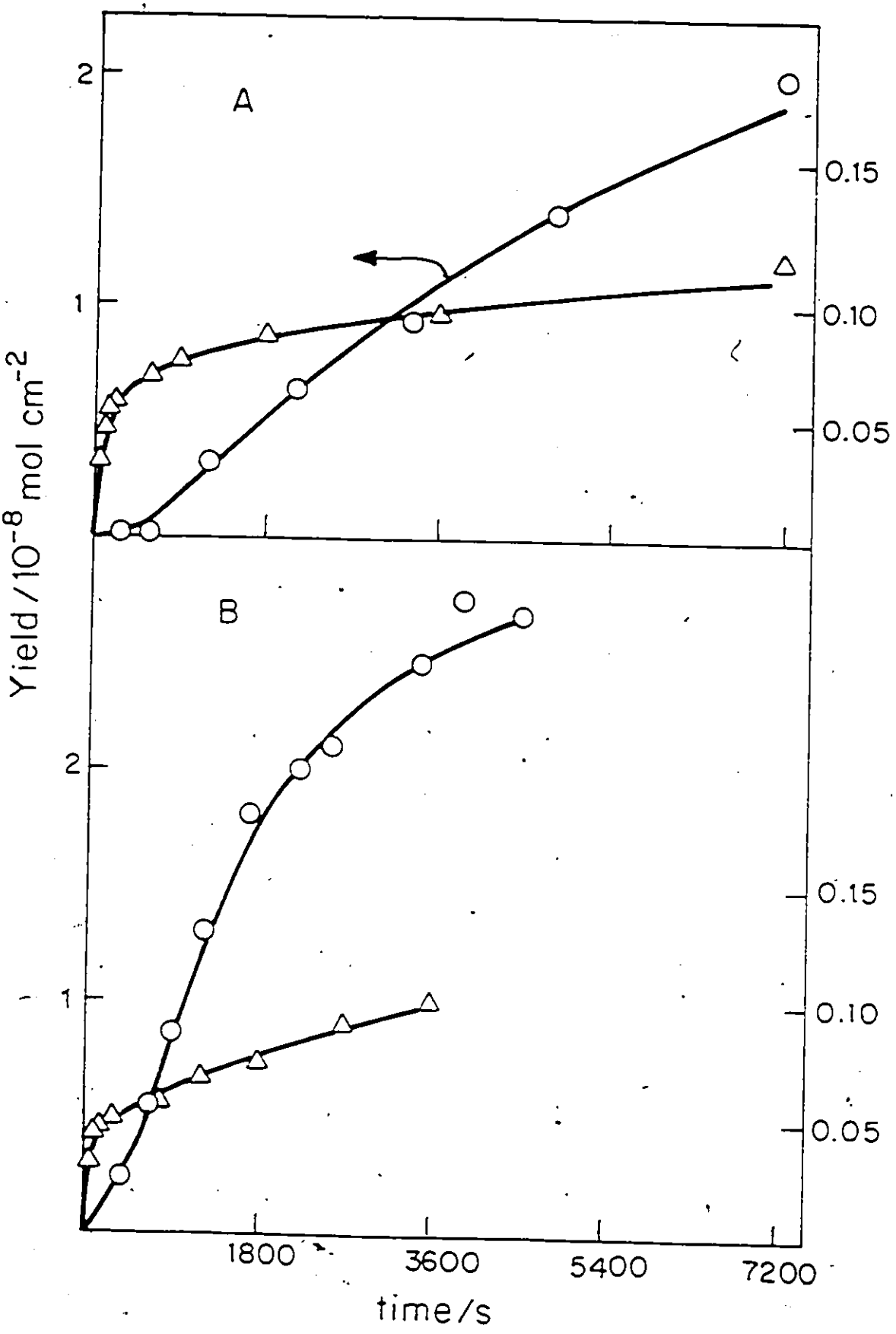
The time course of the reaction with respect to the adsorption of oxygen and to the formation of carbon dioxide is shown for two temperatures in Figure 3.2 where it should be noted that the scale for the adsorption of oxygen is ten times larger than for the yield of carbon dioxide. The reactions were performed at several temperatures. At each temperature it was clearly seen that the formation of carbon dioxide involved an induction period whose magnitude decreased with increasing temperature whereas no induction period was observed for the adsorption

Figure 3.2. Time course of adsorption of oxygen and of formation of carbon dioxide in the low-temperature region. Units apply to both ordinates.

O: CO_2; △ : oxygen adsorbed.

A. Temperature = 848 K; Initial pressure of oxygen = 1.0 Torr.

B. Temperature = 908 K; Initial pressure of oxygen = 0.8 Torr.


A
B
2
1
2
1
0.15
0.10
0.05
0.15
0.10
0.05
Yield / 10^{-8} mol cm^{-2}
1800
3600
5400
7200
time/s

of oxygen. The time course of the disappearance of carbon and of the formation of associated products thus had a sigmoid shape. The results of this series of experiments are summarized in Table 3.3.

The series also showed that the adsorbed oxygen formed the strongly-bound complex. The reaction following the consumption of amounts of carbon in the range 8-20% (amount depended on temperature) was terminated by removing the products and remaining reactant for analysis. At these temperatures the decomposition of the complex is very slow. A temperature-programmed desorption was then performed (as described earlier) to recover the stable complex as gaseous carbon monoxide and carbon dioxide, remaining on the surface after the reaction. The amount of oxygen recovered in this way (calculated from carbon monoxide and carbon dioxide released) was always about 15-30% less than the amount of oxygen adsorbed (calculated from the decrease in the total pressure). Although this difference may be within the combined errors in the measurement, it could suggest that a small fraction of the adsorbed oxygen did not form the stable surface oxide but was removed by evacuation with the reactant and products.

The initial rate of adsorption of oxygen was measured at each temperature. An Arrhenius plot of this rate, normalized with respect to the initial pressure of oxygen (Figure 3.3) gave an activation energy of adsorption of about 11 kcal mol^{-1}. The activation energy of adsorption on a carbon surface is expected to depend on the structural properties of the carbon and if the surface contains more than one type of site, multiple values of the activation energy of adsorption may be obtained. The value obtained in the present study, which probably represents a

Table 3.3. Rates of adsorption and reaction in the low-temperature region

Pressure of oxygen: 1 Torr; $[C]^\circ = 2 \times 10^{-7}$ mol cm^{-2}

Temperature/ K	Initial rate of adsorption of oxygen/ 10^{-12} mol cm^{-2} s^{-1}	Induction period for reaction/ min	Maximum rate of consumption of carbon/ 10^{-12} mol cm^{-2} s^{-1}
748	1.7	60	0.29
778	2.0	45	0.35
798	2.8	15	0.91
848	3.9	10	3.8
	3.8	10	2.7
	4.5	10	4.9
898	5.5	2	13.4
		2	11.5
908	6.8	1	13.4
923		0	21.8

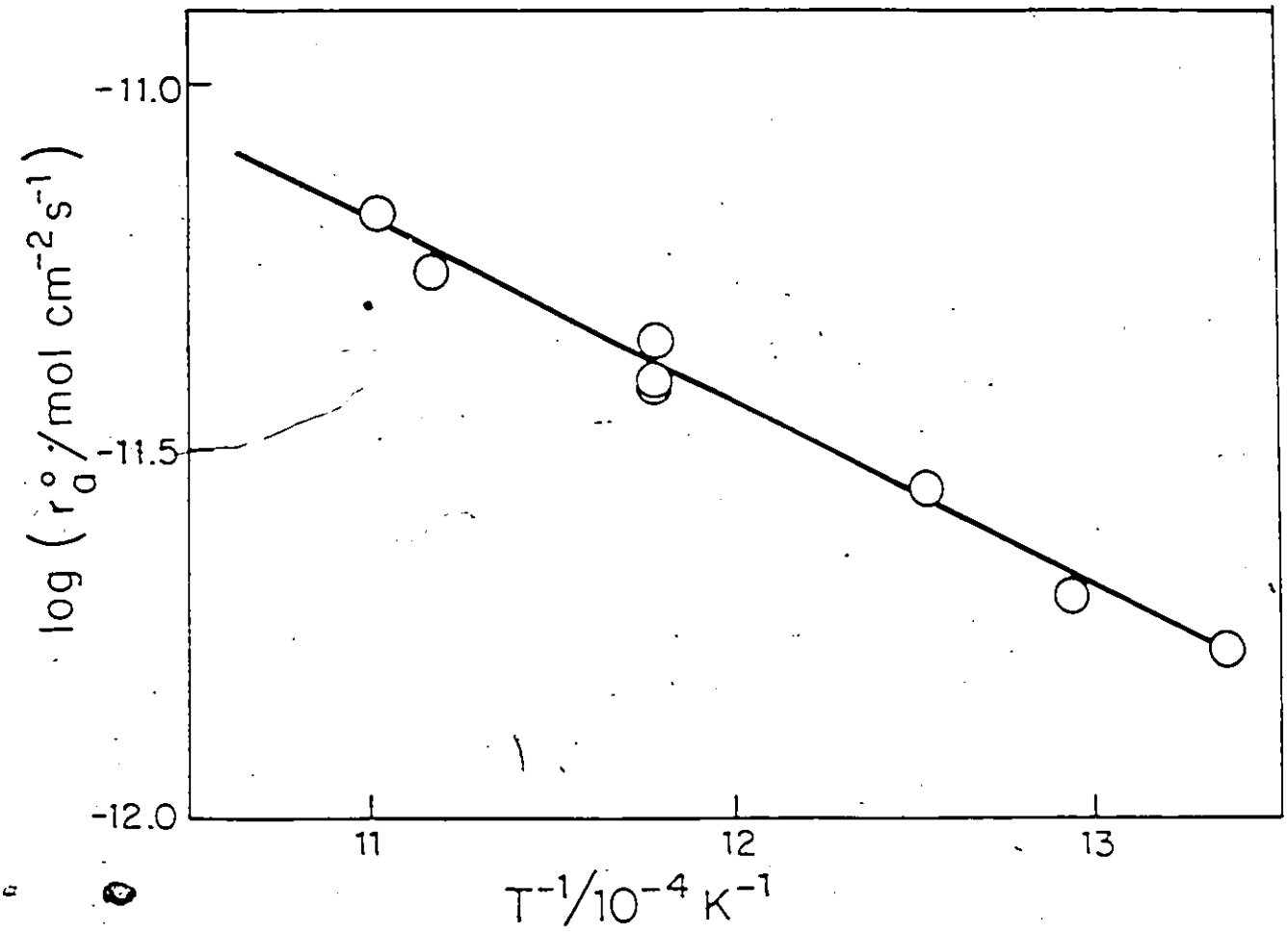


Figure 3.3. Arrhenius plot for the initial rate of adsorption. Initial pressure of oxygen = 1 Torr.

lower limit for a particular type of site (since an increase in the energy of activation with coverage may occur) is similar to the value (7.4 kcal mol^{-1}) obtained by Hart, Vastola and Walker [72] for low-pressure adsorption on Graphon over the temperature range 298-673 K.

The Arrhenius plot of the maximum rate of reaction is shown in Figure 3.4. The activation energy of this rate was 36 kcal mol^{-1}.

3.2.2 923-1173 K

At higher temperatures the general pattern of the time course of the reaction remained the same except that the induction period was gradually shortened and at the highest temperature of the present series of experiments became barely noticeable. At 998 K the yield of carbon monoxide was no longer negligible and in the initial stages amounted to about 25% of the carbon dioxide in the products. At higher conversions of carbon, as carbon monoxide accumulated in the system, some secondary reaction of carbon monoxide with oxygen appeared to become important. The study of this aspect of the reaction is described in Part II. The occurrence of a secondary reaction shows that the product ratio, CO/CO_2 is significant with respect to the primary oxidation only at low conversions. The over-all rate, however, is unambiguously given by the loss of carbon.

Experiments in the low-temperature region, described in the preceding section, suggested that during the course of the reaction the amount of chemisorbed oxygen, or oxygen surface complex residing on the surface, attained a limiting value, which was small compared to the yield of product carbon dioxide. Experiments described later show that the

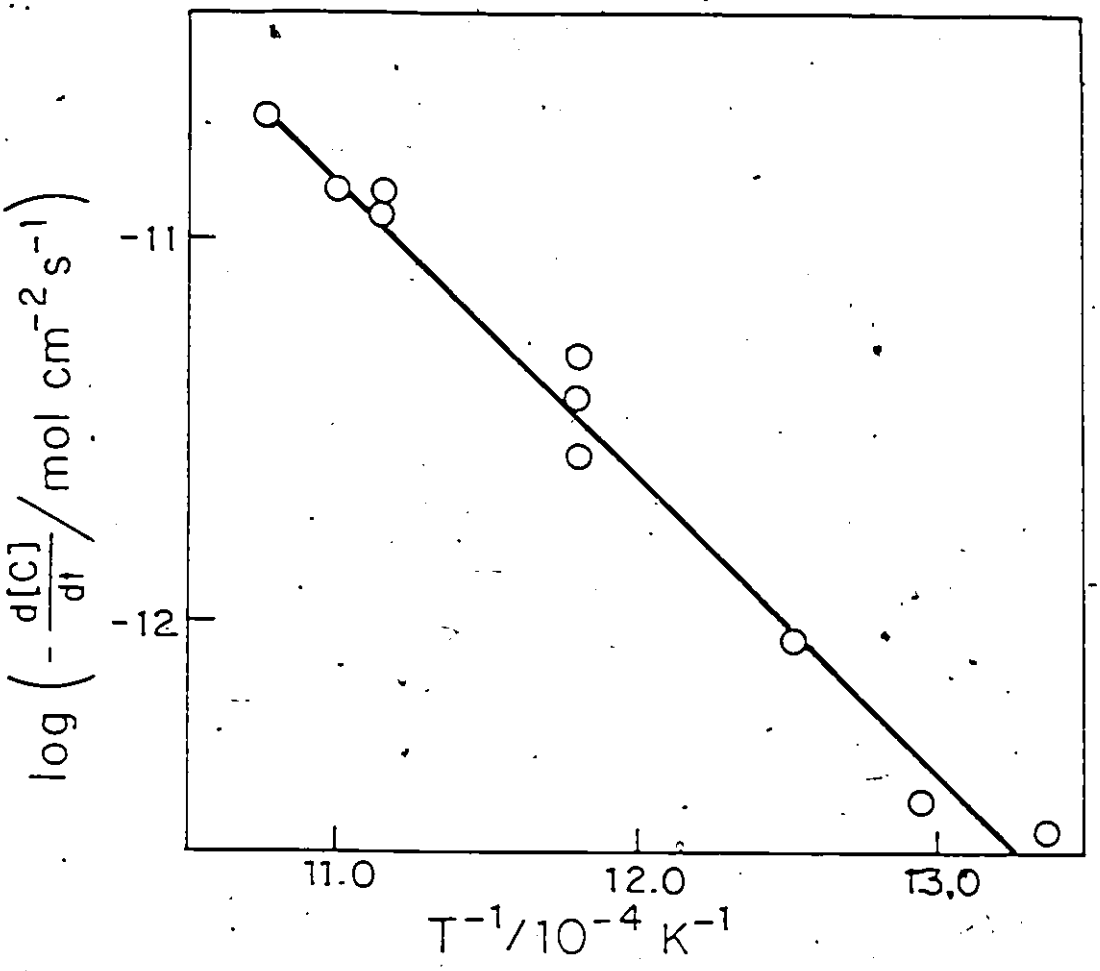


Figure 3.4. Arrhenius plot for the rate of removal of carbon in the low-temperature region. Initial pressure of oxygen = 1 Torr.

same situation prevails in the high temperature region but, as indicated by the shortening of the induction period, the limiting amount is reached within a short period after the commencement of the reaction. If it is assumed that the amount of complex present on the surface during a reaction is approximately equal to the amount recovered by TPD at the end of the reaction then, for example, in a typical experiment illustrated in Figure 3.5A, the total yield of carbon monoxide and carbon dioxide at two minutes ($\sim 4 \times 10^{-6}$ mol or 2.4×10^{-8} mol cm^{-2}) is at least 50 times greater than the concentration of complex on the surface during the reaction. Therefore, in the high temperature region the decrease in pressure due to the formation of the complex becomes negligible compared to the increase associated with the production of carbon monoxide. Under these conditions (3.3) - (3.6) become

$$\Delta n_C = n_{CO_2} + n_{CO} \tag{3.7}$$

$$P = P_{O_2} + P_{CO_2} + P_{CO} \tag{3.8}$$

$$P_{O_2} = P_o - P_{CO_2} - \tfrac{1}{2} P_{CO} \tag{3.9}$$

$$\Delta P = P - P_o = \tfrac{1}{2} P_{CO} \tag{3.10}$$

where additional terms n_{CO} and P_{CO} represent the number of moles of carbon monoxide produced and the corresponding pressure of carbon monoxide. Rates were measured over the temperature range 923-1173 K and at initial pressures of oxygen of 0.5, 1 and 3 Torr. Examples are shown in Figure 3.5. The maximum rates of disappearance of carbon and of formation of carbon monoxide and carbon dioxide were obtained from these measurements. In those cases where there was indication of significant

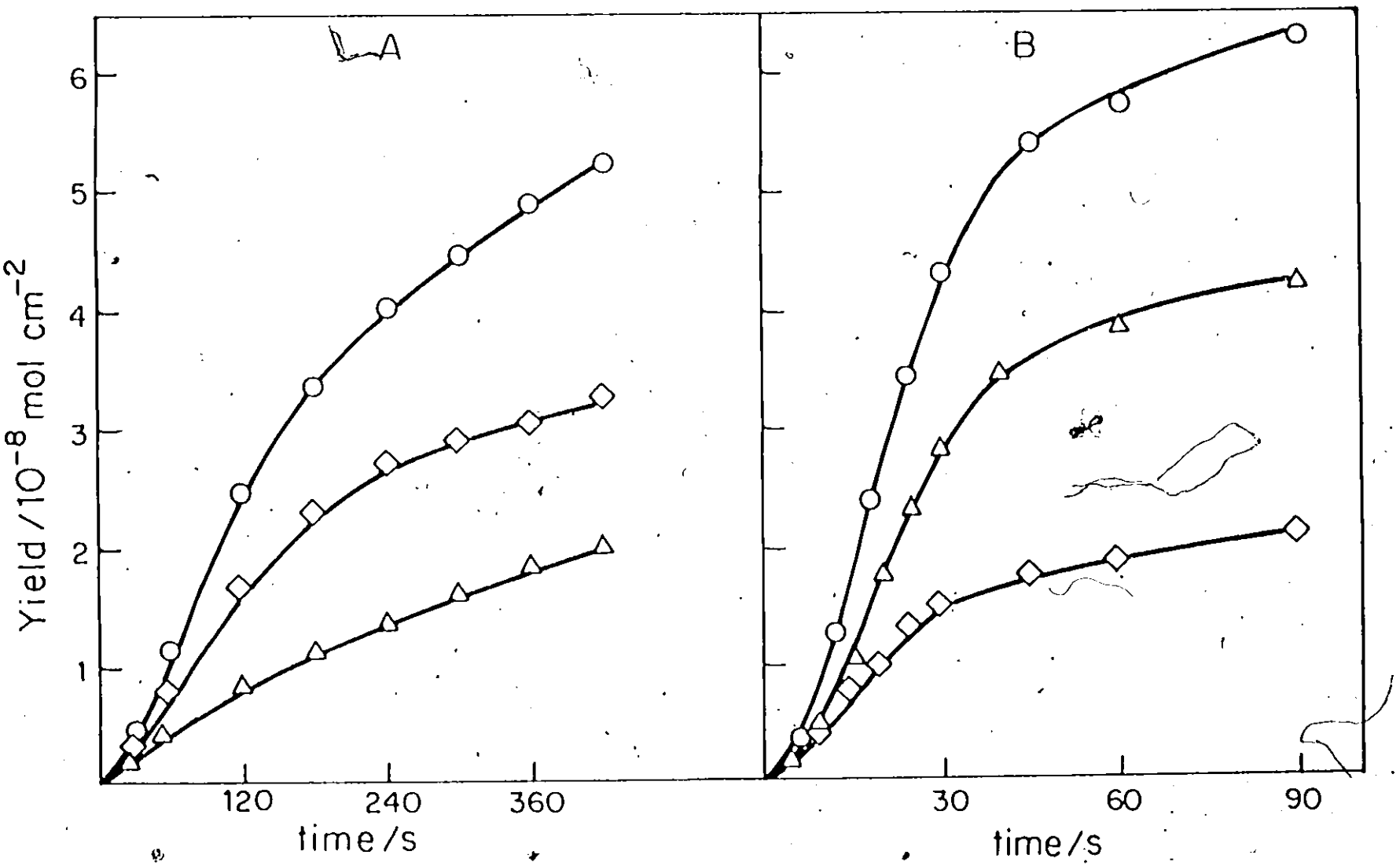


Figure 3.5. Yield-time curves for carbon consumed and products CO and CO_2 formed..

O: carbon removed; △ : CO; ◇ : CO_2

A. Temperature = 1048 K; Initial pressure of oxygen = 1 Torr.

B. Temperature = 1148 K; Initial pressure of oxygen = 3 Torr.

secondary reaction of carbon monoxide before reaching the time at which the maximum rate of loss of carbon occurred, maximum rates of formation of carbon monoxide would be underestimated while those of carbon dioxide would be overestimated. To correct for this; the total rate at the maximum, measured by the loss of carbon, was apportioned between the products carbon monoxide and carbon dioxide according to the ratio measured at low conversion. The maximum rates are shown as Arrhenius plots in Figure 3.6, 3.7 and 3.8. The activation energies obtained from these plots are given in Table 3.4.

Two points are significant from these results. First, the activation energy for the production of carbon monoxide obtained from the measurements below about 1048 K is about the value expected for the desorption of the strongly-bound complex as carbon monoxide, discussed in Section 3.1. Secondly, for pressures of 0.5 and 1 Torr, a significant drop in the activation energy was observed at temperatures above about 1050 K. Both these observations will be discussed in the light of the role of the complex in the reaction pathways of the over-all reaction.

As indicated above, the product ratio CO/CO_2 was measured in the early stages of the reaction at each temperature. At each oxygen pressure the ratio increased with increasing temperature, as is usually observed [11]. For the series of reactions with 1 Torr of oxygen, this ratio is shown as a function of temperature in the Arrhenius plot in Figure 3.9. Although the individual rates of formation of carbon monoxide and carbon dioxide (Figures 3.7 and 3.8) showed departure from the Arrhenius law at temperatures above 1050 K, the ratio displayed an Arrhenius dependence over the whole temperature range 623-1173 K. The

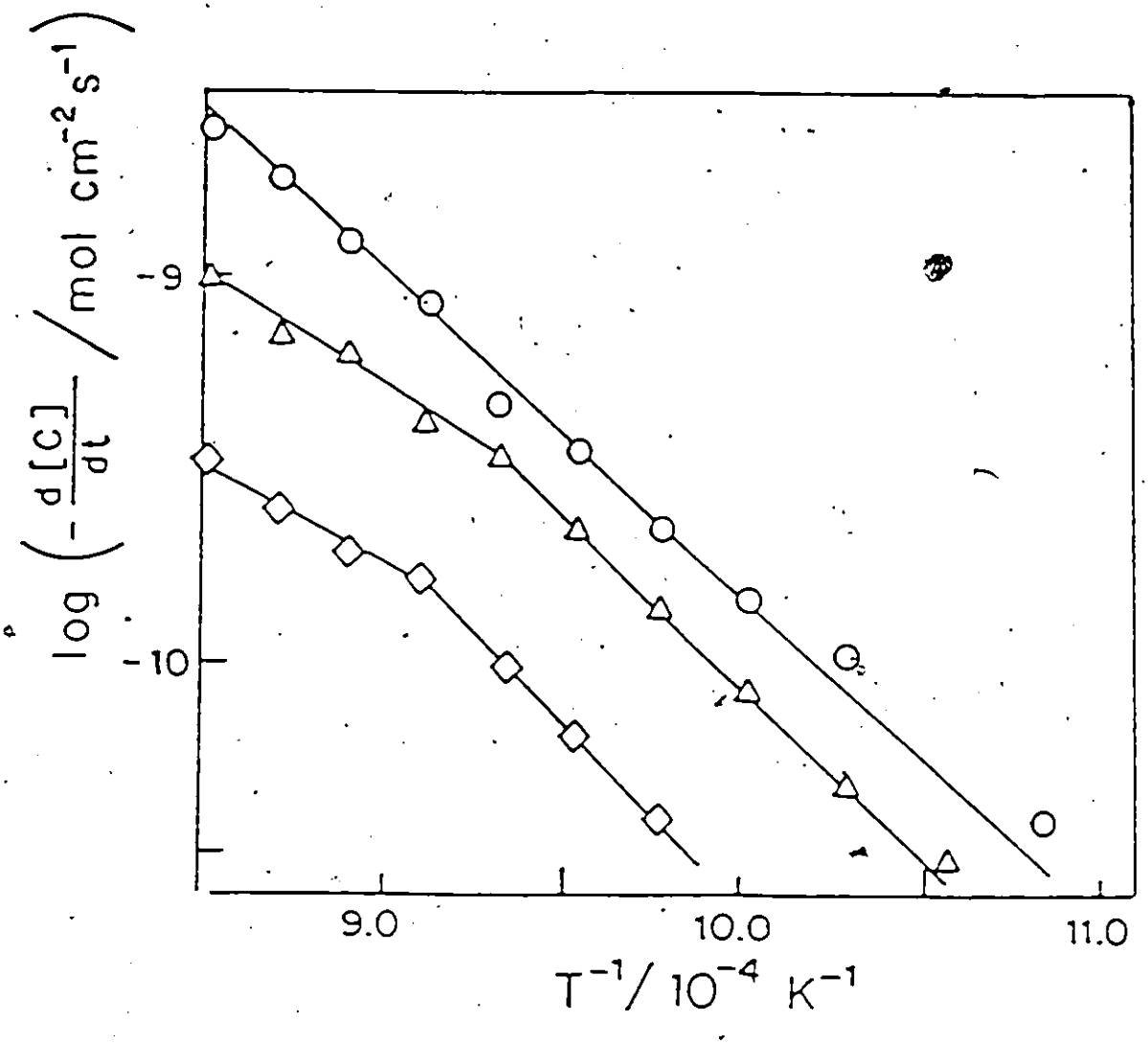


Figure 3.6. Arrhenius plot for the rate of removal of carbon.

Initial pressure of oxygen:

O: 3 Torr; △ : 1 Torr; ◇ : 0.5 Torr.

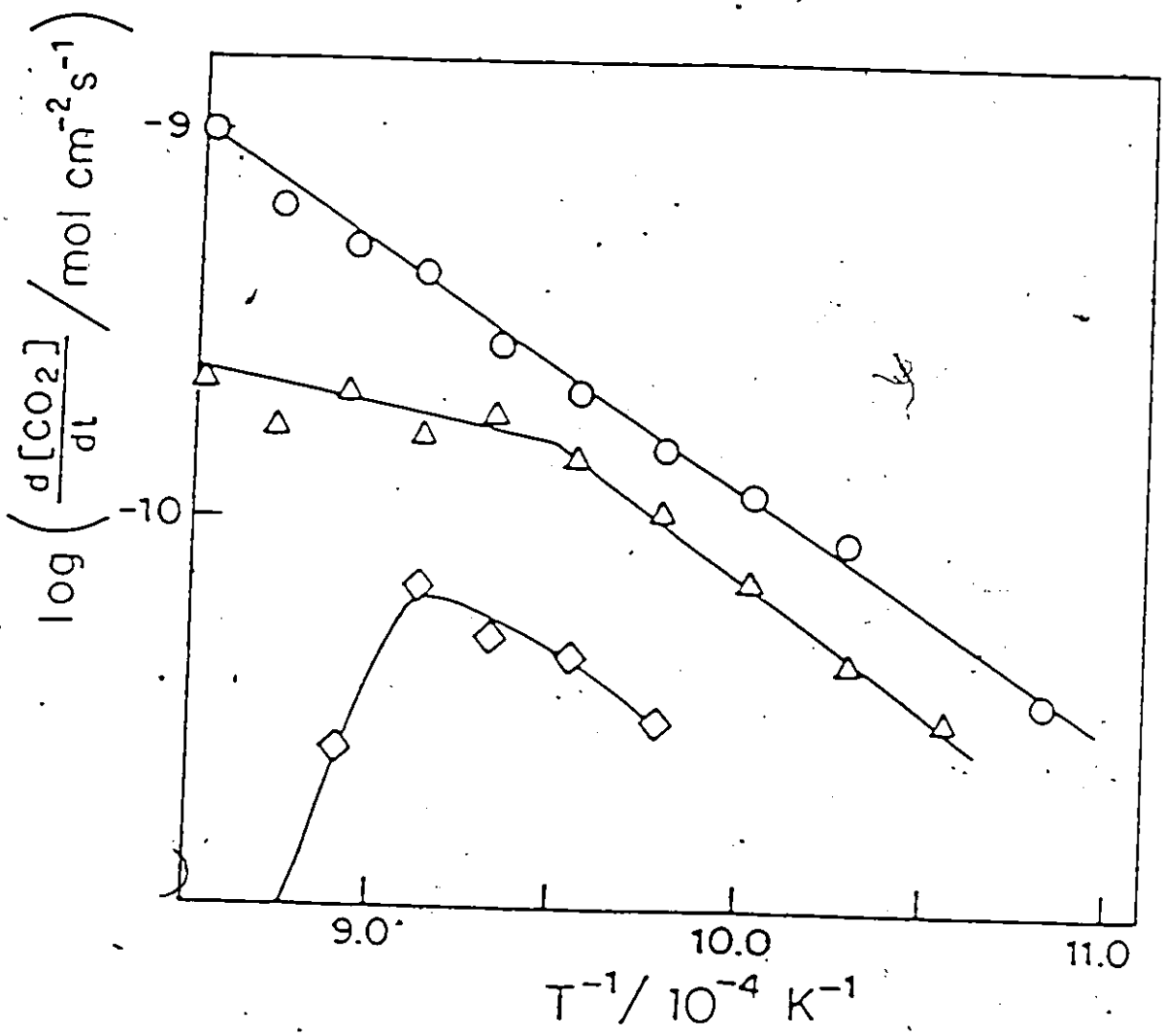


Figure 3.7. Arrhenius plot for the rate of removal of carbon dioxide: Initial pressure of oxygen:
○ : 3 Torr; △ : 1 Torr; ◇ : 0.5 Torr.

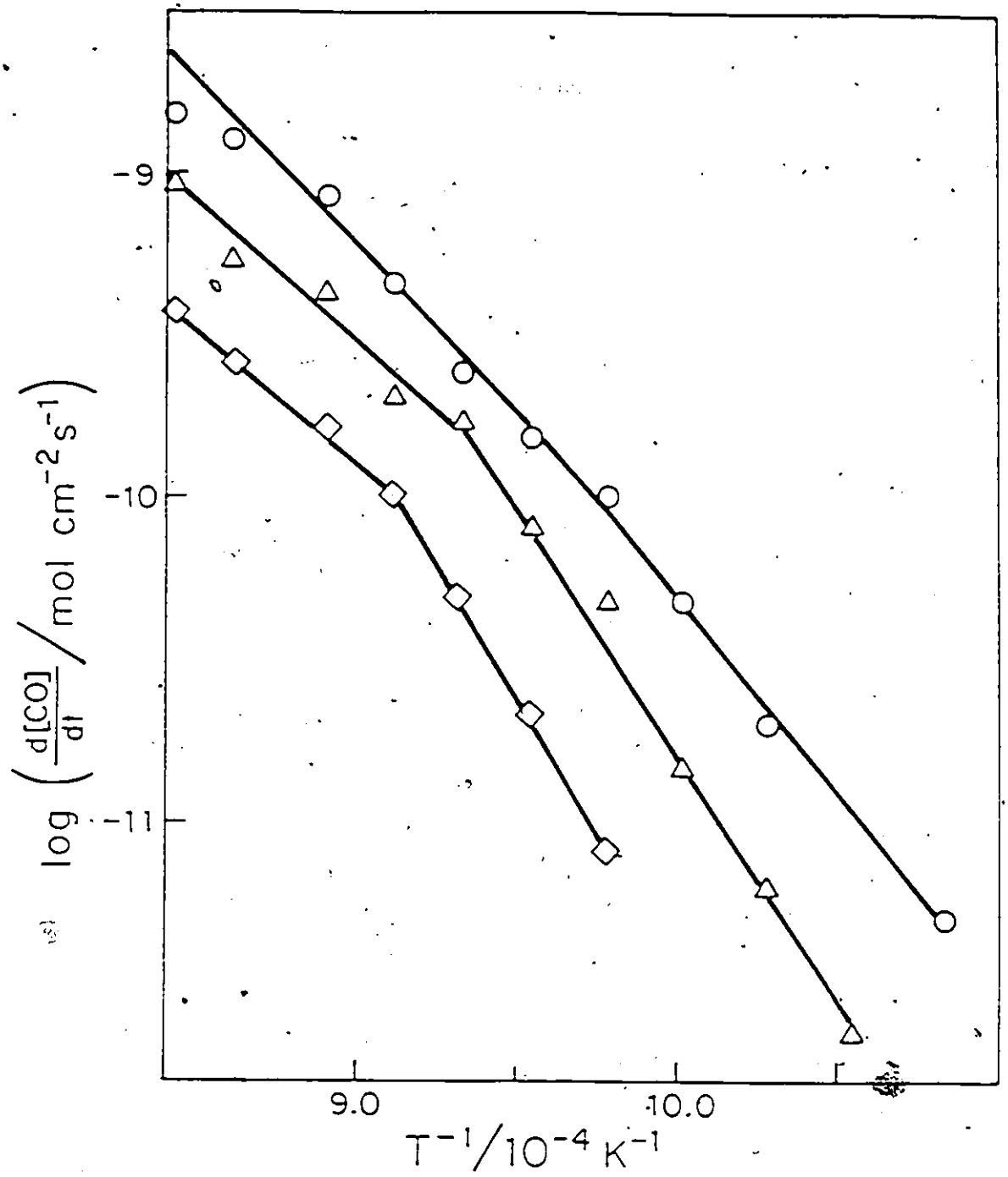


Figure 3.8. Arrhenius plot for the rate of removal of carbon monoxide. Initial pressure of oxygen:

○ : 3 Torr; △ : 1 Torr; ◇ : 0.5 Torr.

Table 3.4. Activation energies of the rates (/kcal mol^{-1})*

Pressure of oxygen/ Torr	$-\frac{d[C]}{dt}$	$\frac{d[CO]}{dt}$	$\frac{d[CO_2]}{dt}$
0.5	43	73	
1	41	68	31
3	39	56	28

* These are maximum values measured in the lower temperature region.

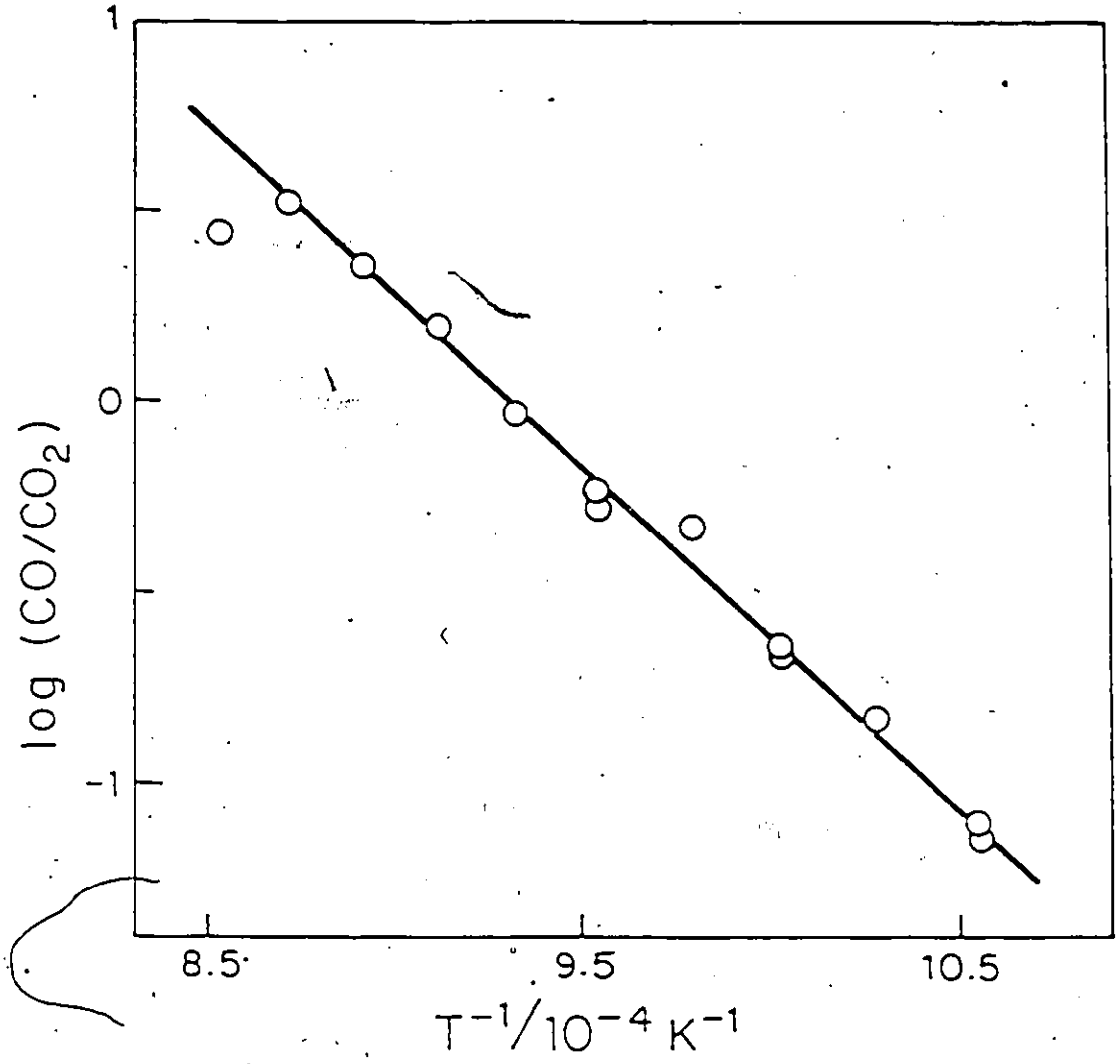


Figure 3.9. Arrhenius plot of the ratio CO/CO_2 in the initial stages of the reaction with new films (stage 1). Initial pressure of oxygen = 1 Torr.

slope of this plot indicates a difference in the activation energy for the formation of carbon monoxide and that of carbon dioxide of 40 kcal mol^{-1}, in good agreement with the difference calculated from the separate determination of each activation energy (37 kcal mol^{-1}).

3.3 Comparison of the kinetics of the reaction in the presence and absence of complex on the surface before the start of the reaction

Several series of experiments were performed at an initial pressure of oxygen of about 1 Torr with the purpose of testing the role of the complex as an intermediate in the oxidation process. In the first series a carbon film was allowed to react with oxygen in two stages, removing about 25-30% of the initial amount of carbon in each stage. In the first stage oxygen was admitted to the system and the rate was measured as described earlier. The reaction was stopped by evacuating the products and remaining reactant. A temperature-programmed desorption to 1223 K was then performed to remove the stable complex remaining on the surface. The temperature of the film was then reduced to the reaction temperature and the oxygen was readmitted for reaction in stage 2.

A second series of experiments with a new film was performed, identical to the first series, except that the complex was not removed after stage 1. Thus the difference between the two series of experiments is that prior to reaction at stage 2 the complex was not present on the surface in the first series but was present in the second series. A typical result of these oxidations is shown in Figure 3.10. This figure shows two important features of this set of experiments. First, the magnitude and the kinetic characteristics of the rate are practically the

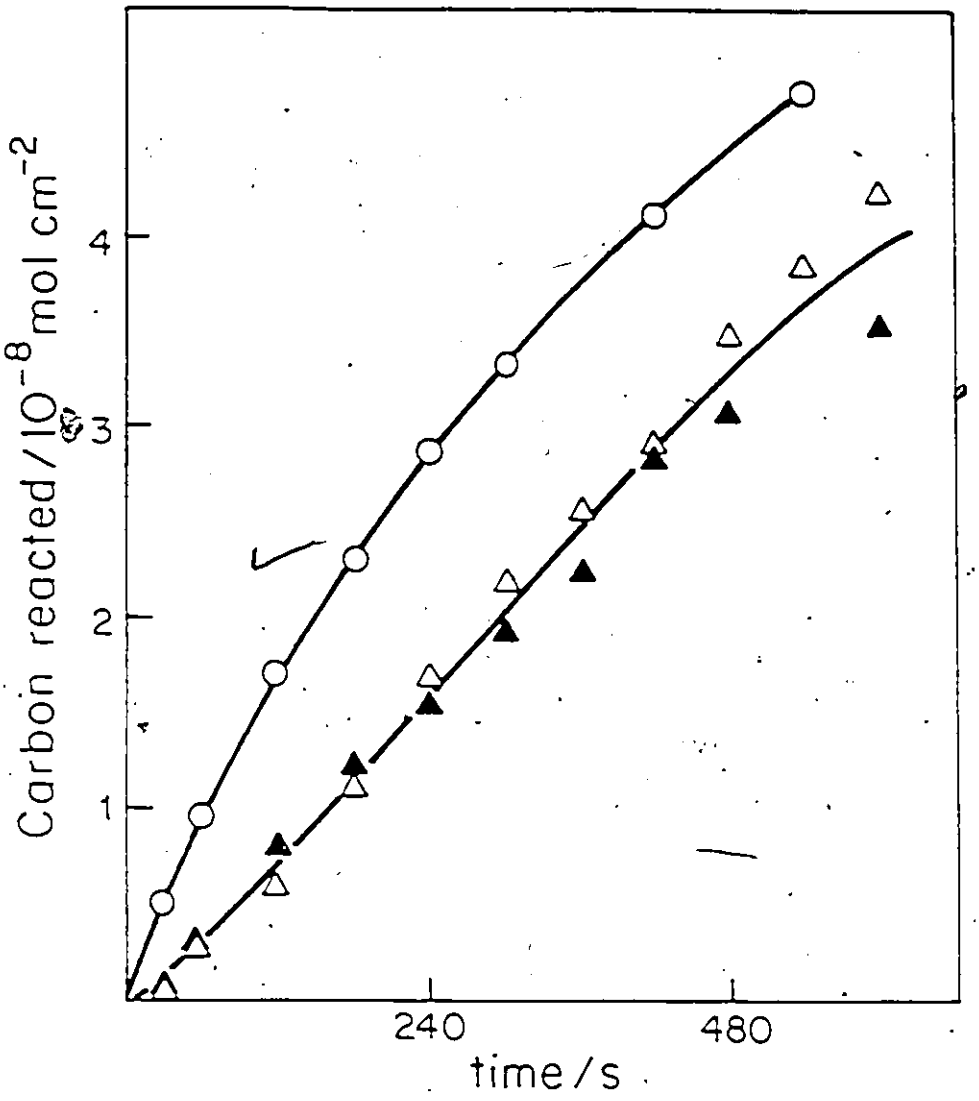


Figure 3.10. The effect of the presence of the complex on the rate of removal of carbon.

Temperature = 998 K; Initial pressure of oxygen = 1 Torr.

△ : stage 1, new film.

▲ : stage 2, complex removed after stage 1.

○ : stage 2, complex not removed after stage 1.

same for the oxidation in stage 1 with a new film and for the oxidation in stage 2 after removal of the complex. Thus the partial oxidation in stage 1 did not noticeably change the ASA, or number of active sites on the surface. Second, the rate was significantly increased when the complex was present on the surface before admission of oxygen.

Further examples of this effect at pressures of 0.5 and 3 Torr of oxygen are given in Figure 3.11. Since the experiments at 1 Torr of oxygen showed that the rate in the absence of the complex was virtually the same at stage 1 and at stage 2, the effect at 0.5 and 3 Torr is shown by comparison of the rate at stage 1 with the rate at stage 2 in the presence of the complex. These series of experiments were performed over a range of temperature and the results are summarized in Tables 3.5, 3.6 and 3.7. The rates of removal of carbon with and without the presence of complex at the start of the reaction are also shown in the form of Arrhenius plots in Figure 3.12. In all cases, the presence of the complex on the surface at the beginning of the reaction had a significant effect on the kinetics of the reaction, viz. the induction period was shortened and the maximum rate of gasification was increased. The decrease in the induction period was most pronounced at low temperatures where the induction period was longest. The increase in the rate was noticeable at all temperatures but the effect was less pronounced above about 1123 K where the concentration of complex present on the surface following stage 1 was small.

In Tables 3.5-3.7 the rates of formation of products carbon monoxide and carbon dioxide in the presence and absence of complex are also included. Although a quantitative assessment of these values is not

Figure 3.11. The effect of the presence of the complex on the time course of the reaction. All curves represent removal of carbon.

△ : stage 1, new film.

○ : stage 2, complex not removed after stage 1.

A. Temperature = 1023 K; Initial pressure of oxygen = 3.0 Torr.

B. Temperature = 1048 K; Initial pressure of oxygen = 0.5 Torr.

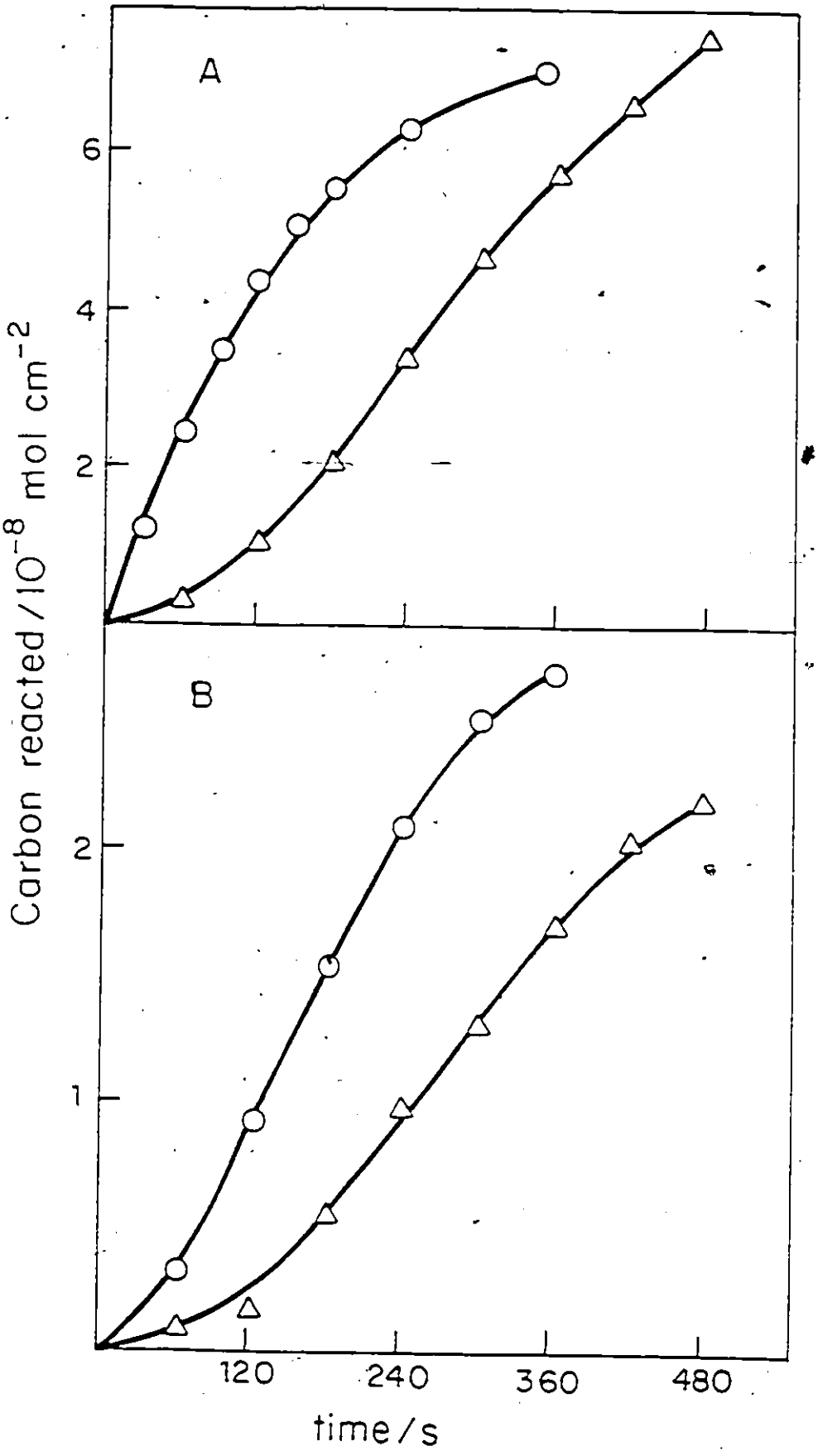

A
B
6
4
2
2
1
120
240
360
480
Carbon reacted / 10^{-8} mol cm^{-2}
time / s

Table 3.5 Rates of removal of carbon and formation of products in the presence and absence of the complex ($[C]^\circ = 2 \times 10^{-7}$ mol cm^{-2})

Initial pressure of oxygen: 1 Torr

Temperature/K	$(-d[C]/dt)/10^{-10}$ mol cm^{-2} s^{-1}			$(-d[CO]/dt)/10^{-10}$ mol cm^{-2} s^{-1}			$(-d[CO_2]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		
	Stage 1	Stage 2		Stage 1	Stage 2		Stage 1	Stage 2	
		complex absent	complex present		complex absent	complex present		complex absent	complex present
948	0.30	0.23		0.021			0.31	0.22	
	0.30		0.41	0.022		0.08	0.28		0.33
973	0.46		0.87	0.062		0.23	0.42		0.67
998	0.83	0.66		0.13	0.08		0.70	0.62	
	0.85		1.70	0.16		0.71	0.69		1.1
1023	1.34		2.46	0.47		1.2	1.0		1.1
1048	2.08	1.64		0.80	0.63		1.3	1.2	
	2.25		4.25	0.81		2.3	1.5		2.0
1073	3.36		5.12	1.7		3.6	1.8		2.0
1098	4.19		7.90	2.0		4.5	2.0		3.6
1123	6.22	5.27		4.3	3.8		2.1	1.5	
	5.99		8.32	3.8		5.9	2.1		2.6
1148	7.00		9.04	5.4		7.4	1.7		2.9
1173	9.88		10.8	9.0		10.4	2.2		2.6

Table 3.6 Rates of removal of carbon and formation of products in the presence and absence of the complex ($[C]^\circ = 2 \times 10^{-7}$ mol cm^{-2})

Initial pressure of oxygen: 3 Torr

Temperature/K	$(-d[C]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		$(-d[CO]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		$(-d[CO_2]/dt)/10^{-10}$ mol cm^{-2} s^{-1}	
	Stage 1	Stage 2 complex present	Stage 1	Stage 2 complex present	Stage 1	Stage 2 complex present
923	0.38	0.77	0.05	0.20	0.32	0.6
973	1.05	2.25	0.20	0.75	0.84	1.5
998	1.44	2.53	0.48	1.0	1.0	2.5
1023	2.22	4.07	1.0	2.2	1.4	2.3
1048	3.65	7.24	1.5	4.1	2.2	3.0
1073	4.79	8.20	2.4	5.1	2.8	3.4
1098	8.74	12.0	4.6	8.5	4.4	4.8
1123	12.6	15.7	8.6	11.6	5.0	4.5
1148	18.1	20.5	12.6	15.3	6.3	9.0
1173	24.5	23.5	15.4	18.3	10.1	11.4

Table 3.7 Rates of removal of carbon and formation of products in the presence and absence of the complex ($[C]^\circ = 2 \times 10^{-7}$ mol cm^{-2})

Initial pressure of oxygen: 0.5 Torr

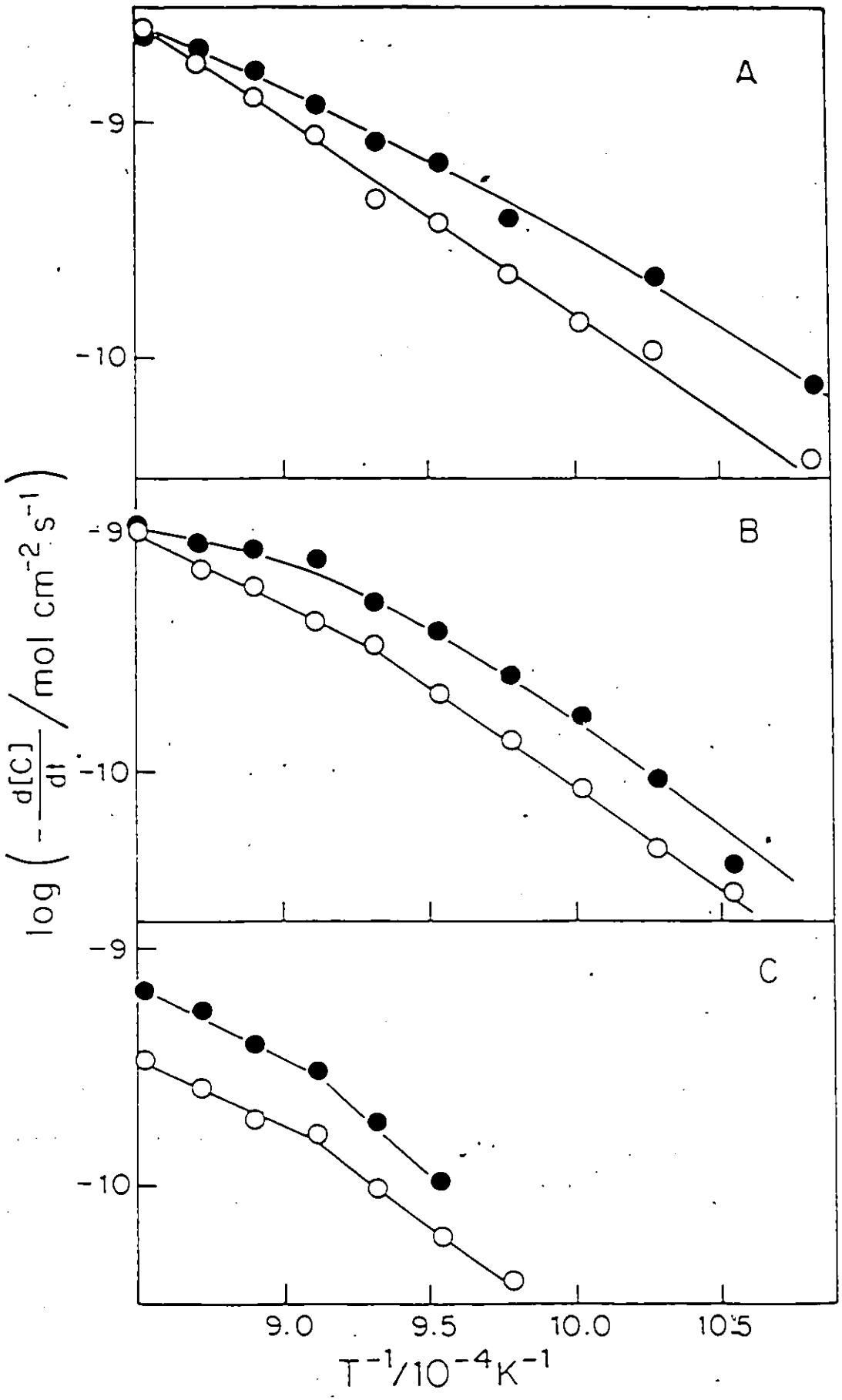
Temperature/K	$(-d[C]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		$(-d[CO]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		$(-d[CO_2]/dt)/10^{-10}$ mol cm^{-2} s^{-1}	
	Stage 1	Stage 2 complex present	Stage 1	Stage 2 complex present	Stage 1	Stage 2 complex present
1023	0.38		0.08		0.30	
1048	0.63	1.02	0.21	0.60	0.45	0.50
1073	0.95	1.83	0.48	1.1	0.50	0.60
1098	1.68	3.01	1.0	1.6	0.65	1.5
1123	1.84	3.82	1.6	2.5	0.25	1.1
1148	2.47	5.28	2.5	2.9	0	2.3
1173	3.41	6.23	3.7	3.6	0	2.5

Figure 3.12. Arrhenius plots for the rate of removal of carbon in the presence and absence of the complex.

O: absence of the complex; ● : presence of the complex.

Initial pressure of oxygen:

A. 3 Torr; B. 1 Torr; C. 0.5 Torr.


A
B
C
-9
-10
-9
-10
-9
-10
9.0
9.5
10.0
10.5
$T^{-1}/10^{-4}K^{-1}$
$\log\left(-\frac{d[C]}{dt}/\text{mol cm}^{-2}\text{s}^{-1}\right)$

attempted, yet the results clearly suggested that the retention of the complex after stage 1 increased the rate of gasification and shortened the induction period (not shown in Tables) for formation of each product.

A note of clarification regarding the slight drop in the rate in stage 2 compared to that in stage 1 when the complex was removed is, perhaps, desirable here (Table 3.5). Because of minor differences in procedure, it was realized that some reactions in stage 1 (using a new film) might have been performed in the presence of a tiny amount of the surface oxygen complex. When care was taken to ensure that no complex was present, the maximum rate in the first stage approached very closely to that of the second stage. The sets of experiments at 0.5 and 3 Torr in the two series of experiments described above and also the third, fourth and fifth series of experiments described below were done carefully avoiding the formation of the complex on newly deposited films.

The third series of experiments again involved oxidation in two stages but this time with films containing various initial amounts of carbon. With each initial amount of carbon, reaction in stage 2 was done as before both with and without the removal of the complex after reaction in stage 1. Again, a shortening in the induction period and an increase in the rate was observed during reaction in stage 2 when the complex was not removed after stage 1. The results are summarized in Table 3.8.

A fourth series consisting of three sets of experiments, each involving the oxidation of carbon in nine stages were performed. For this series the films contained an initial amount of carbon about twice

Table 3.8 Rates of removal of carbon and formation of products in the presence and absence of the complex; films contain different initial amounts of carbon [$(1 - 5) \times 10^{-7}$ mol cm^{-2}]

Temperature: 1048 K; Initial pressure of oxygen: 1 Torr

$[C]^\circ/10^{-7}$ mol cm^{-2}	$(-d[C]/dt)/10^{-10}$ mol cm^{-2} s^{-1}			$(-d[CO]/dt)/10^{-10}$ mol cm^{-2} s^{-1}			$(-d[CO_2]/dt)/10^{-10}$ mol cm^{-2} s^{-1}		
	Stage 1	Stage 2		Stage 1	Stage 2		Stage 1	Stage 2	
		complex absent	complex present		complex absent	complex present		complex absent	complex present
0.85	1.32		0.94	0.34		0.66	1.0		0.39
1.45	1.62	1.10		0.48	0.40		1.1	0.68	
	1.50		2.40	0.40		1.2	1.1		1.4
1.95	1.60	1.65		0.51	0.50		1.1	1.1	
	1.60		4.00	0.55		2.1	1.1		1.8
3.25	1.41	1.28		0.60	0.53		0.95	0.72	
	1.44		3.78	0.56		2.4	0.98		1.4
4.50	1.28	1.22		0.62	0.60		0.62	0.69	
	1.20		3.17	0.60		2.8	0.60		

as that used in the first and second series. Three sets were done as follows:

1. the complex was removed by TPD following each stage.
2. the complex was not removed after any stage of the reaction.
3. the complex was removed after stages 1, 3 and 5.

This series served to compare the maximum rates of reaction under the various conditions. The rates were measured from figures similar to Figure 3.5 and the results are given in Table 3.9 and Figure 3.13A. The x-axis shows the decreasing amount of carbon in the film as the reaction proceeds through the stages. It is clear that the rate changed very little as the carbon was consumed when the complex was removed after each stage. It should be emphasized that the rate and the amount of carbon monoxide recovered following temperature-programmed desorption at each stage, given in Table 3.9, are not divided by the total amount of carbon remaining on the surface. The increase in both quantities therefore appears not as pronounced as has been observed with other carbons [36,37]. Also the fact that very little increase in rate was observed when the complex was removed is not explained by a deactivation or annealing of active sites during TPD of the complex. Consecutive measurements of the ASA of a carbon film (new or oxidized to a certain burn-off), without oxidation between measurements, showed no decrease in the number of active sites (Section 3.1, series 3). This is not surprising since the maximum temperature attained in TPD was only 1223 K and the film was not held for long periods at this temperature.

On the other hand, when the complex was allowed to remain on the surface and only the products and reactant were removed after each stage

Table 3.9. Oxidation of a carbon film in stages

Temperature: 1048 K; Pressure of oxygen: 1 Torr

Stage	[C]/ 10^{-7} mol cm^{-2}	-d[C]/dt/ 10^{-10} mol cm^{-2} s^{-1}	CO recovered after TPD/ 10^{-7} mol
Nine-stage reaction:			
(a) Complex removed after each stage (set 1)			
1	4.51	1.29	0.62
2	4.08	1.11	0.94
3	3.67	1.03	1.05
4	3.24	1.02	1.10
5	2.75	1.20	1.30
6	2.20	1.68	1.10
7	1.56	1.56	1.05
8	1.00	1.38	1.00
9	0.51	1.06	
(b) Complex not removed at any stage (set 2)			
1	4.54	1.19	
2	4.17	3.17	
3	3.70	7.98	
4	3.19	8.07	
5	2.58	11.6	
6	1.93	10.9	
7	1.37	8.68	
8	0.86	6.95	
9	0.36	3.35	
(c) Complex removed after stages 1, 3 and 5 (set 3)			
1	4.70	1.26	0.60
2	4.31	1.34	
3	3.86	3.03	1.14
4	3.32	1.65	
5	2.77	3.32	1.43
6	2.20	1.51	
7	1.59	3.27	
8	1.00	3.52	
9	0.43	1.92	

Table 3.9. (Continued)

Stage	[C]/ 10^{-7} mol cm^{-2}	-d[C]/dt/ 10^{-10} mol cm^{-2} s^{-1}	CO recovered after TPD/ 10^{-7} mol
Six-stage reaction:			
(a) Complex removed after stage 1 and 3 (set 1)			
1	3.24	1.41	0.60
2	2.74	1.16	
3	2.23	3.78	1.05
4	1.58	1.75	
5	0.97	2.76	
6	0.37	1.73	
(b) Complex not removed at any stage (set 2)			
1	3.24	1.44	
2	2.74	3.77	
3	2.13	6.95	
4	1.45	5.99	
5	0.87	5.45	
6	0.32	2.28	

Figure 3.13. The rate of consumption of carbon at each stage in several-stage reaction. The x-axis shows the amount of carbon on the surface at the beginning of each stage.

T = 1048 K; Initial pressure of oxygen = 1 Torr.

A. Nine-stage reaction. $[C]^\circ = 4.5 \times 10^{-7}$ mol cm^{-2}.

○ : complex removed after each stage;

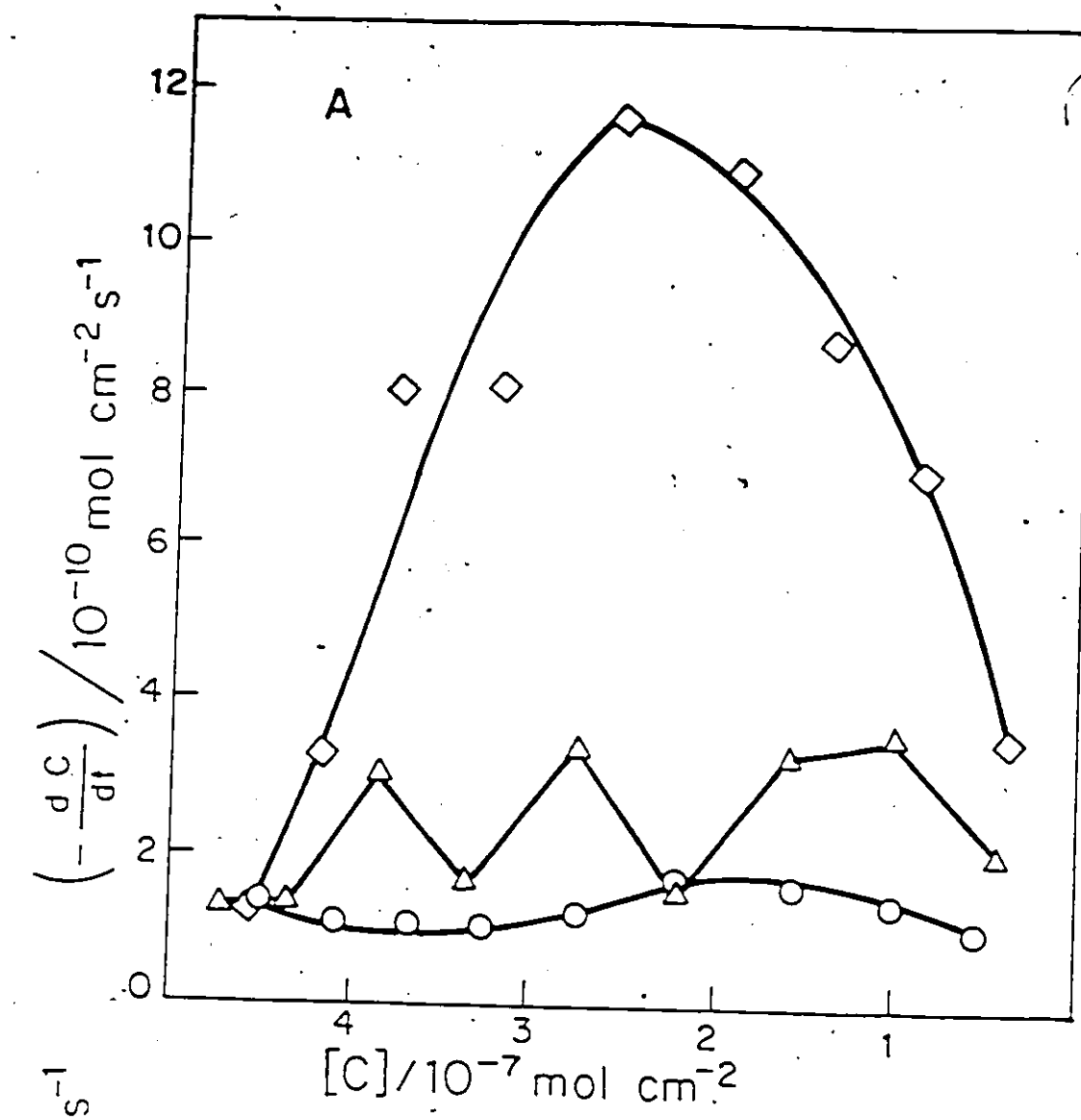
◇ : complex not removed after any stage;

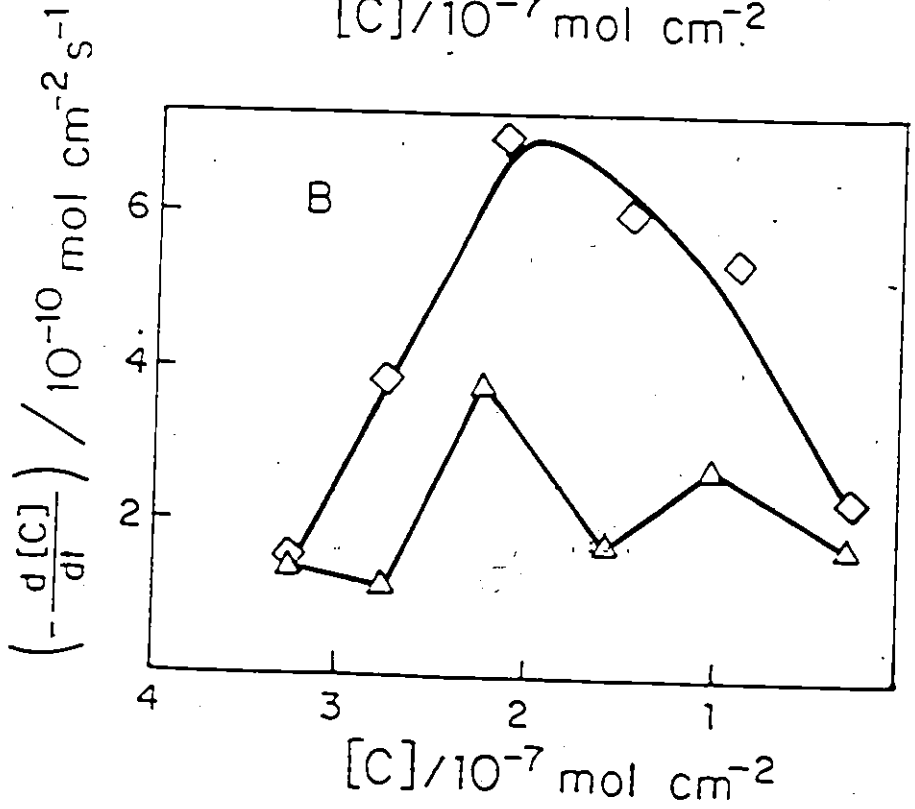
△ : complex removed after stages 1, 3 and 5.

B. Six-stage reaction. $[C]^\circ = 3.2 \times 10^{-7}$ mol cm^{-2}.

◇ : complex not removed after any stage;

△ : complex removed after stages 1 and 3.


A
12
10
8
6
4
2
0
$\left(-\frac{dC}{dt}\right) / 10^{-10}$ mol cm^{-2} s^{-1}
4
3
2
1
[C]/10^{-7} mol cm^{-2}


B
6
4
2
$\left(-\frac{d[C]}{dt}\right) / 10^{-10}$ mol cm^{-2} s^{-1}
4
3
2
1
[C]/10^{-7} mol cm^{-2}

(second set, ◇), the rate was significantly increased. The yield-time curves at each stage of this second set of experiments are given in Figure 3.14. The effect of the presence of the complex is further substantiated by the results of the third set of the present series of experiments. After removal of the complex following stage 1, the rate in stage 2 was unchanged, but when the complex was not removed after stage 2, the rate was significantly increased in stage 3.

The results of a fifth series of two sets of experiments, shown in Figure 3.13b and given in Table 3.9 displayed similar behaviour.

A final test of the effect of the complex on the rate of oxidation was made by allowing the complex to form on the surface before the reaction. A new film of carbon was saturated with the complex at 673 K by adsorption from 300 Torr of oxygen for 15 hours. The temperature of the film was then quickly raised to 898 K and the time course of the reaction with 30 Torr of oxygen was measured. This was then compared with a similar oxidation without pre-adsorbing oxygen. The results shown in Figure 3.15 clearly demonstrate a significant shortening in the induction period by the presence of the complex.

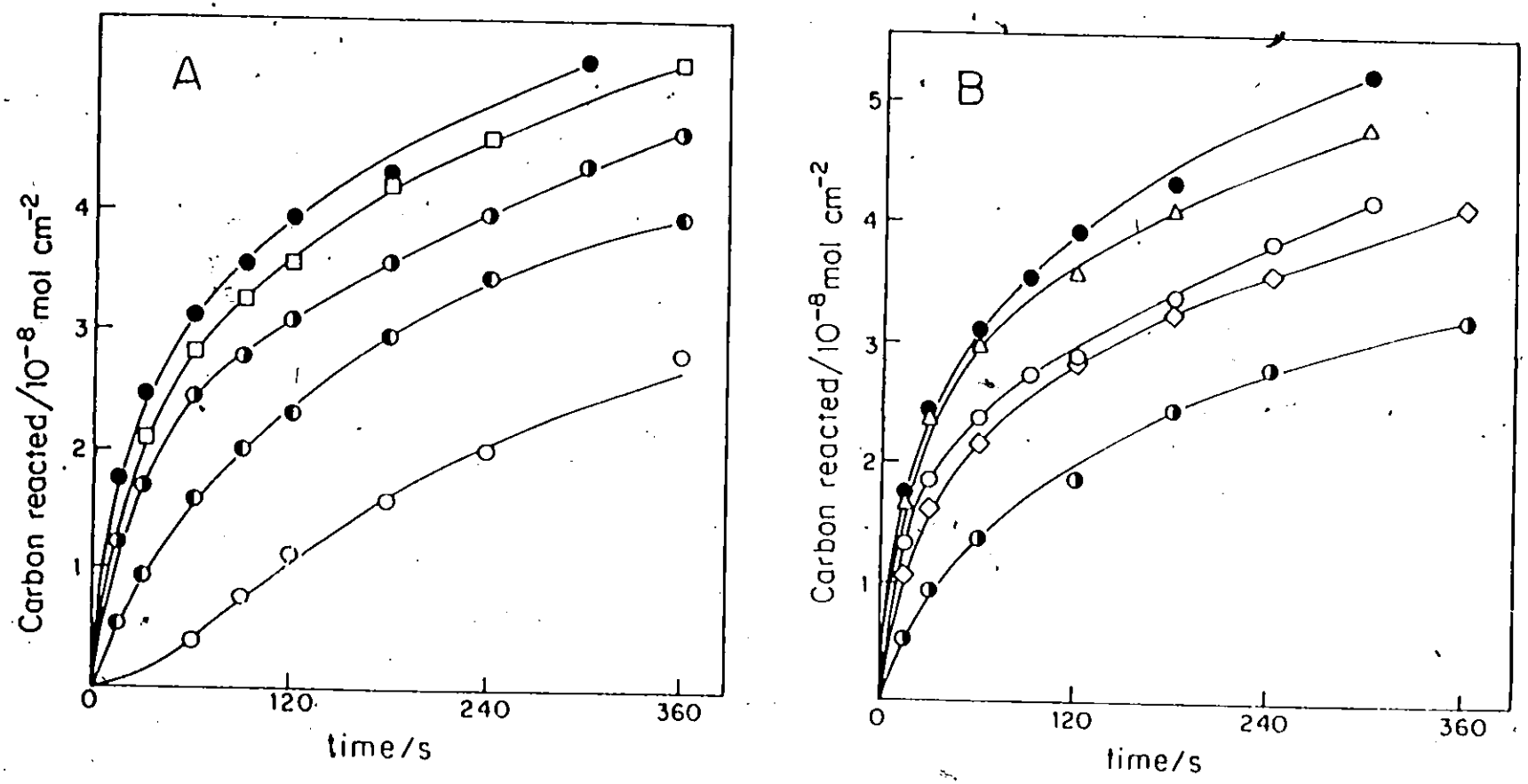


Figure 3.14. Yield-time curves in set 2 of the nine-stage reaction.

Temperature = 1048 K; Initial pressure of oxygen = 1 Torr.

A. Stages 1 thru 5.

○: stage 1; ◐ : stage 2; ◑ : stage 3;

□ : stage 4; ● : stage 5.

B. Stages 5 thru 9. Stage 5 included for sake of convenience in comparison.

● : stage 5; △ : stage 6; ○ : stage 7;

◇ : stage 8; ◑ : stage 9.

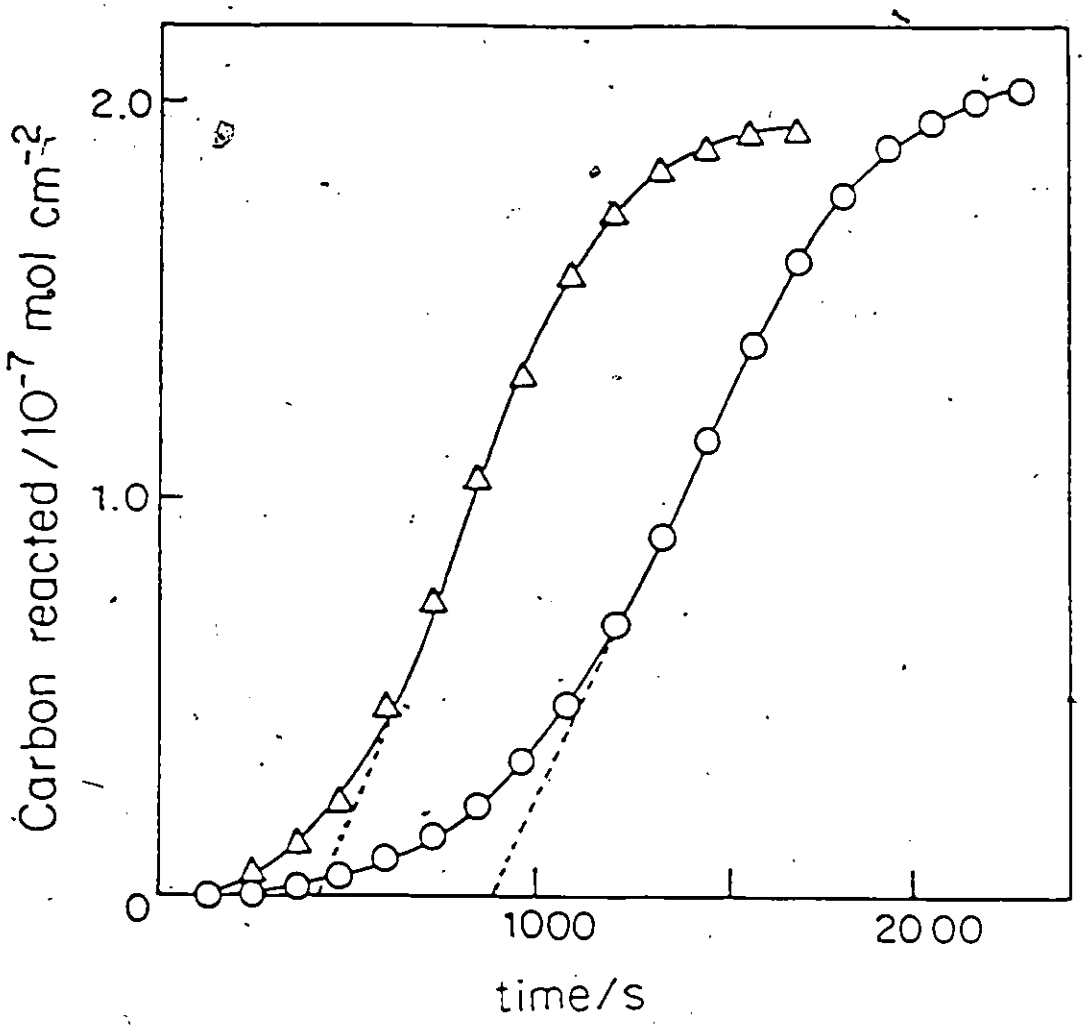


Figure 3.15. The effect of the presence of the complex on the yield-time curve for removal of carbon.

Temperature = 898 K; Initial pressure of oxygen = 30 Torr.

○ : complex not present on the surface before reaction.

△ : complex present on the surface before reaction.

CHAPTER 4

DISCUSSION

4.1 Kinetics and mechanism

The time course of the reaction obtained in the low-temperature region clearly shows that the adsorption commences immediately after the exposure of the carbon film to oxygen and that the amount adsorbed rapidly approaches a limiting value. On the other hand, the formation of the product carbon dioxide (negligible carbon monoxide is formed in this region) is associated with an induction period and a sigmoid-type yield-time curve. Furthermore, the two curves are related in that the maximum rate of formation of carbon dioxide is observed approximately at the time when the adsorbed oxygen attains its maximum value. These results strongly suggest that the adsorbed oxygen is a precursor to the formation of carbon dioxide.

The next question which must be considered is the role of the complex in the processes following adsorption and leading to formation of carbon dioxide. Previous studies of the adsorption of oxygen on carbon and the present measurements of TPD of the complex (discussed in Section 3.1) provide conclusive evidence that adsorption is followed by rapid conversion to the stable complex. The stages in this conversion are not known but probably involve migration, and rearrangement steps. Since the initial adsorption step involves not simply a physisorbed oxygen molecule but a loosely chemisorbed species, the subsequent steps may well be rapid. Thus, although the kinetic measurements link the initially adsorbed oxygen and the product carbon dioxide, it can reasonably be

suggested that the stable complex is the precursor or intermediate in the formation of carbon dioxide at these temperatures.

The induction period gradually decreased as the temperature of the reaction was raised. This suggests that the rates of the reactions following adsorption, either surface migration or rearrangement processes leading to formation of the complex or further reactions leading to formation of carbon dioxide, increase with increasing temperature and hence involve an activation barrier. In the neighbourhood of the highest temperature of measurement of the present study (Figure 3.5B), the induction time was reduced to a few seconds.

This interpretation of the role of the complex in the oxidation reaction is supported by the results of measurements of the rate in the presence and absence of the complex (Tables 3.5, 3.6 and 3.7). The presence of the complex on the surface before the introduction of the reactant had a significant effect on the kinetics of the reaction. Over the entire temperature range of measurement the induction period was shortened. At low pressures an increase in the maximum rate was also observed. Both these effects, evident in the formation of each individual product, indicate that the complex participates directly in the reaction as an intermediate in the formation of products.

The effect of the complex on the over-all rate is clearly shown by the three sets of experiments involving nine stages of reaction and also by the two sets of experiments involving six stages of reaction. In both series, when the complex was removed after each stage the rate was hardly changed. On the other hand, when the complex was left on the surface after each stage the effect appeared to be cumulative and in the case of

the nine-stage reaction, the rate in stage 5 was about 10 times greater than that observed in stage 1. In the six-stage experiment, the increase was a factor of 5 and was attained during stage 3 of the reaction. The maximum effect was, in both series, observed at a concentration of carbon on the surface of about 2×10^{-7} mol cm^{-2}. It is interesting that a maximum in the rate of oxidation, under somewhat different conditions, was observed in a previous study of the reaction of oxygen with carbon films [38]. This result will not, however, be discussed further here.

The experiments in set 3 of the nine-stage reaction (Figure 3.13A) show that the retention of the strongly-bound complex after stages 2, 4 and 6 caused an increase in the rate in stages 3, 5 and 7 but removal of the complex after each of these stages brought the rate back down to the values observed in set 1. Similar effects were also observed in the second set of the six-stage reaction (Figure 3.13B). It is important to point out that these rates are not normalized with respect to the total amount of carbon in the film. During the nine stages (Figure 3.13A, set 1), the film was successively gasified until almost none remained. Nevertheless, after each stage the amount of complex recovered during TPD to 1223 K remained very similar, as did the rate. This is compelling evidence that the property of the surface most directly related to the rate is the ASA and not the total quantity of carbon. It should be noted that the amount of complex recovered at this temperature is not equal to the amount formed during adsorption at 673 K, since only a fraction of the total ASA will remain occupied with the complex after oxidation at 1048 K. The ASA will, however, be proportional to the amount of complex recovered.

The picture that emerges of the gasification of carbon with oxygen consists of rapid adsorption of oxygen on the carbon surface followed by surface reorganization of the adsorbed oxygen into the strongly-bound surface oxygen complex; formation of the gaseous products, carbon monoxide and carbon dioxide, occurs after the accumulation of the complex on the surface. This picture is described by the following mechanism:

$$C_F + O_2 \longrightarrow C(O_2) \quad (1)$$

$$C_F + C(O_2) \longrightarrow 2\,(CO)_c \quad (2)$$

$$(CO)_c \longrightarrow CO(g) + C_F \quad (3)$$

$$C_F + (CO)_c + O_2 \longrightarrow CO_2 + (CO)_c + 2\,C_F \quad (4)$$

$$(CO)_c + C(O_2) \longrightarrow CO_2 + (CO)_c + C_F \quad (5)$$

$$(CO)_c + (CO)_c \longrightarrow CO_2 + C_F \quad (6)$$

where C_F refers to a peripheral carbon atom (a free site on the surface), $C(O_2)$ to an adsorbed oxygen molecule before the formation of the complex takes place, and $(CO)_c$ to the stable oxide complex. It has been pointed out that the processes involved in transformation of the adsorbed oxygen into the surface complex are not known and have therefore been described in a simple manner by reaction (2). The free sites on the carbon surface have been included in the stoichiometry of the reaction by assuming that the formation of a gasified molecule, either carbon monoxide or carbon dioxide, has not changed the number of free sites. This exact balance is, however, only an approximation.

There are two important features of this mechanism which account for

some aspects of the reaction.

(1) Formation of both products, carbon monoxide and carbon dioxide, is preceded by the formation and accumulation of the complex on the surface. Direct desorption of the complex by reaction (3) gives the product carbon monoxide. Carbon dioxide is produced by reactions (4) - (6), which describe pathways, in addition to the simple desorption (3), by which the complex could take part in the reaction leading to formation of products. These surface processes involve the interaction of the complex with oxygen in three different forms, gaseous, molecularly adsorbed and dissociatively adsorbed. A consequence of these reactions, particularly reaction (4), is that at high pressures of oxygen the rate would remain dependent on the concentration of oxygen even when the surface was fully covered by the complex, and many studies have shown that the rate of oxidation is first-order in oxygen pressure. These reactions may, on the other hand, be of less significance at very low pressures of oxygen and this aspect will be discussed later.

(2) The formation of a product molecule, carbon monoxide or carbon dioxide, is associated with the production of a new free site and subsequent formation of another complex. The concentration of complex on the surface, or the portion of ASA filled with the complex, thus, attains a steady-state value as the reaction proceeds due to the balance between formation and disappearance. This steady-state concentration of complex on the surface is a function of temperature and pressure of oxygen. The situation is analogous to the behaviour of active sites in a heterogeneous catalytic reaction where a small steady-state number of continuously renewable sites causes the over-all reaction through the formation of adsorbed intermediates. The active sites on the carbon

surface may therefore be compared to the active sites on a heterogeneous catalyst although in the carbon reaction the formation of a product molecule is not accompanied by regeneration of the old site but by formation of a new carbon atom as an active site, the old active site being permanently lost as a gaseous molecule. Based on this comparison, a 'turnover number' for the reaction may be expressed as follows:

$$\text{TON } (s^{-1}) = \text{Rate of Reaction/ASA}$$

This equation relates the number of product molecules produced per unit time to the number of active sites on the surface. In this calculation the same units must be used for the rate and for the ASA so that the TON has the unit of sec^{-1}. This concept has recently been used by Yang and Wong [67,68], Yang and Yang [69], and Yang [70] in their studies of the gasification of carbon with oxygen, steam and carbon dioxide, using the technique consisting of etch-decoration followed by examination with transmission electron microscopy. Their results showed the development of edge carbon sites as the reaction progressed and they described a turnover frequency as the rate of atoms reacting divided by the number of edge sites.

Values of the TON obtained in the present study are compared with those calculated from the data in the literature in Table 4.1. Values were calculated only for those studies where the ASA of the carbon was reported or a meaningful value could be estimated from the data provided. For the purpose of comparison, the present data were converted to the conditions of temperature and pressure at which the data in the

Table 4.1. Comparison of turnover numbers

T/K	Pressure of oxygen/ Torr	Carbon	Reference	TON/s^{-1}	
					Present Work
648	152	Saran char	Taylor [48]	$6 \rightarrow 4 \times 10^{-5}$	6.8×10^{-5}
773	76	Synthetic Graphite	Gulbransen and Andrew [73]	6.3×10^{-4}	57×10^{-4}
773	20	Graphon	Tucker and Mulcahy [16]	$2.4 \quad 1.8 \times 10^{-4}$	15×10^{-4}
823	152	V3G	Taylor [48]	2×10^{-3}	58×10^{-3}
898	3.9×10^{-2}	Graphon	Laine, Vastola and Walker [37]	4.4×10^{-3}	0.12×10^{-3}
900	30	Pyrolytic Carbon Films	Tong, Pareja and Back [38]	0.15	0.11
919	4.3×10^{-2}	Synthetic Graphite	Bonnetain, Duval and Letort [49]	1.3×10^{-3}	0.22×10^{-3}
923	152	Single-Crystal Graphite	Yang and Wong [67]	0.93	0.99

literature were reported, using the measured activation energy and assuming that the rate of reaction is first-order with respect to oxygen. Because of these extrapolations or interpolations, agreement can only be approximate. In addition, the carbons used in these studies probably contain several types of sites with different reactivities. The TON, calculated from the measured rate, may therefore reflect contribution from a particular type of site or represent the net effect of all classes of sites present. The measurement of the ASA may also, under these situations, be of doubtful significance since whether all sites or only a specific type would be saturated depends upon the conditions of adsorption. These ambiguities may, at least in part, be responsible for the differences in TON between the present results and some of those listed in Table 4.1. Indeed, Yang [70] observed that the turnover frequency for gasification with oxygen on the multilayer edges was higher than that on single-layer edges by about an order of magnitude, and suggested the existence of different types of chemisorbed species as a probable reason for the difference. It should also be mentioned that much greater discrepancies are observed when comparison is made between rates normalized to the weight of carbon used in the experiment. The rates g^{-1} measured with the thin films used in the present experiments are orders of magnitude greater than most of the other values.

4.2 The role of the complex

In this section, the conclusions discussed in the preceding section regarding the role of the complex in the over-all oxidation process are compared with the ideas expressed by other authors, usually from rather

different types of experiments. Attention will be focussed on kinetic studies of the reaction rather than spectroscopic investigations.

Bonnetain et al. [49-52] studied the oxidation of synthetic graphite with oxygen at temperatures between 673-973 K and at pressures in the range 10^{-4}-10^{-1} Torr. They observed that the ratio of CO/CO_2 obtained during the course of oxidation was similar to that found during thermal desorption (at the same temperature) of the stable oxide remaining on the surface after oxidation. This led them to conclude that gasification with oxygen proceeds by continuous formation and decomposition of a surface oxide intermediate. Glassy carbon also demonstrated similar behaviour so that the crystallinity of carbon apparently did not affect the mechanism of oxidation [52]. Bonnetain et al. [49-52] also observed that when the graphite surface was cleaned by outgassing at 1223 K between successive runs, reaction began at a high rate which subsequently dropped to a steady value. The authors attributed the initial high rate to the unsaturated, reactive "dangling" carbon atoms left on the surface after thermal decomposition of the surface oxides.

Tucker and Mulcahy [16], from their studies on the formation of the surface oxide on Graphon by reaction with oxygen at 773 K followed by desorption at 873-1023 K, suggested that the surface complexes have large differences in reactivities depending on the type of carbon site occupied. They proposed the existence of labile sites and differentiated among arm-chair, zig-zag and labile sites. The yield-time curve of their reaction was similar to that observed by Bonnetain et al. [49-52], and was characterized by a fast, transient rate followed by a slower, steady

rate. The stable surface oxide was observed to form exclusively during the initial transient period of fast reaction. They proposed the following mechanism

$$\gg C + O_2 + C^{*}— \longrightarrow \; > (CO)_C + CO(g) \qquad (7)$$

where C* represents a 'labile' atom (initially present on the surface) and C an arm-chair atom. Thus the initial fast transient reaction corresponded to the formation of the stable complex at an arm-chair atom. They further concluded that only at higher temperatures (above 820 K) would this oxide descrb, generate another labile atom and allow oxidation to continue. At low temperatures where desorption does not occur the reaction would cease when all the labile atoms had reacted. To explain the experimental fact that gasification did continue at a steady rate at 773 K after the surface had become saturated with the oxide, they suggested that direct gasification at the zig-zag edges of carbon surface could occur without the intermediate formation of the surface oxide. In the present study a fast transient rate, which in the experiments of both Bonnetain et al. [49-52] and Tucker and Mulcahy [16] were a few 10-fold higher than that of the subsequent steady rate, was not observed under any conditions so that the presence or generation of surface irregularities such as 'dangling' or 'labile' carbon atoms need not be postulated. Rodriguez-Reinoso, Thrower and Walker [71] who also observed an initial fast transient rate with pyrolytic graphite, but only with a new specimen and not after desorption of the complex at 1223 K, suggested that the surface irregularities described above may be introduced during cutting or polishing of a graphite sample. Therefore, it may not be

surprising that the carbon films produced by decomposition of methane do not retain labile or dangling atoms. Nevertheless, the idea of the involvement of the surface complex in the oxidation process suggested in the present study is consistent with the view of Mulcahy and Tucker [16] that to sustain oxidation the formation and decomposition of the stable complex is essential. Reaction (4) of the present scheme is similar to reaction (7) except that in reaction (4) the interaction involves a complex instead of a 'labile' carbon atom.

A somewhat different view of the role of the complex was presented by Walker, Vastola and associates [11,36,37,43-48] from studies of the kinetics of the reaction at low pressures (below 10^{-2} Torr) of oxygen using Graphon. From measurements of the yields of surface complex, carbon monoxide and carbon dioxide as a function of time, Laine et al. [36,37] showed that all three were primary products of the reaction and all rates declined with time in a similar manner. They explained their results by suggesting that the stable complex, rather than being a reaction intermediate, retarded the reaction by occupying a part of the active sites. The reaction occurred through an unstable "fleeting" complex on the part of the surface not covered by the stable complex. The amount of this "fleeting" complex was, however, too small to be measured. The present results are actually not in contradiction to these earlier results when the quantities of products and of complex are compared. In the experiments of Laine et al. [36,37], where the pressure of oxygen was about 10^{-3} Torr, the yields of carbon monoxide and carbon dioxide were both comparable to that of the complex. In the present experiments, the sensitivity of detection for the formation of

carbon monoxide or carbon dioxide (by loss of carbon) was much less than for the formation of the complex (by pressure decrease). Yields of carbon monoxide and carbon dioxide comparable to the amount of complex formed would have been undetectable and could have been formed during the induction period. Yields of carbon dioxide formed after the induction period were considerably greater, as evident from Figure 3.2. This secondary increase was not observed in the experiments of Laine et al. [36,37] because the pressure of oxygen was too low. In fact, it seems likely that reactions (4) and (5) were not important in their system and carbon dioxide was formed by a reaction analogous to reaction (6) as they suggested later [46]. The present results indicate that with pressures of oxygen greater than about 1 Torr, reactions (4) and (5) should be important in the over-all reaction. Subsequent experiments of Vastola, Hart and Walker [43] using O^{18} as a tracer suggested that some direct participation of the stable complex through continuous decomposition and reformation may occur even at pressures of 10^{-3} Torr. Later studies by Rodriguez-Reinoso et al. [71] indeed suggested that at higher pressures of oxygen the role of the strongly-bound complex in the over-all reaction could be different from that at low pressures.

Marsh and Foord [53,54] emphasized the importance of the mobility of the complex in controlling relative yields of the products. Again they concluded that on any carbon surface there must be different types of carbon-oxygen complexes with different degrees of mobility and suggested that the reaction proceeds through the direct participation of these mobile complexes. Marsh [1] summarized these ideas in a general mechanism involving some reactions similar to those of the present

scheme. Substantial evidence for surface diffusion of adsorbed oxygen atoms was provided by two powerful experimental techniques. From results obtained with a modulated molecular beam and pyrolytic graphite, Olander, Seikhaus, Jones and Schwarz [63] proposed a two-site model in which dissociative adsorption and gasification occurs from site A but site B reacts only with adsorbed oxygen atoms which have migrated from site A. Yang and Wong [67] used the etch-decoration technique with transmission electron microscopy and a single-crystal graphite. They interpreted their results to indicate two independent pathways for reaction with the edge carbon atoms, viz. by direct collision of O_2 and by reaction following chemisorption on the basal plane and migration of the adsorbed oxygen atoms. Both these models tacitly assume that gasification occurs through direct involvement of the stable oxygen complex. The idea of the participation of the complex in the gasification process thus permeates the various mechanisms proposed for the reaction. Because the complex may exhibit different characteristics in terms of reactivity or mobility on various types of carbon under different conditions of reaction, the exact manner of its participation is difficult to define. In the present mechanism this problem is partially accommodated through reactions (4), (5) and (6), which represent different types of reactions whose relative importance will be sensitive to experimental conditions of temperature, pressure and characteristics of the carbon surface.

The mechanism proposed is currently being tested by computer modelling techniques in collaboration with Prof. J.M. Roscoe of Acadia University. Although the results of this study do not form part of this thesis, it may be mentioned that the kinetic data are best accommodated

through the introduction of two types of sites on the surface, with different adsorbing properties. The basic mechanism, however, appears to account for the results.

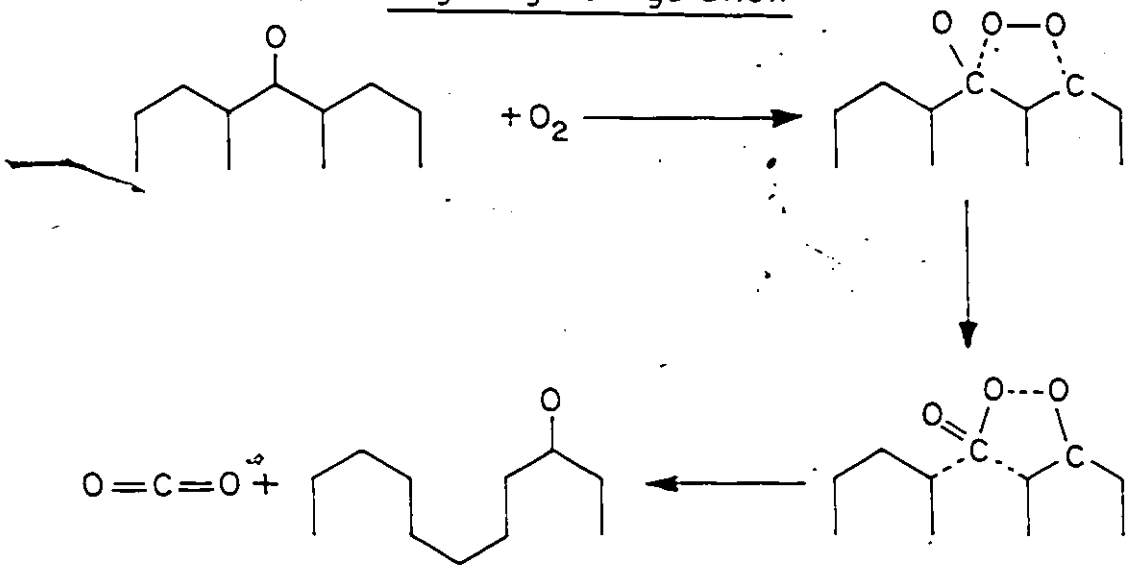
Finally, the reader should not be left here with the impression that the sigmoid-type yield-time curve is characteristic only of thin pyrolytic carbon films used in the present study. When the reaction was accompanied by considerable burn-off, the sigmoid shape of the time course was often observed, for example, with saran char [48], anthracene and phenazine cokes [74] and activated carbons [75]. The mechanism involving secondary interaction of the complex with oxygen proposed in the present study may therefore be applicable to many other types of carbon.

4.3 The effect of temperature

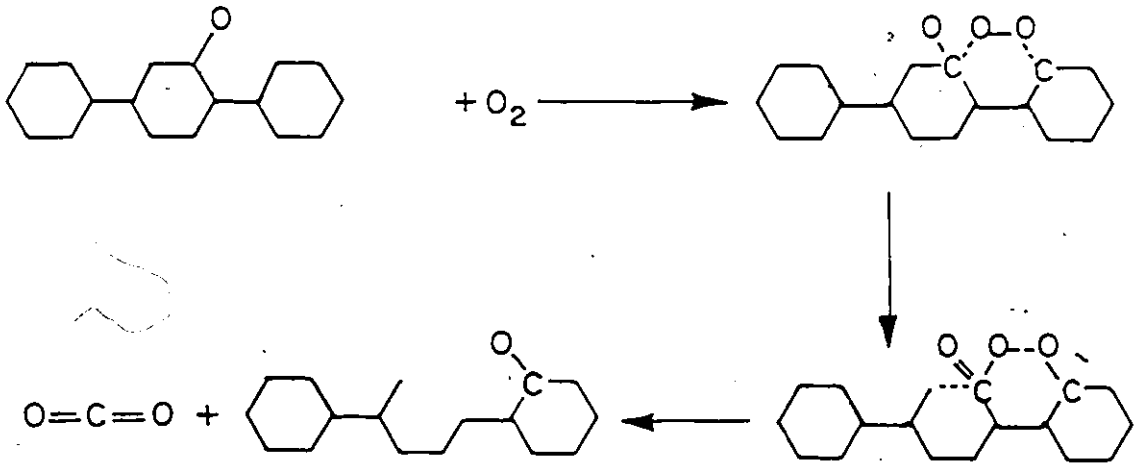
The mechanism outlined in Section 4.1 accounts for many aspects of the dependence of the rate on the temperature. Activation energies for the over-all rate of gasification of carbon with oxygen in the range 40-50 kcal mol^{-1} have been reported. Such values are much lower than the 70 kcal mol^{-1} required for desorption of the complex. The energy barrier for reactions (4) - (5) could be considerably lower than required for simple desorption of the complex. For example, reaction

(4), which may have the highest barrier of these, may be described as follows:

Zig-zag configuration



Arm-chair configuration



In each of these sequences two C-C bonds of graphite and the O_2 bond are broken, while one new carbonyl bond in carbon dioxide is formed, with

possible strengthening in the second, and one new $(CO)_c$ bond of the surface complex is formed. Since the bond strength of the complex is not known, an estimate of the endothermicity can be only approximate. It could, however, be less than for desorption where two C-C bonds of graphite are broken and the carbon monoxide bond is strengthened.

In the present study, the activation energy measured for the production of carbon monoxide over the temperature range 950-1050 K was in the neighbourhood of 70 kcal mol^{-1}. This value is consistent with formation by a direct desorption process, reaction (3). At higher temperatures and at pressures below 1 Torr, the rates of consumption of carbon and formation of products dropped below the values expected from extrapolation of the rates at lower temperatures (Figures 3.6,3.7,3.8,3.12). Similar phenomena, observed in catalytic processes [76], have been explained by depletion of the concentration of a surface intermediate from a critical value required to maintain the reaction. This usually occurs at high temperatures where the rate of dissociation of the intermediate has exceeded its rate of formation, under particular conditions. During the gasification of carbon with oxygen, the complex plays the part of a surface intermediate. Its rate of disappearance both by direct desorption and by secondary surface processes increases with temperature faster than does the rate of adsorption. At some temperature therefore the critical steady-state concentration on the surface may not be maintained, particularly at low pressures. In the present experiments, with pressures of oxygen of 1 Torr, the rate fell below the Arrhenius extrapolation at about 1050 K. This effect is quite different from the decrease in the rate observed in other experiments at

temperatures above about 1200 K which has been accounted for by mass transfer effects [77].

4.4 Summary

Measurements of the formation of the oxygen surface complex and products, carbon monoxide and carbon dioxide, as a function of time along with comparison of the kinetics of the reaction in the presence and absence of the complex have clearly established the direct participation of the complex to a substantial extent in the over-all gasification process. It was suggested that turnover numbers for oxidation could be calculated using the number of active sites, ASA, defined by the formation of the complex and that this quantity provides a better comparison of oxidation rates. A mechanism for the oxidation of carbon was proposed which includes reaction of the complex with oxygen, gaseous or adsorbed, and allows for regeneration of active carbon sites. The relative importance of the various competing reactions leading to gasification will depend on the structural properties of the carbon involved in the reaction as well as the conditions under which the reaction takes place. As a consequence, measured activation energies reported in the literature would be expected to show wide variations, and indeed, values ranging from 40-80 kcal mol^{-1} have been reported [1-3,70]. It is therefore probably not appropriate to argue over a "correct" value or to select a value from the present measurements which may be applicable to only one variety of carbon. On the other hand, investigation into the nature of complexes, particularly the relative stabilities of the complex formed during reactions with both high and low

pressures of oxygen, may provide valuable insights helpful to the development of a general mechanism applicable over extended ranges of temperature and pressure. In this regard, isotopically-labelled oxygen is a useful aid in kinetic studies while improved instruments for measurement of spectra, such as FTIR, will be important in spectroscopic studies.

P A R T II

KINETICS AND MECHANISM OF THE EXPLOSIVE REACTION OF CARBON MONOXIDE AND OXYGEN

CHAPTER 5

INTRODUCTION

In Part I, the kinetics of the reaction of thin films of pyrolytic carbon with pressures of oxygen in the neighbourhood of 1 Torr were examined and a mechanism was outlined which accounted for some important features of the reaction. During these experiments it was observed that as the product carbon monoxide accumulated in the static system, a secondary reaction between the product carbon monoxide and the reactant oxygen sometimes took place. Although this secondary conversion of carbon monoxide was slow under those experimental conditions, it was sufficient to influence the product ratio of the primary oxidation process. When the measurements were extended to higher pressures, it was observed that under certain conditions of temperature and pressure this secondary reaction became so rapid that there appeared no doubt that a gas phase explosion had occurred. Furthermore, the explosion had a dramatic effect on the rate of gasification of the carbon.

The reactions of oxygen with carbon monoxide and hydrogen are of considerable importance both fundamentally and in many industrial applications, but in spite of research dating back to the 19th century, the mechanism of the oxidation of carbon monoxide, including the explosive reaction, is much less clear than that of the oxidation of hydrogen. Because the present experimental method offered a new approach to the study of ignition in mixtures of carbon monoxide and oxygen, with distinct advantages over conventional methods, the measurements were pursued to obtain data covering a wide range of experimental conditions. The results of these studies are described in Part II of this thesis.

The oxidation of carbon monoxide exhibits several interesting features, including spontaneous ignition [78-85], chemiluminescence (or glow) [78,79], and oscillatory behaviour accompanied by chemiluminescence [80,86-88]. The critical conditions for ignition in the carbon monoxide-oxygen system develop through a chain branching reaction mechanism, most convincing evidence for which is the existence of an ignition peninsula with characteristic first and second pressure-temperature limits. Most of the experimental studies on the kinetics of the reaction were made before 1970 and excellent reviews are available [89,90]. The mechanism of the reaction in terms of the elementary steps involved has been discussed by Dixon-Lewis and Williams [91].

Early mechanisms [83,92,93] for the explosion suggested that the branching process involved energy transfer from an electronically excited carbon dioxide molecule by the following sequence of reactions:

$$CO + O \longrightarrow CO_2^*$$

$$CO_2^* + O_2 \longrightarrow CO_2 + 2O$$

It soon became clear, however, from studies by several groups, involving either addition of minute quantities of water [83] or hydrogen [94] to the carbon monoxide and oxygen mixtures or careful reduction of water and hydrogen from the reactants by extensive drying and purification [78,80,81,83], that the position of explosion peninsula was very sensitive to the presence of small amounts of hydrogeneous substances in the system. The peninsula shifts markedly to higher temperatures or contracts significantly as the amount of moisture and other hydrogeneous

materials are reduced. For example, Dickens, Dove and Linnett [80] have shown that the second explosion limit could be displaced to higher temperature by more than 100 K by extensive purification and drying of reactants by fractional distillation and storage at liquid oxygen temperatures. This great sensitivity of explosion limits towards hydrogen containing substances implied that these materials were involved in the chain branching steps. Since only traces of these hydrogeneous compounds may be sufficient to cause explosion and since such amounts, particularly of water, are always present in typical reaction systems, branching by the energy transfer step has generally been rejected in favour of reactions involving hydrogeneous substances. The energy transfer process has also been criticized on theoretical grounds [95-97].

It is now generally agreed that in the presence of hydrogeneous substances, the oxidation of carbon monoxide proceeds through the following chain sequence

$$CO + OH \longrightarrow CO_2 + H$$

$$H + O_2 \longrightarrow OH + O$$

This is an alternating (non-branching) chain sequence accompanied by the production of oxygen atoms. The cycle is branching only if oxygen atoms participate in a subsequent reaction producing more OH radicals. In the presence of hydrogen or water, this can be achieved through the following reactions

$$O + H_2 \longrightarrow OH + H$$

$$O + H_2O \longrightarrow 2OH$$

Explosive conditions may develop with even a few ppm of these substances [98,99]. It is interesting to note that carbon monoxide is not directly involved in the branching reaction but is simply oxidized by the alternating chain sequence during the reaction, either slowly or by an explosion.

Most of the investigations on ignitions in mixtures of carbon monoxide and oxygen were directed at determining the explosion limits, particularly the second limit, in terms of temperature and total pressure. Reactant mixtures with ratios of CO/O_2 in the range 2-0.5 were generally used. Two general methods have been used to determine the explosion limits. A reaction mixture of definite composition is admitted to the reaction vessel at a temperature well below the limit (first or second depending on the pressure) followed by a gradual increase in the temperature until explosion occurs. Alternatively, the mixture is admitted at a pressure above the second limit followed by a gradual reduction in the pressure by withdrawal of the mixture until the explosion. The temperature and total pressure at the explosion are thus determined, but if slow reaction occurs, the composition of the mixture is in some doubt.

Computer modelling techniques have been used to explore various aspects of the reaction. Yang [100,101], and Yang and Berlad [97] attempted to predict the explosion limits and the occurrence of glow for a range of composition, water content, surface efficiency, temperature, and pressure but their attention was focussed mainly, with considerable success, on the mechanism of oscillatory behaviour. Pilling and Noyes [95] discussed the effect of thermal gradients created in the reaction

vessel due to the rapidity of exothermic elementary steps. They concluded that these make an important contribution to the development of instability leading to explosion.

Recently, Gray and coworkers [79,85,88] have renewed interest in the reaction, which they describe as a classic unsolved problem in chemical kinetics, by a careful examination of the phenomena of glow, oscillation and explosion associated with the oxidation of carbon monoxide in the presence of various amounts of added hydrogen. Their experiments emphasized continuous monitoring of the concentration of reactants, temperature and pressure of the system and of the intensity of emitted light during the reaction. Their main objective was the demonstration of the relation between glow and ignition and the relation of both to the oscillatory behaviour.

Indeed, much of the attention given to the oxidation of carbon monoxide has centred on the questions of the glow and the oscillations. Perhaps, for this reason the reactions leading to the ignition have not been quantitatively tested in terms of the general equation describing an explosive condition. As discussed earlier, these reactions are believed to be a variation of the hydrogen-oxygen mechanism and rate constants of these elementary steps are generally reliable. Previous studies, however, have not led to quantitative measurements of the concentrations of reactants at the instant of explosion. The present method has overcome this limitation and one of the main objectives has therefore been to test the mechanism under all experimental conditions through the application of the general equation for an explosion.

During the reaction of oxygen with the thin film of carbon the products carbon monoxide, carbon dioxide and small quantities of water, formed from traces of hydrogen in the carbon film were continuously formed and monitored. Thus measurement of the concentrations of products and reactants was obtained at the instant of explosion.

Explosions took place with ratios CO/O_2 far below those used in any previous study. The additives hydrogen, methane and water promoted the onset of an explosion. The effect of inert gases changed from inhibition at low temperatures to promotion at high temperatures. Low pressure explosion limits, hitherto difficult to measure on a bare quartz surface, were conveniently obtained on the carbon-coated vessel. All the explosions under all conditions of temperature, pressure and reactant concentration used in the present study were accounted for by a simple mechanism involving the branching reactions mentioned earlier, together with suitable termination reactions.

CHAPTER 6

EXPERIMENTAL

6.1 Apparatus

The apparatus used for these experiments has been described in Part I. A modification was made to reduce the volume of the reaction vessel connected to the manifold. The vessel was connected by a 3-way stopcock either to the manifold or to a pressure transducer (MKS Baratron Model 223B, maximum range of 1000 Torr, accuracy 0.25% of the reading). The gauge was operated either absolutely or differentially to follow the pressure in the system during the reaction. The volume of the vessel, as mentioned in Part I, was 149 cm^3 and the volume of the manifold containing the pressure gauge was 10 cm^3.

6.2 Materials

Research grade methane and carbon monoxide (both minimum purity 99.99%) were obtained from Matheson Gas Products Canada, Whitby, Ontario. Carbon dioxide also with a minimum purity of 99.99% was supplied by Union Carbide Canada Limited, Toronto. Oxygen, hydrogen and helium (Industrial high purity grade, purity 99.6%, 99.95% and 99.995% respectively) were obtained from Air Products and Chemicals, Inc. All gases were used as received, except passage through two dry ice traps (195 K) to exclude water*, before admission to the reaction vessel.

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* The vapour pressure of water at 195 K is about 5.6×10^{-4} Torr [102].

Mixtures of additives, usually about 0.1% additive in oxygen, were prepared by introduction of the additive into a spherical flask with minimal dead space followed by addition of the larger pressure of oxygen. All mixtures were allowed to stand overnight to ensure complete mixing. Before preparation of mixtures of water with oxygen, the flask was allowed to remain in contact with about 10 Torr of water vapour (much larger than required to make mixtures of desired composition) overnight. This procedure was an attempt to counteract the slow loss of water from the mixtures by adsorption on the walls of the flask and the manifold containing the pressure transducers. Overnight contact with water vapour reduced this rate of loss to a negligible amount. Furthermore, the mixtures were used for reactions immediately after preparation.

6.3 Formation and detection of the carbon film

Thin films of carbon were deposited, treated and calibrated according to the procedures described in Part I. Most of the experiments were made using films with a total amount of carbon of 3.3×10^{-5} mol (2.0×10^{-7} mol cm^{-2}), which corresponds to an average thickness of about 12 nm. In some experiments, a film of about twice this thickness was used. It should be pointed out that the outgassing of the film at 1223 K for 1.5 hours, as described in Part I, removed adsorbed or occluded hydrogen or other gases so that subsequent evolution of hydrogen at the temperature of the reaction was negligible. The films nevertheless retained small amounts of hydrogen bonded to the carbon as remnants from the polyaromatic precursor molecule. As discussed later, this hydrogen is released into the system as water during the reaction with a large excess of oxygen.

6.4 Experimental procedure

Reaction was commenced by the introduction of the desired pressure of reactant or mixtures of reactants into the quartz vessel coated with the carbon film as described. Both the consumption of carbon, from the absorbance of the film, and the change in pressure in the system from initial value were monitored continuously throughout the course of the reaction and recorded simultaneously with a two-pen strip chart recorder. From these measurements the yields of products, carbon monoxide and carbon dioxide were obtained through the following equations,

$$\Delta n_C = n_{CO} + n_{CO_2} \qquad (6.1)$$

$$\Delta P = \tfrac{1}{2} CO \qquad (6.2)$$

where Δn_C is the molar loss of carbon and n_{CO} and n_{CO_2} are the number of moles of carbon monoxide and carbon dioxide produced in the reaction. The equation (6.2) neglects the formation of water, since, as shown later, the amount is small compared to the yield of carbon monoxide.

The accuracy of measurement of carbon monoxide depends on the measurement of ΔP. Since the yield of carbon monoxide, and hence ΔP is roughly the same in all experiments (2-3 Torr), the fractional change in the total pressure therefore decreases as the pressure of reaction is increased and the measurement of ΔP becomes less accurate at higher pressures. In the range of pressure where explosion was observed (<100 Torr), the uncertainty in the measurement of carbon monoxide, taking into account fluctuations in temperature, was less than 5%.

Figure 6.1 shows the chart record of a portion of the time course of a typical experiment leading to an explosion. As the reaction proceeds,

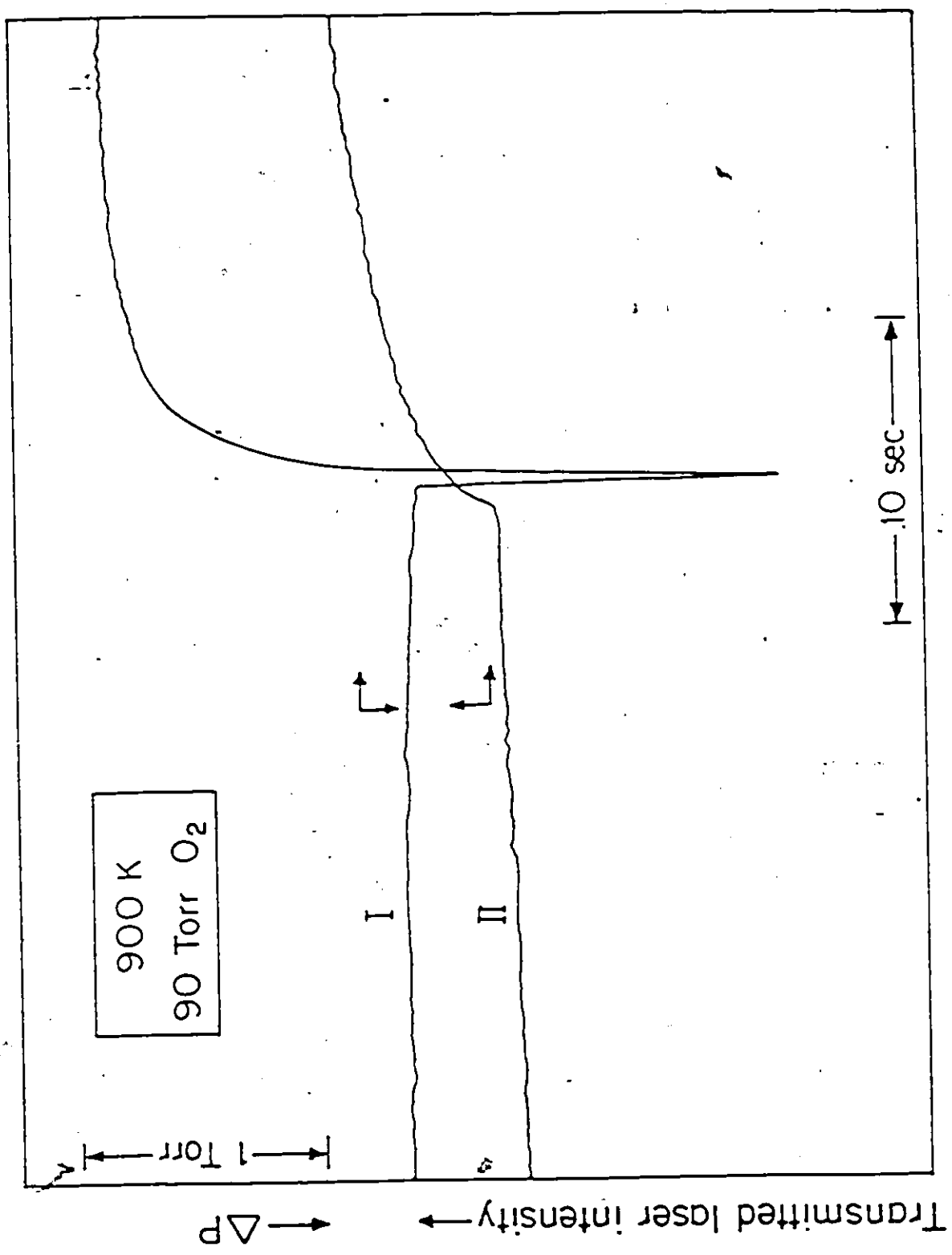


Figure 6.1. Chart-record of the time course of an experiment leading to an explosion.

I: Increase in the pressure; II: Increase in the intensity of the transmitted laser beam.

the intensity of the transmitted laser beam and the pressure in the system increase smoothly. After the reaction of a certain amount of carbon (the amount depending on the conditions of experiment), this smooth continuous course of the reaction was interrupted by a sudden drop in pressure, almost to the initial value, indicating complete conversion of carbon monoxide to carbon dioxide. The conversion typically took place in a fraction of a second, indicating, as discussed by Bond, Gray and Griffiths [79] that an ignition has occurred. A momentary jump in pressure immediately preceding the pressure drop, which has also been observed in previous studies [78-80] of the explosion, has been explained by Bond et al. [79] as the consequence of a temperature pulse due to the exothermic reactions associated with explosion. This pressure pulse is, in fact, a further confirmation of the occurrence of an ignition [79]. In the present study, no attempt was made to measure the increase in temperature. Nevertheless, a rough estimation from the magnitude of ΔP indicated that the momentary rise in temperature could, in some instances, be greater than 50 K. Figure 6.1 also shows that the explosion was accompanied by a dramatic increase in the rate of gasification. This aspect will be discussed further in Part III.

At the end of a reaction (with or without explosion), the products carbon monoxide and carbon dioxide were analysed by gas chromatography (Part I) after removal of water by trapping at 195 K. The quantity of water was then measured by expansion into a calibrated volume and the pressure measured with a pressure transducer (Baratron model 222A) with maximum pressure range 10 Torr. However, the accuracy of this measurement of water is questionable because of loss by adsorption on the walls, and probably represents a lower limit.

CHAPTER 7

RESULTS

This chapter describes measurements of the kinetics of the reaction of oxygen with the film of carbon in the temperature range 848-1048 K with pressures of oxygen between 5 and 700 Torr. Below 900 K explosion was not observed and these experiments will not be discussed further here. Carbon monoxide and carbon dioxide were both major products of the reaction at all temperatures of the present investigation. Water, formed by the reaction of oxygen with traces of hydrogen in the film, was a minor product. The yield of water, measured after each experiment, was consistently about 1% of the total yields of carbon monoxide and carbon dioxide (by mole) indicating that the carbon film contained about 0.2% hydrogen by weight. Analysis of the water at various stages of the reaction showed that the water was produced continuously throughout the course of the reaction.

7.1 Measurements at 935 K

Since several kinetic features of the reaction were so distinctly seen at 935 K, it is advantageous to discuss the results obtained at this temperature first.

7.1.1 REACTIONS WITH PURE OXYGEN.

Based on the kinetic features of the reaction four regions of pressure, shown in Figure 7.1, may be identified at 935 K.

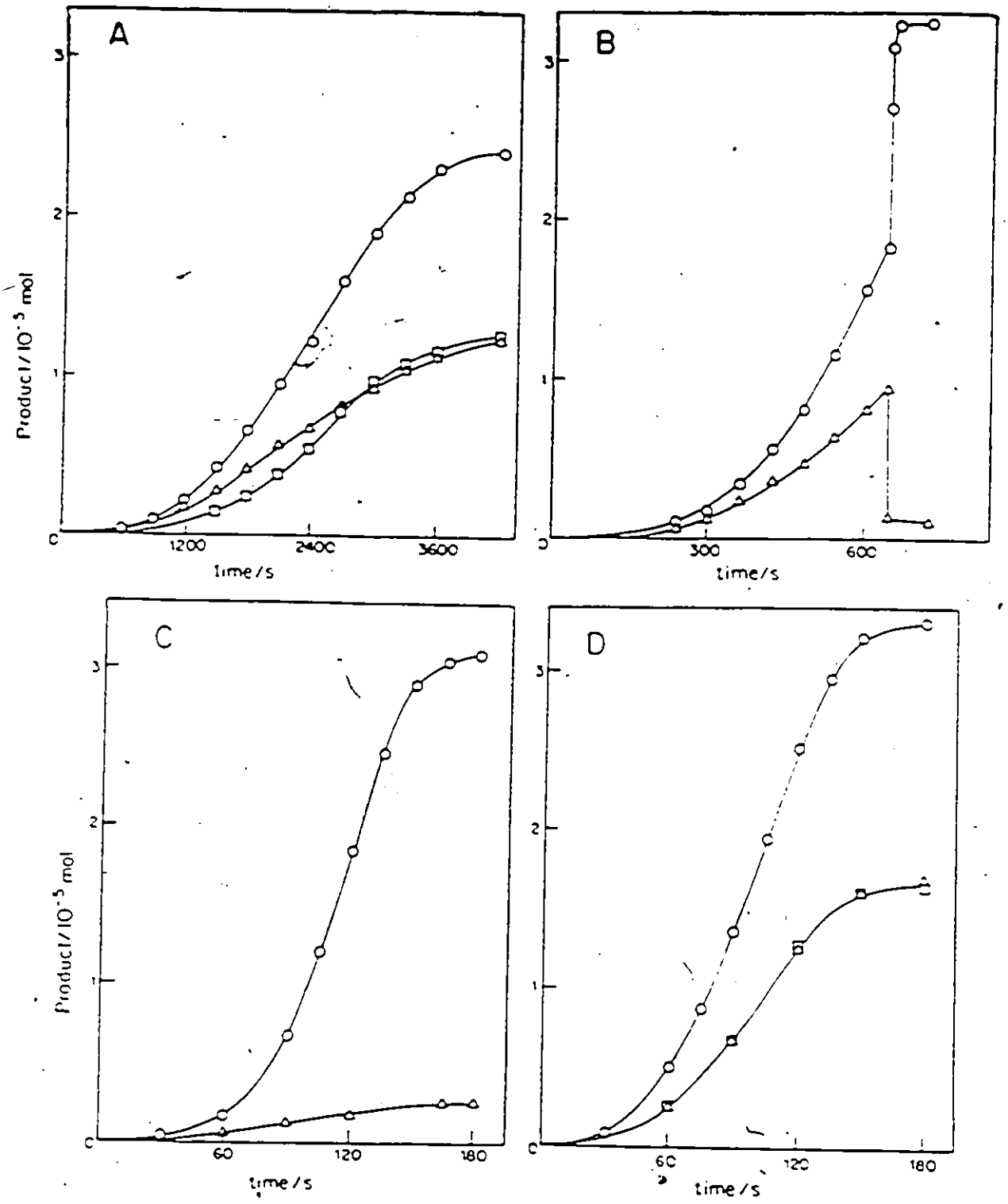


Figure 7.1. Effect of oxygen pressure on the characteristics of the reaction at 935 K. Circles refer to carbon consumed, triangles to carbon monoxide formed and squares to carbon dioxide formed.

Initial pressure of oxygen:

A: 5.2 Torr (Region I);

B: 30 Torr (Region II);

C: 202 Torr (Region III);

D: 410 Torr (Region IV).

In region I, corresponding to pressures of oxygen below 20 Torr (Figure 7.1A), carbon reacted smoothly without explosion at any stage of the complete course of the reaction. The time course of the reaction in this region was characterized by an induction period and a maximum rate, each a function of pressure of oxygen. Carbon monoxide and carbon dioxide were produced in approximately equal amounts at this temperature. This region corresponds to a "normal" reaction between oxygen and carbon. The mechanism of the reaction in this region was described in Part I in terms of various concurrent and consecutive surface processes involving chemisorbed oxygen. The secondary oxidation of carbon monoxide was negligible in this region.

The second region, which is the major region of interest of this study, roughly covered the pressure range 20-100 Torr. In this region an explosion occurred, as illustrated in Figure 7.1B, after the reaction of a particular amount of carbon. The amount decreased with increasing pressure of oxygen (Table 7.1). At the explosion, carbon monoxide was instantaneously converted to carbon dioxide and at the same time the rate of removal of carbon was increased dramatically. This effect of the gas phase explosion on the rate of reaction of carbon with oxygen will be further discussed in a later chapter.

In region III, corresponding to pressures of oxygen above 100 Torr and below 400 Torr, explosions were not observed, but the yield of carbon monoxide remained low ($< 10\%$) throughout the complete course of carbon consumption (Figure 7.1C). The main product of reaction was therefore carbon dioxide.

Table 7.1.* Effect of pressure of oxygen on conditions at the onset of explosion at 935 K

$[C]^{\circ} = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr	Conditions at explosion			
O_2	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
20	3.20	0.21	5.5	11.9
30	1.85	0.12	3.0	25.9
30	1.95	0.13	3.1	24.9
30	1.85	0.12	2.9	25.9
45	0.90	0.060	1.5	43.0
60	0.50	0.032	0.8	59.5
60	0.50	0.032	0.9	58.9
101	0.25	0.016	0.6	100.5

* In this and the following tables in this chapter, the pressure of water was calculated from the relation $H_2O/\Delta C = 0.02$, which will be discussed in Chapter 8.

Beyond 400 Torr of oxygen, region IV, the carbon-oxygen reaction returned to its "normal" behaviour. The yield-time curve did not show any irregularities and, as in region I, both carbon monoxide and carbon dioxide were formed in comparable amounts. Thus the distribution of the products in regions I and IV and also in region II (before explosion) contrasts sharply with that in region III.

It should be pointed out that since the experiments were performed only at selected pressures, the range of pressure ascribed to each region is approximate only.

7.1.2 EFFECT OF ADDITIVES

A. Pressure range 20-100 Torr (Region II)

1. Addition of carbon monoxide

In this region, with increasing initial pressure of oxygen, explosion occurred at lower consumption of carbon and therefore at lower pressure of carbon monoxide. The question then arises, whether the consumption of carbon or the partial pressure of carbon monoxide is the critical factor leading to an explosion. This was tested at two initial pressures of oxygen. Mixtures of carbon monoxide in oxygen (2-20%) were prepared for reaction with the carbon film. At each initial pressure of oxygen, as shown in Table 7.2, explosions occurred after the reaction of nearly the same percentage consumption of carbon even though the concentration of carbon monoxide in the mixtures was different by a factor as large as about 3. It was therefore concluded that the conversion of carbon is the critical factor for the explosion. This may be understood from the estimation of the formation of water, which was

Table 7.2. Effect of pressure of carbon monoxide on conditions at the onset of explosion at 935 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr		Conditions at explosion			
O_2	CO	n_C/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
30	0	1.85	0.12	2.9	25.9
30	0.8	1.80	0.12	3.5	25.0
30	1.6	1.60	0.10	4.1	26.3
30	1.6	1.70	0.11	4.0	25.5
30	6.0	1.40	0.09	8.1	26.7
60	0	0.50	0.032	0.8	59.5
60	0.6	0.70	0.045	1.6	58.6
56	1.5	0.70	0.045	2.4	52.6

proportional to the consumption of carbon. The concentration of water is therefore more important for attaining an explosion condition than the concentration of carbon monoxide.

2. Addition of inert gases

Mixtures of oxygen and helium (1:1), and oxygen and carbon dioxide (1:1) and (1:3) were used for reaction with partial pressures of oxygen of 30, 60 and 100 Torr. In this region, the presence of inert gas inhibited or prevented explosion until a greater amount of carbon had reacted compared to that reacted with pure oxygen. A typical set of experiments illustrating this retarding action of inert gases is shown in Figure 7.2. Carbon dioxide was a more effective inhibitor than helium. The results are given in Table 7.3. Two points are significant.

a. The inhibitive effect was more pronounced at higher pressures of oxygen. For example, with a 1:1 oxygen-carbon dioxide mixture, little effect on the explosion conditions was observed with an initial pressure of oxygen of 30 Torr. With 60 Torr of oxygen the explosion was clearly inhibited while with 100 Torr no explosion at all was observed.

b. At the same partial pressure of oxygen, increasing amounts of an inert gas caused increasing inhibition of the explosion. For instance, addition of 30 Torr of carbon dioxide to 30 Torr of oxygen had a measurable retarding effect while addition of 90 Torr prevented explosion altogether.

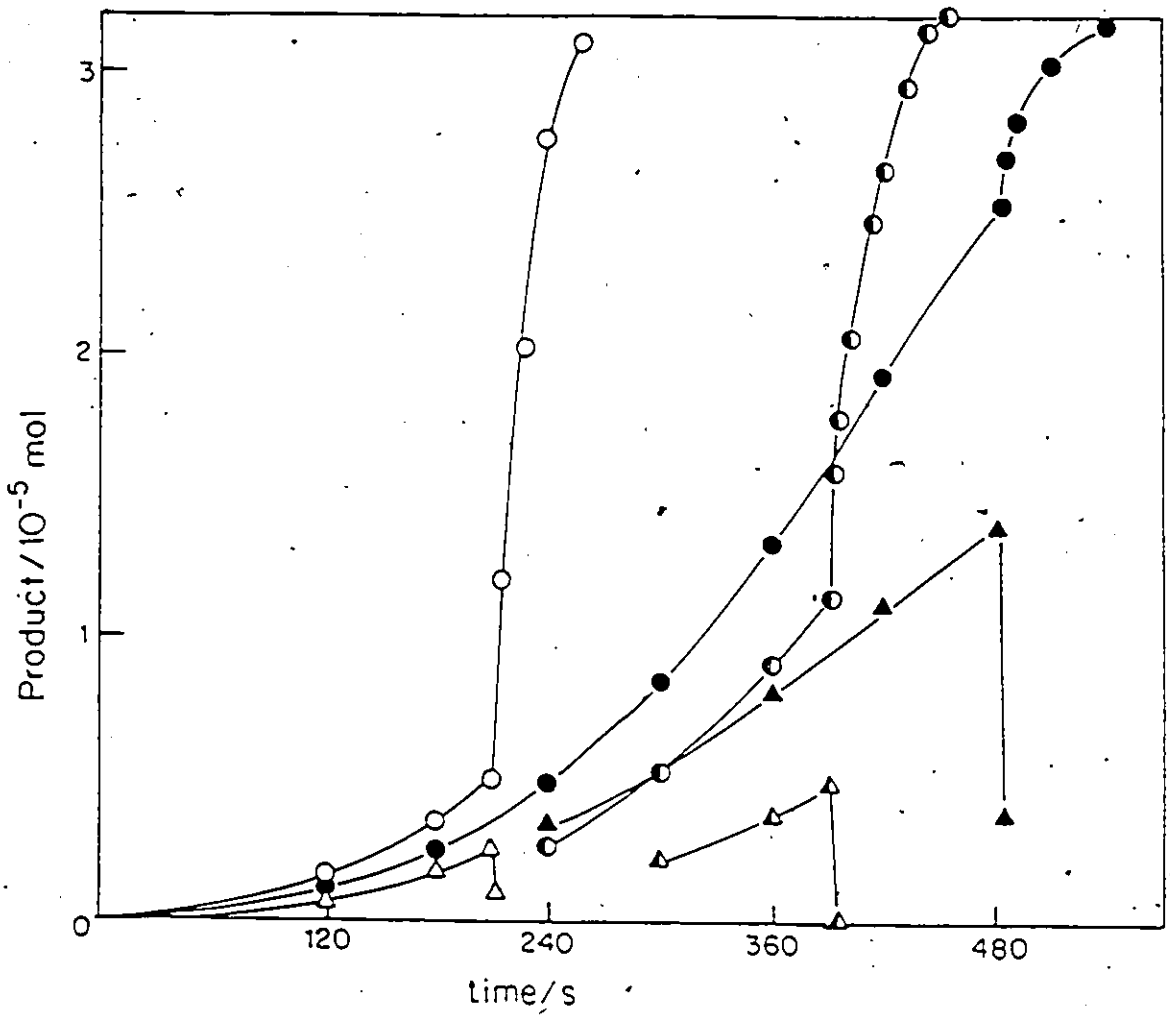


Figure 7.2. Effect of inert gases in region II at 935 K. Circles refer to carbon consumed and triangles to carbon monoxide formed. Initial pressure of oxygen: 60 Torr. Some points in the early stages have been omitted for clarity.

○, △ : O_2; ◐, ◭ : O_2 + He (1:1); ●, ▲ : O_2 + CO_2 (1:1).

Table 7.3. Effect of inert gases on conditions at the onset of explosion at 935 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr		Conditions at explosion			
O_2	Inert gas	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
30	-	1.95	0.13	3.1	24.9
30	30 (He)	2.30	0.15	3.5	24.2
30	30 (CO_2)	2.40	0.15	4.0	24.3
30	90 (CO_2)	No explosion observed			
60	-	0.50	0.032	0.9	58.9
60	60 (He)	1.15	0.074	1.6	57.0
60	60 (CO_2)	2.50	0.16	4.5	53.2
100	-	0.25	0.016	0.6	100.5
100	100 (He)	0.70	0.045	1.2	96.3
100	100 (CO_2)	No explosion observed			

3. Addition of chain-branching agents: hydrogen, methane and water vapour

The effects of these additives on the onset of explosion in region II were investigated using mixtures of oxygen and hydrogen (0.1%), oxygen and methane (0.1%) and oxygen and water (0.3%) at two initial pressures of oxygen. A summary of the results showing the amount of carbon consumed prior to the explosion with different additives is given in Table 7.4. Each of these additives had the effect of inducing an ignition at lower extent of reaction than observed with pure oxygen at the same pressure. In other words, the mixture of reactants and products formed in the presence of each of these additives was more explosive than the mixture formed in its absence. Hydrogen and methane were about equally effective, and more effective than water, as illustrated in Figure 7.3.

B. Pressure range 100-400 Torr (Region III)

1. Addition of carbon monoxide

As shown in Figure 7.1C, the yield of carbon monoxide was barely detectable throughout the course of the reaction. The effect of addition of carbon monoxide to the reactant (0.5%) in this region is shown in Figure 7.4. It is clear that the added carbon monoxide was rapidly oxidized to carbon dioxide even at a very low conversion of carbon. It may therefore be concluded that the low yield of carbon monoxide in this region is the consequence of a rapid secondary conversion of carbon monoxide to carbon dioxide rather than a low primary yield of carbon monoxide.

Table 7.4. Effect of chain-branching additives on conditions at the onset of explosion at 935 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 mm)

Initial pressure/Torr		Conditions at explosion			
O_2	Additive	n_C/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
	-	1.95	0.13	3.1	24.9
30	0.03 (H_2)	0.85	0.055	1.2	28.4
30	0.03 (CH_4)	0.45	0.029	0.7	29.7
30	0.09 (H_2O)	0.50	0.032	1.1	29.6
60	-	0.50	0.03	0.8	59.5
60	0.06 (H_2)	0.1	0.007	0.2	59.8
60	0.06 (H_2O)	0.1	0.007	0.1	60.0

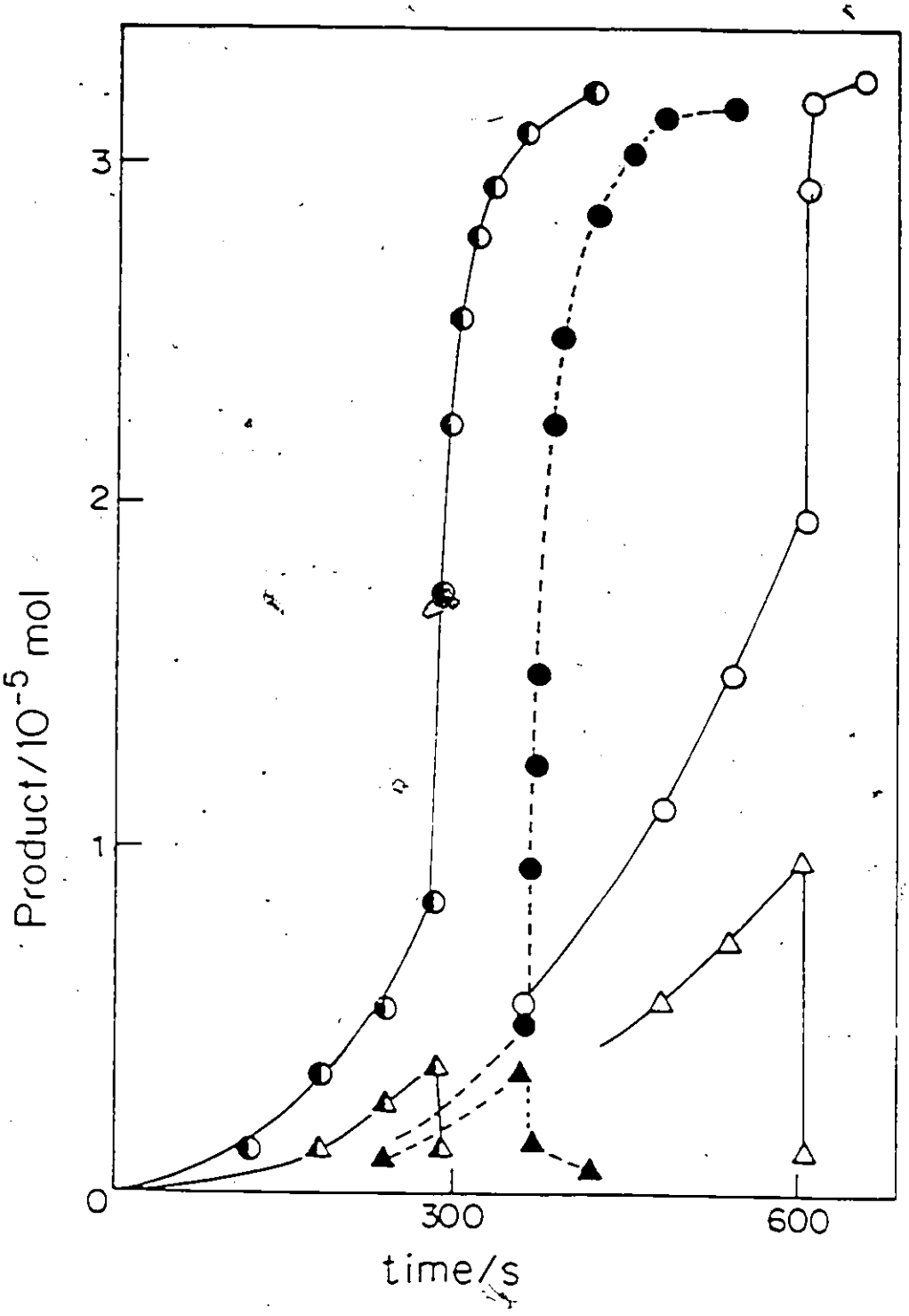


Figure 7.3. Effect of the additives, hydrogen and water, in region II at 935 K. Circles refer to carbon consumed and triangles to carbon monoxide formed. Initial pressure of oxygen: 30 Torr. Some points in the early stages have been omitted for clarity.

○, △ : O_2; ◐, ◭ : O_2 + 0.1% H_2; ●, ▲ : O_2 + 0.3% H_2O.

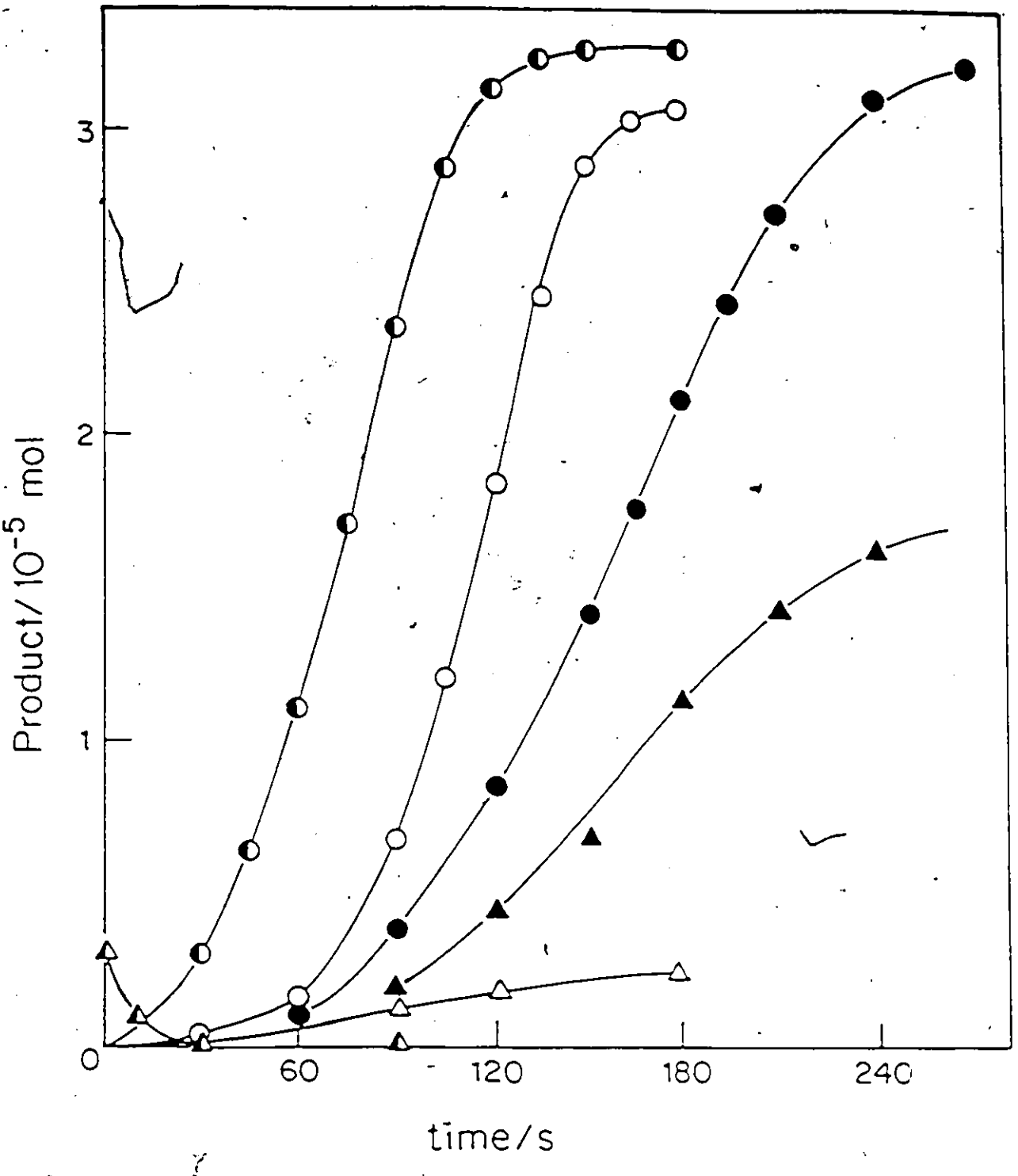


Figure 7.4. Effect of addition of carbon monoxide and carbon dioxide in region III at 935 K. Circles refer to carbon consumed and triangles to carbon monoxide formed. Initial pressure of oxygen: 200 Torr.

○, △ : O_2; ◐, ◭ : O_2 + 0.5% CO; ●, ▲ : O_2 + CO_2 (1:1).

2. Addition of inert gas

Addition of carbon dioxide to oxygen (1:1) in this region had the effect of displacing the reaction into region IV, also illustrated in Figure 7.4. In the presence of added carbon dioxide, the product carbon monoxide accumulated in the system in amounts comparable to the yield of carbon dioxide from the reaction; it was no longer consumed in a rapid secondary process which kept its yield low throughout the reaction.

3. Addition of hydrogen

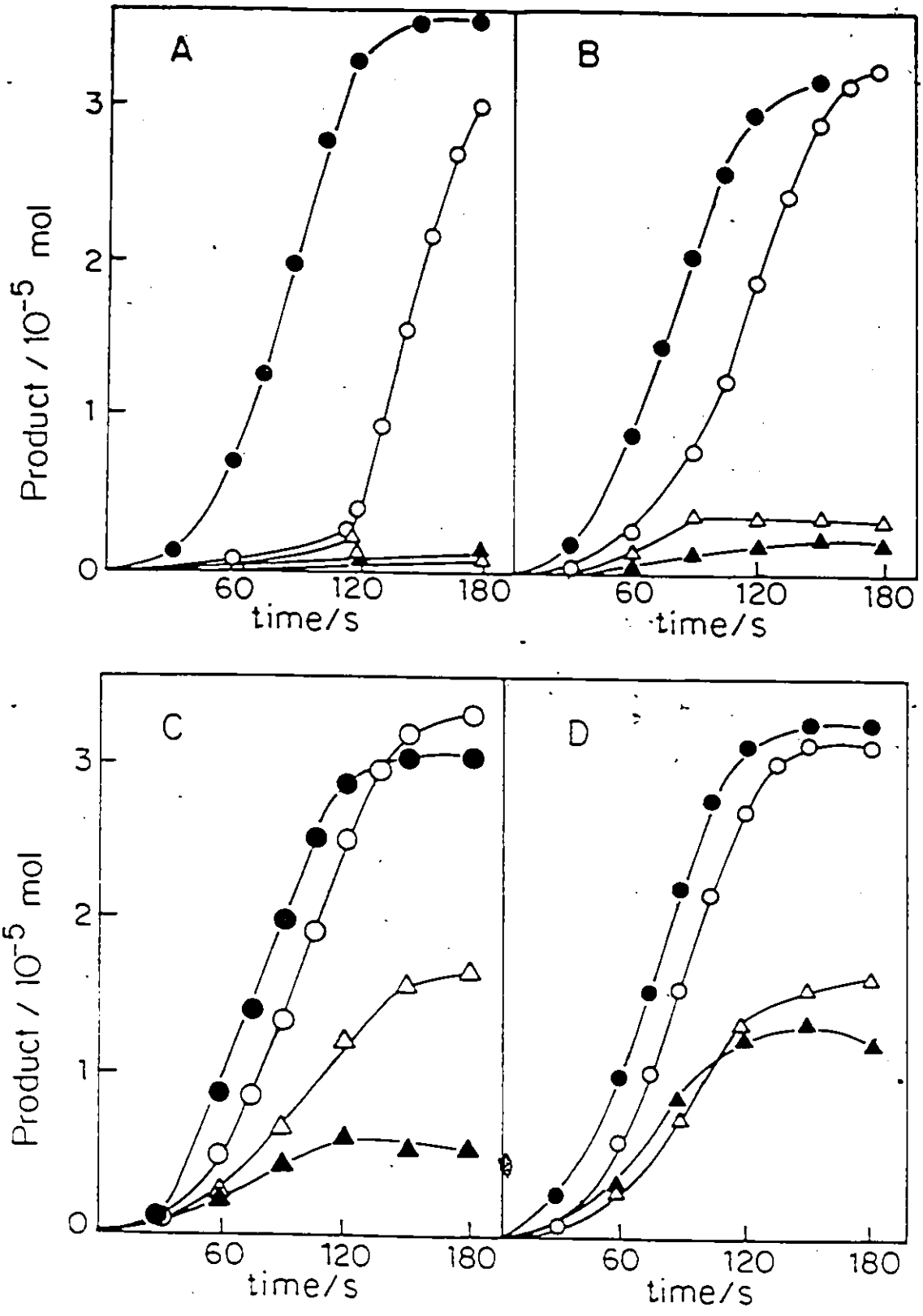
In region II, addition of hydrogen (0.1%) to the reaction mixture caused an explosion after the reaction of a relatively smaller amount of carbon. In region III, where a rapid secondary conversion of carbon monoxide to carbon dioxide occurred, addition of hydrogen caused this conversion to commence at a lower extent of carbon consumption. Thus the effect of hydrogen in region II and III is qualitatively similar. This can be best appreciated by comparison of the reaction in the presence and absence of hydrogen at four pressures, as shown in Figure 7.5. With 100 Torr of oxygen (about the limit of pressure where an explosion was observed), only very little carbon monoxide accumulated in the reaction vessel before the occurrence of the explosion (Figure 7.5A). In the presence of hydrogen, no explosion was observed but rapid secondary reaction occurred at even lower conversion of carbon and the yield of carbon monoxide remained barely detectable throughout the course of the reaction. At 300 Torr (region III in pure oxygen) the presence of hydrogen shortened the induction period (Figure 7.5B), but the maximum rate of carbon disappearance was similar to that observed in pure oxygen.

Figure 7.5. Effect of addition of hydrogen on the reaction in the various regions at 935 °. Circles refer to carbon consumed and triangles to carbon monoxide formed.

Initial pressure of oxygen:

A: 100 Torr; B: 300 Torr; C: 400 Torr; D: 550 Torr.

○ , △ : O_2; ● , ▲ : O_2 + 0.1% H_2.


A
B
C
D
Product / 10^{-5} mol
time/s
0
1
2
3
60
120
180

At 400 Torr in the presence of hydrogen (Figure 7.5C), significant amounts of carbon monoxide accumulated during the reaction, indicating partial transition into region IV. At 550 Torr (region IV in pure oxygen), the effect of hydrogen was no longer significant (Figure 7.5D).

Figure 7.5 emphasizes the gradation in the effect of hydrogen with increasing pressure of oxygen, which is consistent with the action of hydrogen in inducing an explosion or increasing the secondary conversion of carbon monoxide to carbon dioxide. It is clear from the figure that addition of hydrogen expands the range of pressure corresponding to region III at both lower and upper boundaries. The results obtained with oxygen-hydrogen mixtures at 400 and 550 Torr also illustrates the fact that the transition from region III to IV is not sharp but occurs gradually over a range of pressure.

7.1.3 EXPERIMENTS WITH THICK CARBON FILMS (AT 935 K)

Experiments described so far were performed using carbon films of thickness about 12 nm (henceforth called thin films). A corresponding series of experiments was done using films with approximately twice the amount of carbon (24 nm thickness). Qualitatively, the results were similar to those obtained with the thin films. Reactions with characteristics of all four regions of pressure were observed. Explosions were observed with pressures of oxygen of 30 and 60 Torr (Region II) but in both cases, as shown in Table 7.5, ignition took place after the reaction of a smaller amount of carbon than observed with the thin films. This result is explained by the observation that proportionally more water was formed from oxidation of the thick film.

Table 7.5. Effect of the thickness of the film on conditions at the onset of explosion at 935 K

Initial pressure/Torr		Conditions at explosion							
		Thick Film (6.5×10^{-5} mol)*				Thin film (3.2×10^{-5} mol)			
O_2	Inert gas	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
30	-	0.70	0.09	2.3	29.9	1.85	0.12	3.0	25.9
30	30 (CO_2)	0.95	0.12	3.6	29.4	2.40	0.15	4.0	24.3
60	-	0.20	0.026	0.5	60.1	0.50	0.032	0.8	59.5
60	60 (CO_2)	1.00	0.13	3.6	58.5	2.50	0.16	4.5	53.2

* In this table and Table 7.7, the pressure of water for thick films was calculated from the relation $H_2O/\Delta C = 0.04$, which will be discussed in Chapter 8.

At 200 Torr carbon monoxide was confined to a low level during the complete course of the reaction (Region III), and above 400 Torr the reaction returned to "normal" behaviour with continuous accumulation of carbon monoxide and carbon dioxide (Region IV). Addition of carbon dioxide in region II prevented explosion until a greater extent of carbon consumption and the effect was greater at higher pressures. Addition of 200 Torr of carbon dioxide to 200 Torr of oxygen caused the characteristics of the reaction to shift from region III to region IV, as shown in Figure 7.6.

7.2 Measurements at 900 K

The results of the measurements at 900 K were, broadly speaking, similar to those obtained at 935 K. The results will therefore be described briefly, emphasizing the differences observed at the lower temperature.

Explosions were observed in the region of pressure of oxygen 40-120 Torr with a film of thickness of 12 nm. At the lower temperature, region II was thus shifted to higher pressures. At 935 K the extent of carbon consumption prior to the onset of explosion decreased sharply as the pressure of oxygen was increased (Table 7.1). The effect was much less pronounced at 900 K and in fact, the amount of carbon consumption passed through a minimum as the pressure of oxygen was increased (Table 7.6A).

With pure oxygen region III was not observed. Explosion was observed at 120 Torr but at 150 Torr carbon monoxide and carbon dioxide were produced in comparable amounts throughout the course of the reaction, indicating entry into region IV of the reaction. Nevertheless,

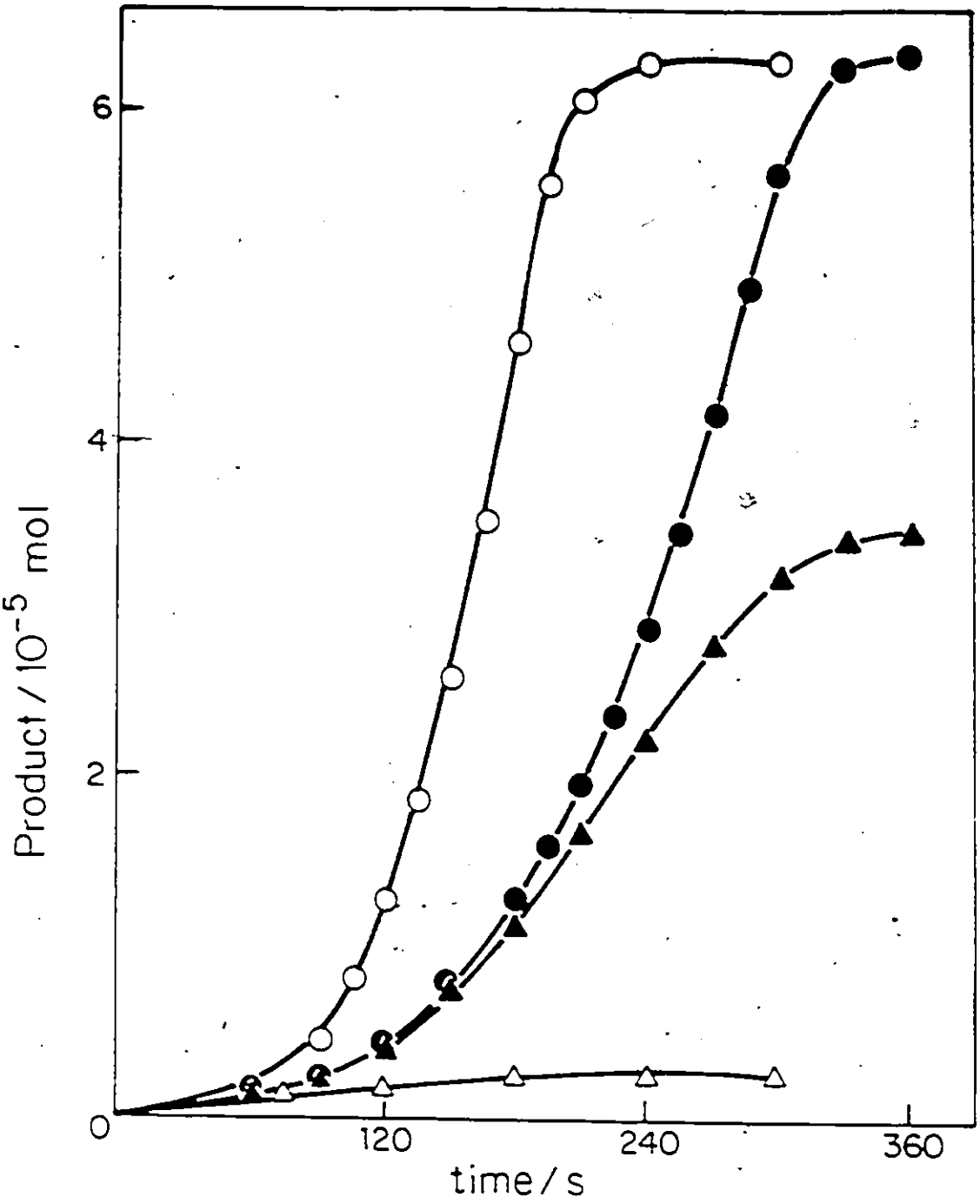


Figure 7.6. Reaction on the thick film of carbon (24 nm) at 935 K. Shift from region III to region IV by addition of an equimolar amount of carbon dioxide to 200 Torr of oxygen. Circles refer to carbon consumed and triangles to carbon monoxide formed.

○, △ : O_2; ●, ▲ : $O_2 + CO_2$ (1:1).

Table 7.6. Effect of oxygen and of various additives on conditions at the onset of explosion at 900 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr		Conditions at explosion			
		n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
A. Effect of oxygen					
O_2					
45		3.20	0.20	4.9	39.4
60		3.00	0.19	4.5	51.8
90		2.40	0.15	3.4	84.0
120		2.70	0.17	3.7	113.5
B. Effect of chain-branching additives					
O_2	additive				
45	-	3.20	0.20	4.9	39.4
45	0.045 (H_2)	0.80	0.050	1.2	43.1
45	0.045 (CH_4)	0.40	0.025	0.5	43.2
45	0.45 (H_2O)	2.85	0.22	4.4	38.4
45	0.135 (H_2O)	1.20	0.21	1.5	41.8
90	-	2.40	0.15	3.4	84.0
90	0.090 (H_2)		shift into Region III		
90	0.090 (CH_4)		shift into Region III		
90	0.090 (H_2O)	0.45	0.12	0.9	86.6
90	0.270 (H_2O)		shift into Region III		
C. Effect of carbon monoxide					
O_2	CO				
90	-	2.35	0.[illegible]	3.2	81.7
90	2.3	2.25	0.14	5.7	84.2
90	4.6	2.70	0.17	8.3	83.7
120	-	2.70	0.17	3.8	113.5
120	3.2	2.50	0.16	6.9	117.9
120	6.3	3.00	0.19	10.7	116.2

on addition of water, methane and hydrogen to 90 Torr of oxygen, a gradual shift in the characteristics of the reaction from those of region II to those of region III occurred, as illustrated in Figure 7.7. In the presence of added water (0.1%), explosion occurred at a lower conversion of carbon than with pure oxygen. In the presence of hydrogen an explosion was not obvious, but the rate was much faster than with pure oxygen and the concentration of carbon monoxide remained low throughout the reaction (Region III). The results are summarized in Table 7.6B.

At 150 Torr in the presence of hydrogen (0.1%), behaviour corresponding to region III was observed whereas with pure oxygen the reaction was in region IV (Figure 7.8A). At 240 Torr the yield of carbon monoxide was significant but still lower than observed with pure oxygen (Figure 7.8B). At 400 Torr (Figure 7.8C) the reaction had the characteristics of region IV both in the presence and absence of hydrogen. Except for a slight reduction in induction period, there was hardly any effect of added hydrogen on the course of the reaction. These results again illustrate that as at 935 K the shift in the characteristics of the reaction from region III to IV was a gradual change.

In the present study, 900 K was the lowest temperature at which explosions were observed. With pure oxygen at 883 K and at all pressures up to 700 Torr, the reaction had the characteristics of region I (or IV). Thus a gradual change in the reaction was observed as the temperature was increased from 883 K, only region I (or IV), to 900 K, regions I, II, IV and above 900 K, regions I, II, III and IV. It should not be forgotten, however, that in pure oxygen, a small amount of water is produced from

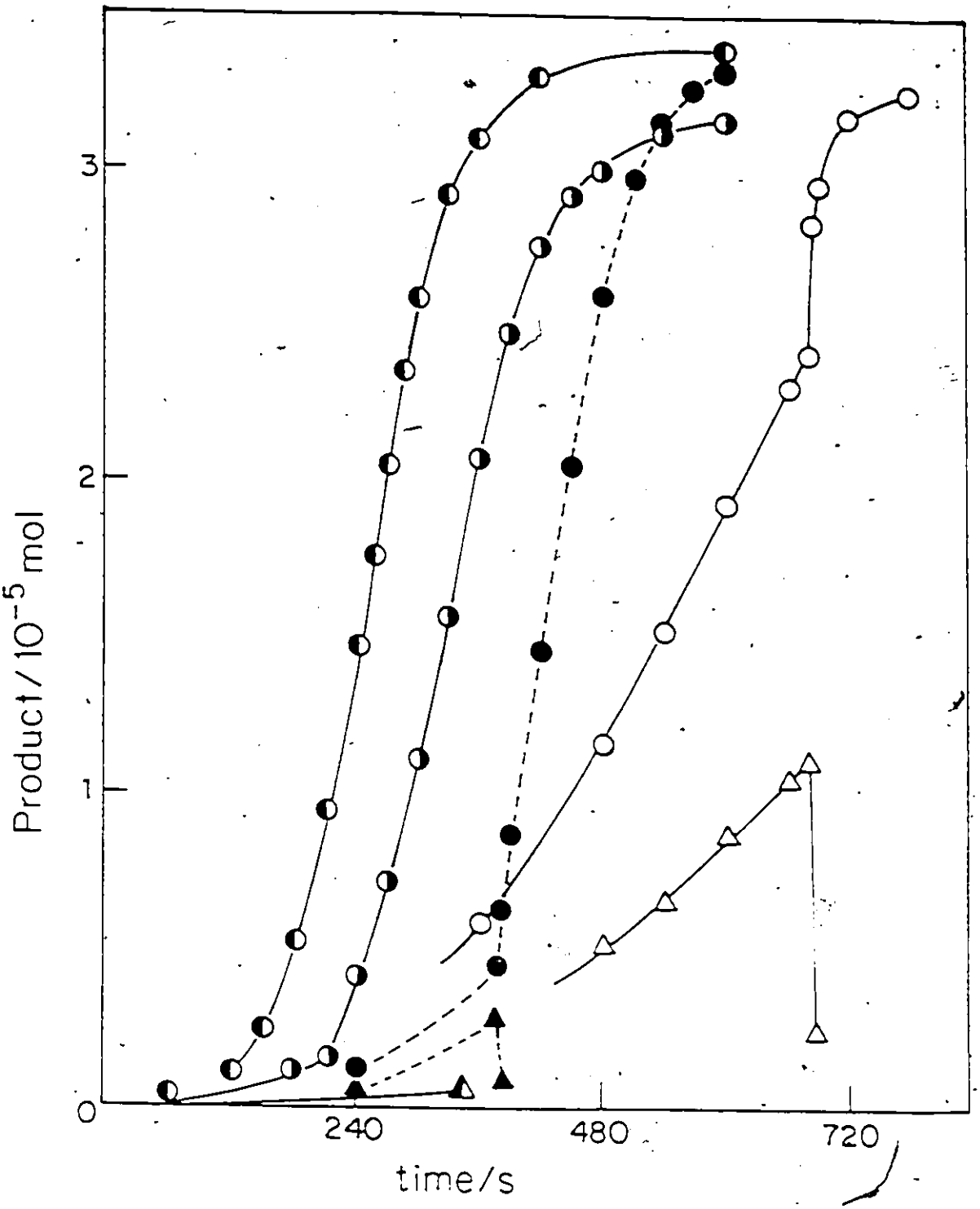


Figure 7.7. Effect of the additives, hydrogen, methane and water, in region II at 900 K. Circles refer to carbon consumed and triangles to carbon monoxide formed. Initial pressure of oxygen: 90 Torr. Some points in the early stages have been omitted for clarity.

○, △ : O_2;
◐, ▲ : O_2 + 0.1% H_2;
◑, ▲ : O_2 + 0.1% CH_4
●, ▲ : O_2 + 0.1% H_2O.

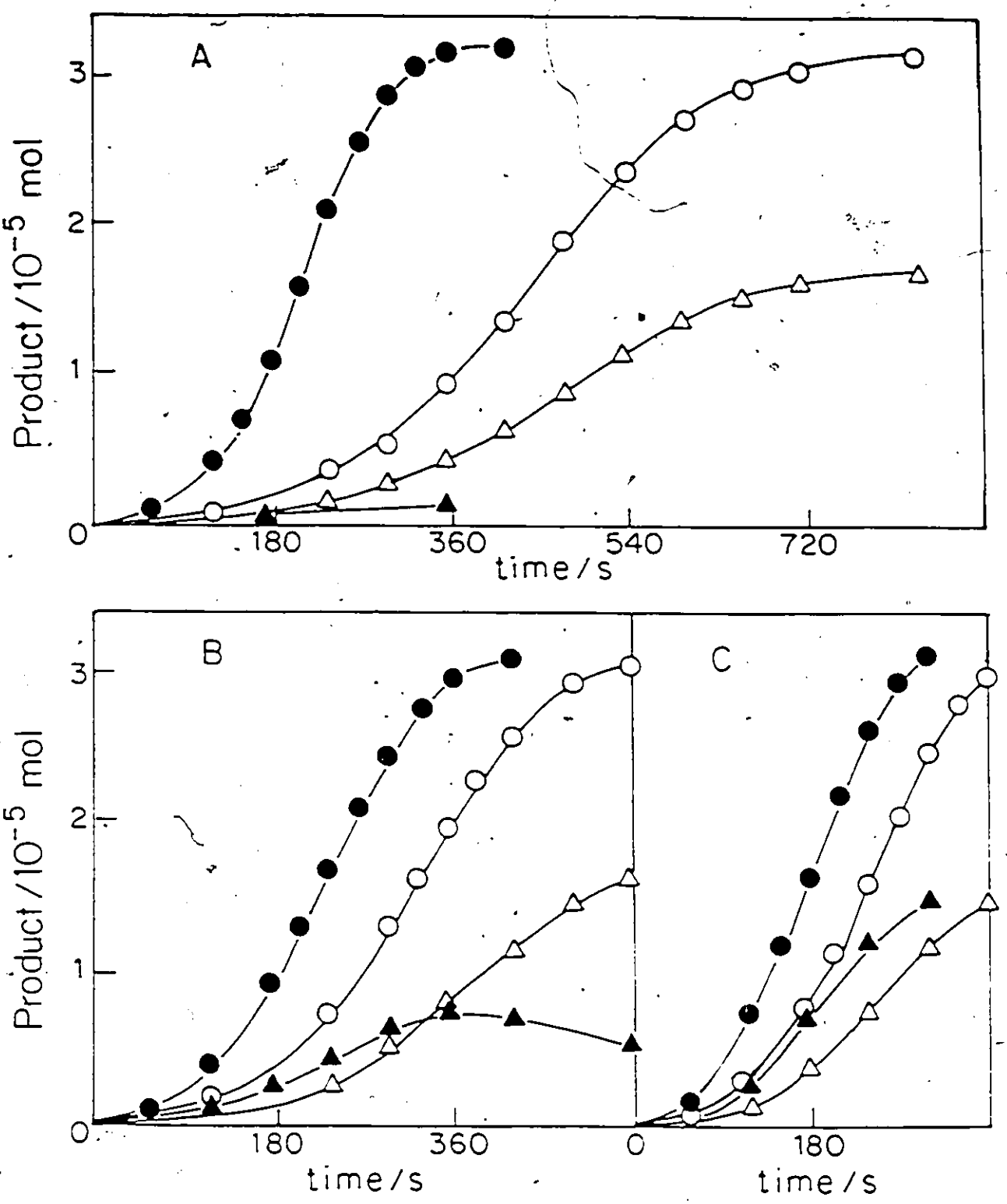
Figure 7.8. Effect of addition of hydrogen on the reaction at 900 K. Circles refer to carbon consumed and triangles to carbon monoxide formed.

Initial pressure of oxygen:

A: 150 Torr; **B:** 240 Torr; **C:** 400 Torr.

○ , △ : O_2; ● , ▲ : O_2 + 0.1% H_2.

(A) illustrates transformation of region IV to III by addition of hydrogen. At higher pressures the transformation is less effective, (B) and (C). In fact, for mixtures of oxygen plus hydrogen, Figure 7.9 A,B,C illustrates a gradual change from region III to region IV.


A
B
C
Product / 10^{-5} mol
time / s
0
1
2
3
180
360
540
720

the traces of hydrogen present in the film and this plays a vital role in the development of conditions both for explosion and for rapid secondary oxidation of carbon monoxide. The fact that at 900 K region III was observed only when hydrogen or methane was added suggests, although not verified experimentally, that explosion or rapid secondary oxidation of carbon monoxide can also be induced at still lower temperatures by addition of a sufficient amount of chain branching additive. This conclusion, of course, is consistent with the established fact [91] that the explosion peninsula expands or shifts to lower temperatures on addition of hydrogen or water.

The effect of inert gases was examined by reaction with equimolar mixtures of oxygen and helium or oxygen and carbon dioxide at a total pressure of 180 Torr. No explosion was observed indicating an inhibiting action of inert gas similar to that observed at 935 K. Addition of carbon monoxide did not have a significant effect on the extent of carbon conversion prior to explosion (Table 7.6C), as also observed at 935 K.

The general trends in the characteristics of the reaction, including the effect of addition of carbon dioxide (Figure 7.9) were also observed using a thicker film (24 nm). The results are summarized in Table 7.7.

7.3 Measurements at 973 K

At 973 K the measurements were made over the range of pressure 5-80 Torr of oxygen. Within this range, regions I, II and III were observed but, compared to the lower temperatures, displaced significantly to lower pressures. For example, region II was observed between 15 and 40 Torr compared to 40-120 Torr at 900 K. Also, for a particular pressure of

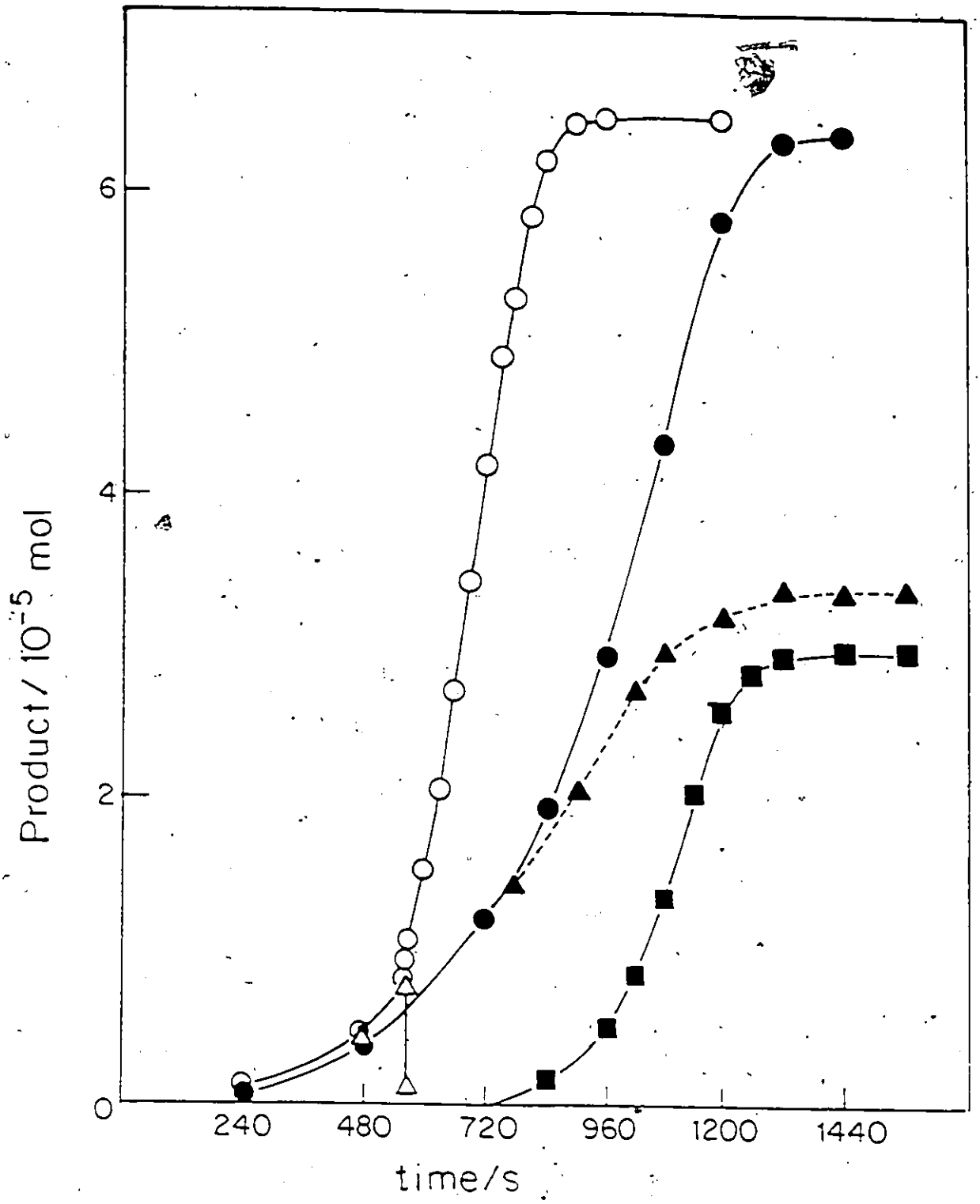


Figure 7.9. Reaction on the thick film of carbon (24 nm) at 900 K. Inhibiting action of inert gas in region II. Initial pressure of oxygen: 90 Torr. Circles refer to carbon consumed, triangles to carbon monoxide formed and squares to carbon dioxide formed.

○, △ : O_2; ○, △, □ : $O_2 + CO_2$ (1:1).

Table 7.7. Effect of the thickness of the film on conditions at the onset of explosion at 900 K

Initial pressure/Torr	Conditions at explosion							
	Thick Film (6.5×10^{-5} mol)				Thin Film (3.2×10^{-5} mol)			
O_2	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr	n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
30	4.60	0.58	9.0	20.6	No explosion observed			
45	1.90	0.24	5.0	36.4	3.20	0.20	4.9	39.4
60	0.90	0.12	2.9	58.9	3.00	0.19	4.5	51.8
90	0.80	0.10	2.3	90.5	2.35	0.15	3.4	84.0
120					2.60	0.17	3.7	113.5
150	0.65	0.08	2.1	149	No explosion observed			

oxygen, explosion occurred at lower conversion of carbon and therefore at lower concentration of water than observed at lower temperatures. This trend reflects the increase in the rate of the branching reactions at higher temperatures.

Hydrogen and methane both made the mixture more explosive. The large inhibiting effect of inert gases observed at 900 and 935 K was, however, not seen at this temperature. Helium had almost no effect on the onset of explosion. In the presence of carbon dioxide (1:1), explosion occurred at a slightly lower conversion of carbon compared to that with pure oxygen. A summary of the experiments at 973 K showing the extent of consumption of carbon prior to the onset of explosion for various conditions is given in Table 7.8.

At 80 Torr of oxygen a low steady-state yield of carbon monoxide, the characteristic feature of region III, was observed. Because of the rapidity of the oxidation of carbon at this temperature, measurements were not extended to higher pressures of oxygen to observe the transition into region IV. Nevertheless, addition of carbon dioxide to 80 Torr of oxygen gave sufficient increase in pressure to approach the characteristics of region IV. This is shown in Figure 7.10. In pure oxygen at 80 Torr, carbon monoxide remained very low throughout the course of the reaction but on addition of carbon dioxide the yield of carbon monoxide gradually increased, accompanied by a corresponding decrease in the rate of removal of carbon. When 240 Torr of carbon dioxide was added, comparable yields of carbon monoxide and carbon dioxide were formed (Region IV).

Table 7.8. Effect of oxygen and of various additives on conditions at the onset of explosion at 973 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr		Conditions at explosion			
		n_C/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
A. Effect of oxygen					
O_2					
15		3.45	0.23	6.7	7.1
20		1.45	0.10	2.8	17.7
30		0.65	0.043	1.0	27.8
40		0.35	0.023	0.5	40.9
B. Effect of carbon monoxide					
O_2	CO				
20	-	1.45	0.10	2.8	17.7
20	2.6	1.35	0.090	4.0	16.7
20	3.3	1.10	0.073	5.4	17.6
C. Effect of chain-branching additives					
O_2	additive				
15	-	3.45	0.23	6.7	7.1
15	0.015 (H_2)	2.95	0.20	5.8	8.3
20	-	1.45	0.10	2.8	17.7
20	0.02 (H_2)	1.10	0.073	2.0	17.2
20	0.02 (CH_4)	0.85	0.056	1.5	17.5
D. Effect of inert gases					
O_2	Inert gas				
20	-	1.45	0.10	2.8	17.7
20	20 (He)	1.35	0.09	2.7	17.0
30	-	0.65	0.043	1.0	27.8
30	30 (He)	0.55	0.037	0.9	28.2
30	30 (CO_2)	0.35	0.023	0.7	29.7

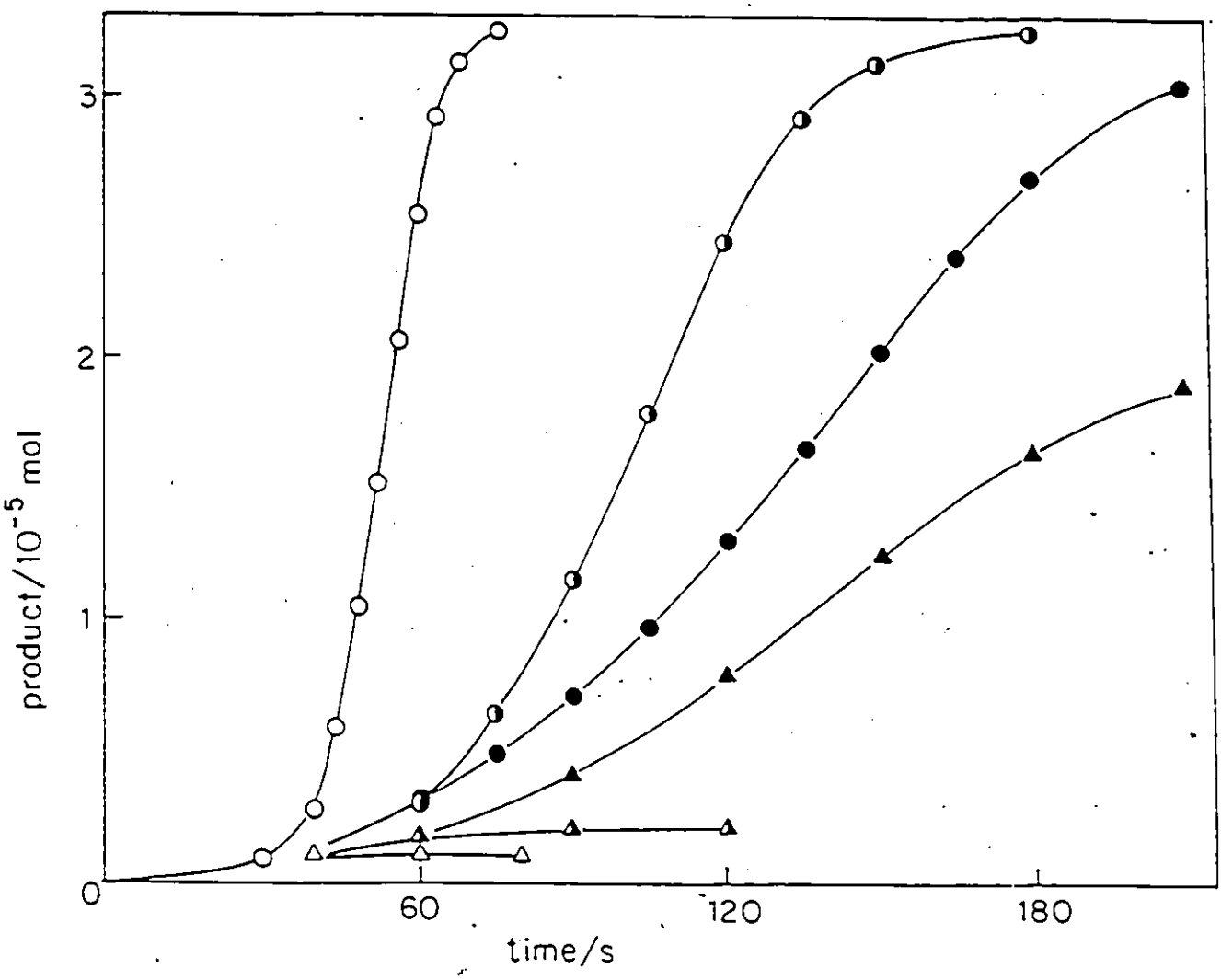


Figure 7.10. Effect of inert gas in region III at 973 K. Initial pressure of oxygen: 80 Torr. Circles refer to carbon consumed and triangles to carbon monoxide formed. Some points in the early stages have been omitted for clarity.

○, △ : O_2; ◑, ▲ : $O_2 + CO_2$ (1:1); ●, ▲ : $O_2 + CO_2$ (1:3).

7.4 Measurements at 1048 K

At 1048 K the reaction was studied at several pressures of oxygen in the range 3-30 Torr. Explosions were observed with initial pressures of oxygen between 12 and 30 Torr. Thus region II was again shifted to lower pressures. At this temperature several interesting changes in the behaviour of the system were observed.

7.4.1 EFFECT OF ADDITIVES

1. Addition of inert gas

Contrary to the inhibitive effect observed at temperatures below 950 K, both inert gases (carbon dioxide and helium) caused explosion at lower conversion of carbon than required for pure oxygen. Carbon dioxide was more effective than helium, as illustrated in Figure 7.11. Thus from 900 K to 1048 K, a complete reversal in the effect of inert gas on the explosion occurred. The very small effect of inert gases at 973 K is therefore the result of the balance between the inhibiting and promoting effects. This reversal in the effect of inert gas on the explosion clearly illustrates the dominance of heterogeneous termination in the development of an explosive condition at low pressures. The results are summarized in Table 7.9.

At a partial pressure of 15 Torr of oxygen, experiments with mixtures of oxygen plus carbon dioxide were performed with ratios O_2/CO_2 of 1:1, 1:3, 1:5, 1:10, 1:20 and 1:40. With 1:1 and 1:3 mixtures, the promoting effects described above were observed. Further additions of carbon dioxide (1:5, 1:10 and 1:20 mixtures), however, caused a shift in the characteristics of the reaction from region II to III where a rapid

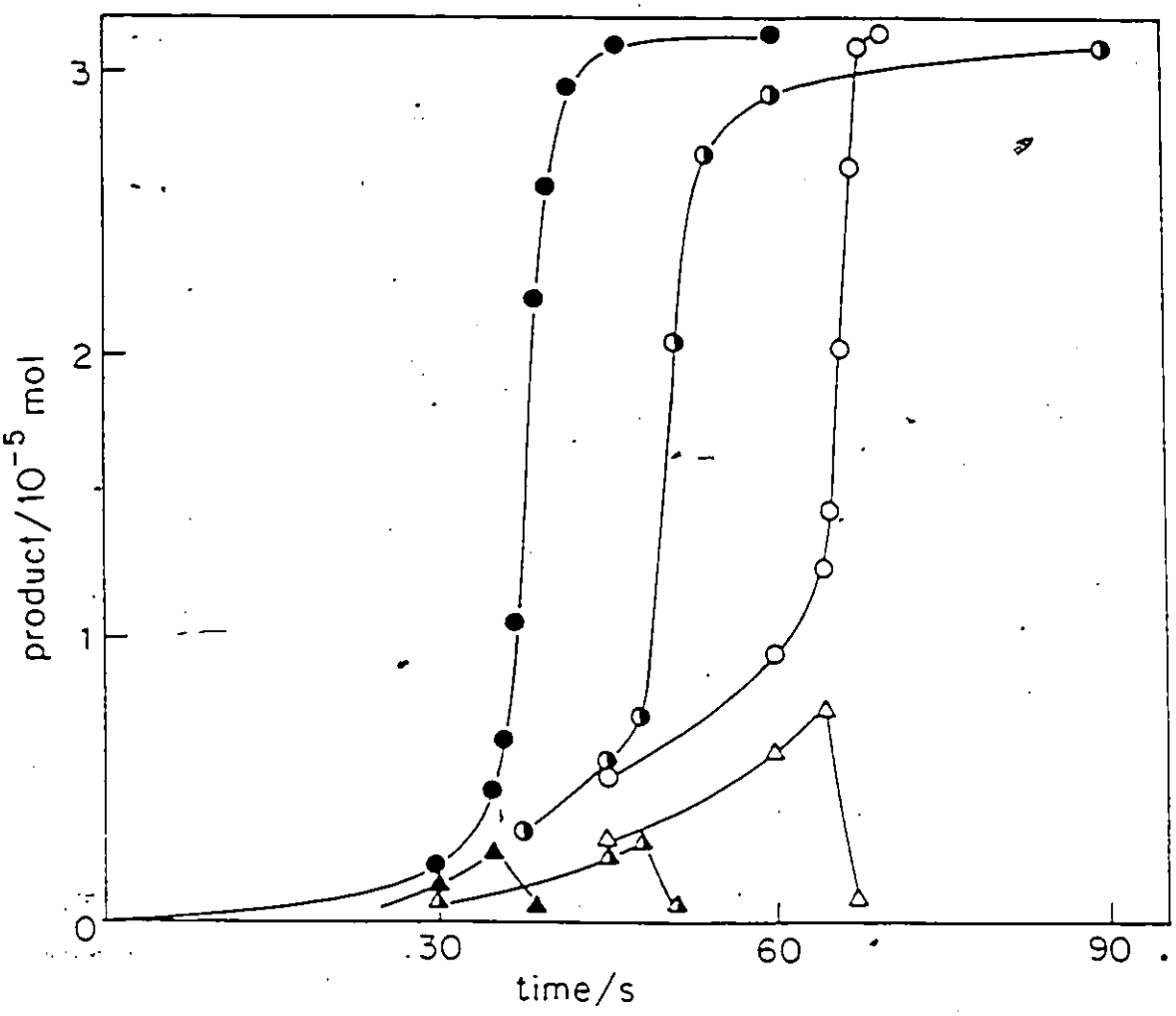


Figure 7.11. Promoting effect of inert gases on the onset of explosion at 1048 K. Initial pressure of oxygen: 15 Torr. Circles refer to carbon consumed and triangles to carbon monoxide formed. Some points in the early stages have been omitted for clarity.

○ , △ : O_2; ◑ , ◭ : O_2 + He (1:3); ● , ▲ : O_2 + CO_2 (1:1).

Table 7.9. Effect of oxygen and of various additives on conditions at the onset of explosion at 1048 K

$[C]^\circ = 3.2 \times 10^{-5}$ mol (2×10^{-7} mol cm^{-2}; average thickness = 12 nm)

Initial pressure/Torr		Conditions at explosion			
		n_c/ 10^{-5} mol	P_{H_2O}/ Torr	P_{CO}/ Torr	P_{O_2}/ Torr
A. Effect of oxygen					
O_2					
12		3.05	0.22	6.7	4.0
15		1.2	0.085	2.7	12.3
20		0.7	0.050	1.5	18.4
30		0.5	0.035	0.8	29.0
B. Effect of inert gases					
O_2	Inert gas				
12	-	3.05	0.22	6.7	4.0
12	36 (He)	0.8	0.056	1.4	9.7
12	12 (CO_2)	0.6	0.043	1.3	10.8
12	36 (CO_2)	0.3	0.021	0.6	11.3
15	-	1.2	0.085	2.7	12.3
15	45 (He)	0.5	0.035	1.0	13.7
15	15 (CO_2)	0.5	0.035	0.85	15.0
15	45 (CO_2)	0.2	0.014	0.35	14.5
C. Effect of carbon monoxide					
O_2	CO				
15	-	1.2	0.085	2.7	12.3
15	2.3	0.9	0.064	4.0	12.2
15	6.4	0.5	0.035	6.9	15.0
20	-	0.7	0.050	1.4	18.4
20	1.5	0.6	0.043	2.3	18.5
20	3.2	0.45	0.032	3.6	19.0

secondary oxidation kept the concentration of carbon monoxide low throughout the course of the reaction and explosions did not occur. When 15 Torr of reactant oxygen was further diluted with carbon dioxide to a composition of 1:40, the reaction was shifted to region IV where both carbon monoxide and carbon dioxide were formed in comparable yields. It is interesting to note that when the inert gases inhibit the explosion, below 950 K, a direct transition in the characteristics of the reaction from region II to IV occurred, without passage through region III. On the other hand, when inert gases promoted an explosion, at 1048 K, a gradual shift from region II to III to IV occurred. This trend is in agreement with the observations during the series of experiments with pure oxygen and with oxygen plus 0.1% hydrogen mixtures. In each case upon increasing the pressure of reactants, at first explosion occurred at progressively lower extent of carbon consumption (promoting effect), then the system entered into region III, and eventually at sufficiently high pressures shifted into region IV.

2. Addition of carbon monoxide

At all temperatures described so far, addition of carbon monoxide to the reactant oxygen exerted very little effect on the extent of carbon consumption prior to the onset of explosion. This was, however, not the case at 1048 K. As shown in Table 7.9 and in Figure 7.12, addition of carbon monoxide caused explosions at lower extent of carbon conversion than observed with pure oxygen. The effect became more important as the pressure of carbon monoxide in the initial mixture was increased. In

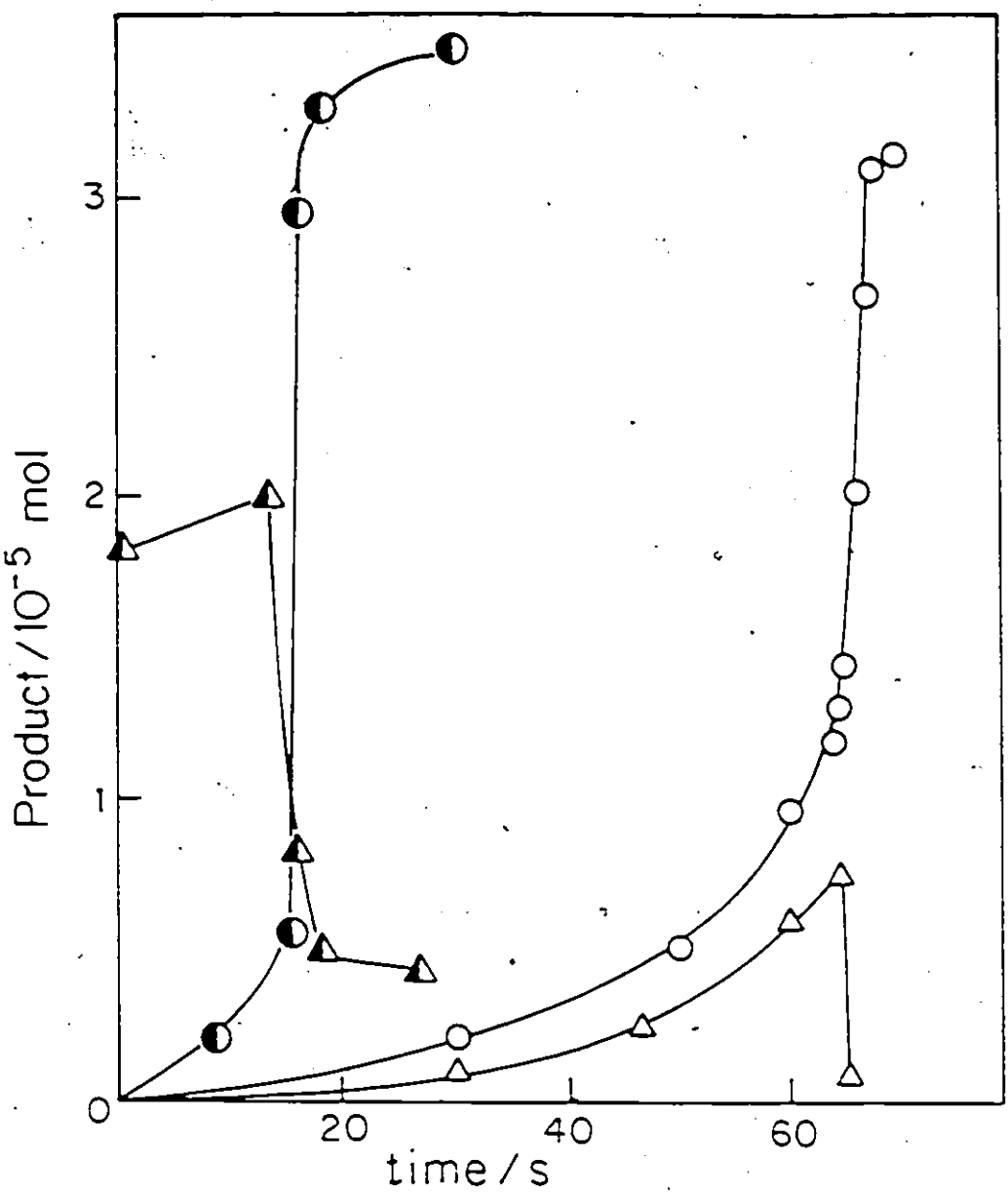


Figure 7.12. Effect of addition of carbon monoxide in region II at 1048 K. Initial pressure of oxygen: 15 Torr. Circles refer to carbon consumed and triangles to carbon monoxide formed.

○ , △ : O_2; ◐ , ◭ : O_2 + CO (Pressure of added CO: 6.5 Torr).

acting thus as a promoter for the explosion at this temperature, carbon monoxide played the role of an inert gas. This result again shows the importance of the surface termination at these low total pressures.

7.4.2 EFFECT OF EXPOSURE OF QUARTZ SURFACE

At 1048 K no explosion was observed in the reactions with initial pressures of oxygen less than 12 Torr as long as the surface of the vessel was covered by carbon. Under some conditions, however, an explosion occurred at the instant of complete consumption of carbon. Examples of these experiments are given in Table 7.10 and illustrated in Figure 7.13. The explosion occurred either after one stage of reaction, where all carbon was consumed while still some oxygen remained (experiments 2,3,4 and 5) or after two stages, where, if oxygen was not sufficient to remove all carbon in stage 1, a second charge of oxygen was admitted after removal of products (experiments 1 and 6). In each of these experiments, explosion was not observed until the carbon was almost completely removed and the quartz surface was exposed, even though different initial amounts of carbon were used, giving different concentrations of oxygen, water and carbon monoxide, and reactant mixtures contained inert gases, giving different rates of diffusion of chain carriers. It must be concluded that the exposure of the quartz surface drastically reduced the efficiency of termination at the surface, leading immediately to an explosion. This effect clearly shows the very high efficiency of the carbon surface for removal of radicals. Explosion under these conditions was observed only at 1048 K, although at the lower temperatures, especially 973 K, a slow secondary reaction of carbon monoxide was noticed after complete removal of carbon.

Table 7.10. Effect of the surface conditions on the occurrence of an explosion at pressures below 12 Torr at 1048 K

Initial conditions				Fractional removal of carbon at explosion
Expt #	O_2/Torr	Inert gas/Torr	C^o/mol	$\Delta C/C^o$
1	6	0	3.1×10^{-5}	0.99
2	6	0	1.9×10^{-5}	1.00
3	9	0	3.1×10^{-5}	0.99
4	9	0	1.9×10^{-5}	1.00
5	9	9 (CO_2)	3.1×10^{-5}	0.99
6	9	27 (He)	3.1×10^{-5}	0.98

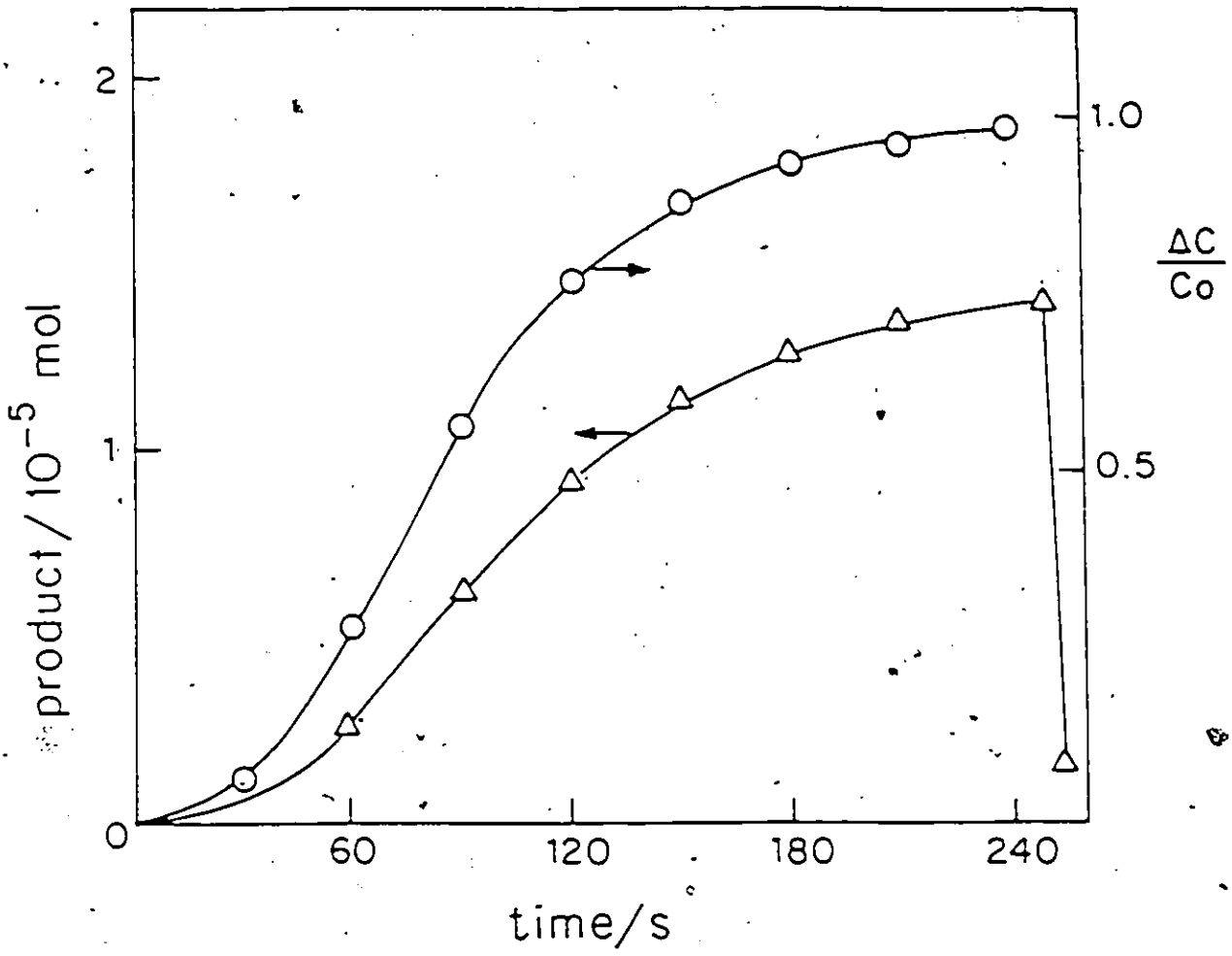


Figure 7.13. Explosion following complete consumption of carbon 1048 K. Initial pressure of oxygen: 9 Torr.

○ : ratio of carbon consumed to initial concentration of carbon;

△ : carbon monoxide.

CHAPTER 8

DISCUSSION

8.1 Characteristics of the present system

The experimental conditions of the present investigation on the explosive reaction of oxygen with carbon monoxide are quite distinct in many respects from those of previous studies of this reaction. Most earlier studies were confined to ratios of CO/O_2 of 1:2, 1:1, and 2:1 whereas in the present study this ratio achieved a very different range of values, summarized in Table 8.1. Measurements were thus extended to a realm of composition not previously investigated, illustrating that explosions could occur at a ratio of CO/O_2 as low as 5×10^{-3} or less than 1 Torr of carbon monoxide in the present system. This result is perhaps significant for studies on oxidation of hydrocarbons where it has long been known that the oxidation of carbon monoxide may contribute appreciably to the later stages of the reaction.

It is also interesting to note that despite these low ratios of CO/O_2, the total pressure of reactants where explosions were observed in the present study was not very different from that where explosion occurred with the higher pressures of carbon monoxide. This further substantiates the conclusion that the pressure of carbon monoxide is not necessarily a critical factor in the development of the conditions for an explosion.

The carbon-coated quartz surface used in the present study has properties different from the acid-washed quartz surface used in most of the previous studies. First, the carbon by its reaction with oxygen,

Table 8.1 Ratio CO/O_2 at the explosion

Temperature/K	Ratio, CO/O_2
900	0.2 - 0.03
935	0.46 - 0.006
973	0.94 - 0.017
1048	1.9 - 0.02

provides the products, carbon monoxide and water, which act as reactants for the explosion. As the reaction proceeds, these products are formed at measurable rates and accumulate in the system until the critical concentrations for the onset of an explosion are attained. This technique of gradually approaching the explosion condition through in situ generation of reactants in the vessel has distinct advantages, particularly at high temperatures, over the conventional method of admitting pre-mixed reactants to a hot reaction vessel. In the latter procedure, whether the pressure is lowered or the temperature is raised after admission, considerable reaction may take place before the explosion limit is reached. As a result, the concentrations of reactants at the onset of explosion may be uncertain and the extent of reaction at explosion, which is a useful characteristic to identify an explosion and to distinguish it from other phenomenon associated with the oxidation of carbon monoxide [79], is not clearly defined. With the present method, the concentrations of oxygen and carbon monoxide and the extent of reaction at ignition were determined unambiguously. The concentration of water at the explosion was, as discussed earlier, more uncertain. Nevertheless, because water was formed continuously throughout the course of the reaction, the error in its estimation was a systematic one. The problem of the accurate measurement of such small quantities of water is, of course, not peculiar to the present study.

Another unique feature of the system is that the carbon surface provides an efficient terminating agent for oxygen atoms, which are chain carriers in the reaction. In fact oxygen atoms are probably removed at every collision with the carbon surface, making termination a diffusion-

controlled reaction. A similar assumption was made for salt-coated vessels in the hydrogen-oxygen reaction [96] and the carbon surface should be at least equally active. On the other hand, the carbon surface will be unreactive towards the products carbon monoxide, carbon dioxide and water, and secondary reactions of these products will occur only through homogeneous gas phase reactions.

8.2 Mechanism of the reaction

The formation of water during the course of the oxidation showed that the carbon film retained a small amount of hydrogen which was not released in the outgassing treatment and is probably in the form of C-H bonds. Formation of water undoubtedly takes place on the surface, but if even a small fraction of oxygen molecules abstract hydrogen and desorb as HO_2, subsequent dissociation of this radical could provide an initiation step for the chain reaction.

$$-C-H + O_2 \longrightarrow -C- + HO_2 \longrightarrow OH + O$$

The identification of the initiation step, or its rate, is not, however important in the development of conditions for an explosion so that its exact description need not concern us here.

The main features of the explosion reaction, including the effect of inert gases and of chain branching additives, may be qualitatively explained by a simple mechanism. The reactions, except the initiation step (1) and the surface destruction step (7), are those suggested in

previous studies, particularly Buckler and Norrish [94] and Brokaw [98], and included in the modelling schemes of Yang [100,101], of Yang and Berlad [97] and of Pilling and Noyes [95].

(1)	$-C-C-H + O_2 \longrightarrow HO_2 \longrightarrow OH + O$	Initiation
(2)	$CO + OH \longrightarrow CO_2 + H$	Propagation
(3)	$H + O_2 \longrightarrow OH + O$	
(4)	$O + H_2O \longrightarrow 2\ OH$	Branching
(5)	$O + H_2 \longrightarrow OH + H$	
(6)	$O + CH_4 \longrightarrow OH + CH_3$	
(7)	$O + -C-C- \longrightarrow CO + -C-$	Termination
(8)	$O + CO + M \longrightarrow CO_2 + M$	
(9)	$H + O_2 + M \longrightarrow HO_2 + M$	

Reactions (2) and (3) represent the oxidation of carbon monoxide by the linear chain sequence with net production of oxygen atoms. Reaction (3), however, is also a branching reaction if oxygen atoms generate further OH radicals for the propagation reaction (2). In the presence of hydrogeneous substances, this is achieved through reactions (4), (5) and (6) which are also then branching reactions. The effectiveness of these branching reactions, including reaction (3), depends on their rates relative to the termination reactions (7), (8) and (9), of which reaction (7) is a heterogeneous termination reaction and the remaining two are gas phase termination reactions.

8.3 Attainment of explosive conditions

A critical factor in the relative importance of the various branching and termination reactions is the ratio H/O in the system. From a steady-state solution for O atom concentrations, excluding reactions involving the additives hydrogen (reaction (5)) and methane (reaction (6)), this ratio is given by the following equation:

$$(A) \qquad \frac{[H]}{[O]} = \frac{k_4[H_2O] + k_7 + k_8[CO][M]}{k_3[O_2]}$$

With the progress of the reaction, the concentrations of water and carbon monoxide in the system increase and therefore the ratio H/O also increases. In order for an explosion to occur, the total rate of branching must exceed the total rate of termination. In other words, when the ratio of the sum of the rates of the branching reactions to the sum of the rates of the termination reactions exceeds unity, an explosion will take place. Without the additives, hydrogen and methane, (3) and (4) are the branching reactions and (7), (8) and (9) are the termination reactions. The explosion condition or the 'criticality for explosion' may therefore be expressed as follows:

$$(B) \qquad \frac{[O]}{[H]} \frac{k_3\frac{[H]}{[O]}[O_2] + k_4[H_2O]}{k_7\frac{[O]}{[H]} + k_8\frac{[O]}{[H]}[CO][M] + k_9[O_2][M]} \geq 1$$

The value of this ratio at the explosion may be calculated using the values of rate constants from the compilation of Pilling and Noyes [95], summarized in Table 8.2, and making an estimate of the concentration of water and of the value for k_7.

The direct measurement of the concentration of water at the completion of a reaction represents a lower limit, since water is easily lost in the system. A better estimate was obtained by comparison of the amounts of carbon reacted prior to the onset of explosion in the presence and absence of added water (Figures 7.3 and 7.7). Assuming that water was produced at a uniform rate during the consumption of carbon and that the total concentration of water at the explosion was the same in the presence and absence of added water, the concentration of water at the explosion is given as follows:

$$(C) \qquad [H_2O]_E = [H_2O]_E^o = [H_2O]_i + [H_2O]_E^o \cdot \frac{[\Delta C]_E}{[\Delta C]_E^o}$$

where the subscript E indicates the concentrations at the explosion and the superscript indicates the reaction in pure oxygen. ΔC represents the extent of carbon conversion and $[H_2O]_i$ is the initial concentration of water in the experiment with the additive. From all experiments with added water, an average value of 0.020 was obtained for the ratio $H_2O/\Delta C$ at the explosion. The direct measurements, however, indicated a ratio in the range 0.01 - 0.015, and an uncertainty in the ratio of a factor of 2 must therefore be accepted. The estimate based on the experiments involving addition of water was considered a more reliable measurement and this ratio was used in all subsequent calculations. Both

Table 8.2 Values of rate constants used in the calculation of equation (A) and ratio (B)

	Reaction	Rate constant	units
(3)	$H + O_2$	$2.24 \times 10^{11} e^{-16800/RT}$	$L\ mol^{-1} s^{-1}$
(4)	$O + H_2O$	$5.75 \times 10^{10} e^{-18000/RT}$	$L\ mol^{-1} s^{-1}$
(5)	$O + H_2$	$1.74 \times 10^{10} e^{-9450/RT}$	$L\ mol^{-1} s^{-1}$
(7)	O + -C-C-	50 (20 Torr)	s^{-1}
(8)	$O + CO + M$	1.0×10^{8}	$L^2\ mol^{-2} s^{-1}$
(9)	$H + O_2 + M$	$3.2 \times 10^{9} e^{1000/RT}$	$L^2\ mol^{-2} s^{-1}$

$R = 1.987\ cal\ mol^{-1}\ deg^{-1}$

measurements, however, show that the pressure of water in the system during the reaction is negligible compared to the total pressure and confirms the validity of the calculation of carbon monoxide from the pressure measurements.

An estimate of K_7, the rate constant for termination on the carbon surface, was more difficult. As mentioned earlier, removal of an oxygen atom at the carbon surface should occur at each collision and k_7 could therefore represent a first-order rate of diffusion to the surface. Because of the large temperature gradients in the system at the explosion which would aid mixing, this value could be considered a lower limit. An empirical estimate of k_7 was first made from the results at 900 and 935 K by selecting a value of k_7 which would bring ratio (B) close to unity over the entire range of pressure where explosions were observed, assuming that k_7 is inversely proportional to the pressure. At 20 Torr the value obtained was 50 s^{-1} which is larger by a factor of about 5 than a value estimated by a rate of diffusion. Since the diffusion rate is a lower limit it was concluded that the empirical value was reasonable and was therefore used in the calculations of ratio (B) for all experiments.

Using the estimated value for k_7 and the ratio $H_2O/\Delta C = 0.020$ at the explosion, values of the ratio H/O, equation (A) and of the ratio of the sum of the rates of branching to the sum of the rates of termination, ratio (B), were calculated as a function of time for a typical experiment in region II. The results are given in Table 8.3 which clearly show the gradual increase in the ratio H/O and the approach of ratio (B) to the explosive condition as the reaction proceeds.

Table 8.3. Values of equation (A) and ratio (B) during the course of a reaction leading to an explosion

Temperature: 900 K; Initial pressure of O_2 90 Torr

Time/sec	$(H/O)/10^{-4}$	Branching/s^{-1}		Terminations/s^{-1}			Ratio
		$k_3[H/O][O_2]$	$k_4[H_2O]$	$k_7[O/H]$	$k_8[O/H][CO][M]$	$k_9[O_2][M]$	(B)
240	4.20	12.5	0.49	26450	1910	14160	0.72
360	5.07	14.8	1.4	21890	4520	14070	0.79
480	6.40	18.4	2.8	17350	7130	13990	0.86
600	8.31	23.4	4.7	13350	9240	13670	0.93
619 (at explosion)	9.63	26.8	5.9	11520	10180	13570	0.96

Values of equation (A) and ratio (B) at the explosion were calculated for all experiments where an explosion was observed at temperatures of 900, 935, 973 and 1048 K and are summarized in Tables 8.4 - 8.7.

The tables show the values calculated for the contribution of each branching reaction and each termination reaction as well as the ratio H/O at the explosion. It is immediately apparent that termination at the surface is important even at the highest pressures obtained in the low temperature range. This result emphasizes the high efficiency for radical destruction at the carbon-coated surface. The influence of the surface on the second explosion limit was also reported in previous studies of the reaction in quartz vessels [80,103] although the behaviour was somewhat erratic. Results in the present system were entirely reproducible.

8.3.1 PURE OXYGEN

Considering first the experiments with pure oxygen, the values obtained for ratio (B) were close to unity except for experiments with pressures below 15 Torr (Tables 8.6 and 8.7) where values up to 2 were obtained. This range is well within the errors expected in the calculation. Besides the uncertainty discussed in k_7 which is particularly important at low pressures, the uncertainty suggested in k_4 is a factor of 2 [104]. A reduction in k_4 by a factor of 2 reduces the value of ratio (B), for experiments at 12 Torr at 1048 K, from 2.0 to 1.4. The uncertainty in the concentration of water at the explosion has already been discussed. A reduction in the concentration

Table 8.4. Concentrations of reactants and products at the explosion and calculated values of equation (A) and ratio (B) at 900 K.

Reactant	n_t/ 10^{-5} mol	P_{CO}/ Torr	P_{O_2}/ Torr	$(H/O)/10^{-3}$	Branching/s^{-1}			Terminations/s^{-1}			Ratio
					$k_3[H/O][O_2]$	$k_4[H_2O]$	$k_5[H_2]$	$k_7[O/H]$	$k_8[O/H][CO][M]$	$k_9[O_2][M]$	(B)
$P^o_{O_2}$ = 30 Torr											
O_2 + 1% H_2	3.20	4.8	21.8	10.9 (6.36)	78.7 (46.2)	8.7 (10.0)	34.3	3030 (4930)	301 (754)	828 (1230)	2.7 (1.3)
$P^o_{O_2}$ = 45 Torr											
O_2	3.22	4.9	39.4	2.80	36.7	8.8		7230	2750	3460	1.2
O_2 + 0.1% H_2	0.80	1.2	43.1	6.39 (1.93)	91.4 (27.7)	2.1 (4.1)	67.7	3130 (11400)	257 (881)	3240 (3490)	3.8 (1.1)
O_2 + 0.1% H_2O	2.84	4.4	38.4	2.92	37.4	9.7		7220	2260	3230	1.3
O_2 + 0.3% H_2O	1.17	1.5	41.8	2.29	33.3	9.1		9210	921	3380	1.3
$P^o_{O_2}$ = 60 Torr											
O_2	2.96	3.9	51.5	1.87	32.1	8.1		8810	4000	5560	1.2
*O_2	0.92	3.0	58.8	1.28	27.1	5.0		11700	4260	6460	1.0
$P^o_{O_2}$ = 90 Torr											
O_2	2.35	3.2	81.7	0.979	26.6	6.4		11500	9190	12900	1.0
O_2 + 0.1% H_2	0.2	0.3	88.8	5.21 (0.556)	153 (16.5)	0.5 (4.4)	141	2110 (20100)	164 (1520)	14080 (14100)	3.5 (1.1)
O_2 + 0.1% H_2O	0.45	0.9	86.6	0.665	18.9	5.1		17250	3820	13600	1.1
O_2 + 0.2% H_2O	0.2	0.3	88.8	0.818	24.2	12.3		12580	1040	14020	1.5
O_2 + 2.7% CO	2.26	5.7	84.2	1.21	33.8	6.2		8960	13900	13900	1.0
*O_2	0.80	2.4	90.4	0.739	22.3	4.4		14600	9590	14900	1.0
$P^o_{O_2}$ = 120 Torr											
O_2	2.62	3.65	111.9	0.79	29.5	7.1		11300	17800	22900	0.9
O_2 + 2.7% CO	2.48	7.0	118.0	1.05	41.1	6.7		7620	25000	21300	0.8

* Experiments with thick films

Table 8.5. Concentrations of reactants and products at the explosion and calculated values of equation (A) and ratio (B) at 935 K.

Reactant	n_c/ 10^{-5} mol	P_{CO}/ Torr	P_{O_2}/ Torr	$(H/O)/10^{-3}$	Branching/s^{-1}			Terminations/s^{-1}			Ratio
					$k_3(H/O)[O_2]$	$k_4[H_2O]$	$k_5[H_2]$	$k_7(O/H)$	$k_8(O/H)[CO][M]$	$k_9[O_2][M]$	(B)
$P^\circ_{O_2}$ = 20 Torr											
O_2	3.20	5.5	11.9	11.3	61.1	12.6		3980	319	429	1.4
O_2 + 1% H_2	3.02	5.2	13.0	17.3 (10.2)	102 (60.5)	11.9 (13.1)	36.7	2890 (4290)	175 (336)	421 (478)	2.5 (1.4)
$P^\circ_{O_2}$ = 30 Torr											
O_2	1.86	2.9	25.9	3.51	41.3	7.3		8820	769	1340	1.2
O_2 + 0.1% H_2	0.85	1.2	28.4	7.21 (7.24)	93.0 (39.3)	2.9 (5.2)	56.0	4580 (10800)	150 (361)	1400 (1420)	3.4 (1.2)
O_2 + 0.3% H_2O	0.50	1.1	29.6	2.96	39.8	7.5		10600	351	1630	1.3
O_2 + 2.6% CO	1.82	3.5	25.0	3.76	42.7	7.2		8590	851	1250	1.2
O_2 + 5.3% CO	1.73	4.0	25.5	3.69	42.8	6.8		8760	976	1280	1.2
O_2 + 19.5% CO	1.41	8.1	26.7	3.42	41.5	5.6		7930	2560	1590	1.1
O_2 + He (1:1)	2.29	3.5	24.2	3.53	38.8	9.0		7070	1490	2000	1.3
O_2 + CO_2 (1:1)	2.39	4.0	24.3	2.97	32.7	9.4		4380	3330	3310	1.3
O_2 + CO_2 (1:3)	No explosion observed										
*O_2	0.70	2.3	29.9	2.83	38.5	5.5		10900	777	1570	1.2
*O_2 + CO_2 (1:1)	0.95	3.6	29.4	2.20	29.4	7.5		5820	4140	4090	1.2
$P^\circ_{O_2}$ = 60 Torr											
O_2	0.49	0.8	59.5	0.754	20.4	1.9		22500a	1860	5720	1.0
O_2 + 0.1% H_2	0.1	0.2	59.8	4.70 (0.78)	128 (21.2)	0.5 (4.2)	110	3610 (21400)	75 (448)	5840 (5800)	5.3 (1.2)
O_2 + 1.0% CO	0.73	1.7	58.6	0.835	22.3	2.9		19600	3590	5780	1.0
O_2 + 2.7% CO	0.7	2.4	52.6	0.975	23.3	2.8		18300	2770	4760	1.0
O_2 + He (1:1)	1.14	1.6	57.0	0.860	22.2	4.5		15500	5140	9140	1.1
O_2 + CO_2 (1:1)	2.53	4.5	53.2	1.78	43.0	10.0		3760	14250	16460	0.9
*O_2	0.19	0.6	60.1	0.691	18.9	1.5		23700	1450	5930	1.0
*O_2 + CO_2 (1:1)	1.02	3.6	58.5	1.22	32.4	8.0		5330	14700	15900	0.9
$P^\circ_{O_2}$ = 100 Torr											
O_2	0.26	0.6	100.5	0.254	11.6	1.0		39400	2360	16300	0.9
O_2 + He (1:1)	0.68	1.2	96.3	0.383	16.8	2.7		20800	15400	25900	0.9
O_2 + CO_2 (1:1)	No explosion observed										

* Experiments with thick film

Table 8.6. Concentrations of reactants and products at the explosion and calculated values of equation (A) and ratio (B) at 973 K.

Reactant	n_c/ 10^{-5} mol	P_{CO}/ Torr	P_{O_2}/ Torr	$(H/O)/10^{-3}$	Branching/s^{-1}			Terminations/s^{-1}			Ratio
					$k_3(H/O)[O_2]$	$k_4[H_2O]$	$k_5[H_2]$	$k_7(O/H)$	$k_8(O/H)[CO][M]$	$k_9[O_2][M]$	(B)
$P^{\circ}_{O_2}$ = 15 Torr											
O_2	3.45	6.7	7.1	17.5	77.4	19.8		3080	194	193	1.6
O_2 + 0.1% H_2	3.00	5.8	8.3	20.9 (14.7)	108.0 (76.0)	17.0 (18.3)	33.0	2640 (3730)	137 (194)	220 (220)	2.5 (1.5)
$P^{\circ}_{O_2}$ = 20 Torr											
O_2	1.45	2.8	17.7	4.98	54.9	8.2		9050	342	580	1.3
O_2 + 0.1% H_2	1.10	2.0	17.2	9.27 (5.33)	99.3 (57.1)	6.3 (8.0)	43.8	5180 (9000)	123 (214)	527 (527)	2.8 (1.3)
O_2 + 8% CO	1.35	4.1	16.8	5.18	54.2	7.6		8500	495	559	1.3
O_2 + He (1:1)	1.35	2.7	17.0	4.72	50.0	7.7		8480	481	769	1.3
$P^{\circ}_{O_2}$ = 30 Torr											
O_2	0.65	1.3	27.9	2.17	37.7	3.7		15200	488	1220	1.1
O_2 + He (1:1)	0.55	0.9	28.2	1.79	31.4	3.1		15100	695	2020	1.1
O_2 + CO_2 (3:1)	0.45	0.9	29.1	1.42	25.7	2.6		15500	789	2000	1.1
O_2 + CO_2 (1:1)	0.35	0.8	29.7	0.907	16.8	2.0		14300	2030	3700	1.0
O_2 + CO_2 (1:3)	0.45	0.9	29.2	0.719	13.1	2.6		8350	6180	6180	1.0
O_2 + CO_2 (1:4)	0.65	1.5	28.7	1.02	14.4	3.5		4690	9740	10200	0.9
O_2 + CO_2 (1:6)	No explosion observed										
$P^{\circ}_{O_2}$ = 40 Torr											
O_2	0.35	0.7	40.7	1.06	26.9	2.1		22700	700	2490	1.1

Table 8.7. Concentrations of reactants and products at the explosion and calculated values of equation (A) and ratio (B) at 1048 K

Reactant	n_c/ 10^{-5} mol	P_{CO}/ Torr	P_{O_2}/ Torr	$(H/O)/10^{-3}$	Branching/s^{-1}			Terminations/s^{-1}			Ratio
					$k_3(H/O)[O_2]$	$k_4[H_2O]$	$k_5[H_2]$	$k_7(O/H)$	$k_8(O/H)[CO][M]$	$k_9[O_2][M]$	(B)
$P^\circ_{O_2}$ = 12 Torr											
O_2	3.26	7.4	4.0	24.1	103.6	35.7		2690	111	76	2.0
O_2	3.05	6.7	4.7	19.8	99.9	33.4		3240	124	89	2.0
O_2 + 0.1% H_2	3.00	6.5	4.7	26.5 (20.0)	135.0 (102.0)	33.1 (35.0)	34.7	2450 (3240)	87 (115)	89 (89)	2.9 (2.0)
O_2 + He (1:3)	0.8	1.4	9.7	5.54	57.6	8.4		8670	206	405	1.3
O_2 + CO_2 (1:1)	0.6	1.4	10.8	3.50	40.6	6.6		9440	292	426	1.3
O_2 + CO_2 (1:3)	0.3	0.6	11.3	1.59	19.3	3.3		9400	670	1050	1.3
$P^\circ_{O_2}$ = 15 Torr											
O_2	1.2	2.9	12.1	5.86	76.2	13.1		10600	188	240	1.4
O_2 + 0.1% H_2	1.0	2.1	12.5	8.67 (5.66)	116.4 (76.0)	10.9 (13.2)	42.7	7130 (11000)	91 (40)	244 (244)	2.6 (1.4)
O_2 + 13% CO	0.9	4.0	12.2	5.33	69.9	9.9		11000	300	254	1.3
O_2 + 40% CO	0.5	7.0	15.0	3.35	54.1	5.5		13400	1070	405	1.2
O_2 + He (1:3)	0.5	1.0	13.7	2.88	44.9	5.7		13200	376	816	1.2
O_2 + CO_2 (1:1)	0.5	0.8	13.7	2.26	33.3	5.5		11900	358	679	1.3
O_2 + CO_2 (1:3)	0.2	0.3	14.5	0.98	15.2	2.4		12300	800	1690	1.2
$P^\circ_{O_2}$ = 20 Torr											
O_2	0.6	1.4	19.0	2.69	54.9	6.1		17900	257	486	1.2
$P^\circ_{O_2}$ = 30 Torr											
O_2	0.3	0.8	29.7	1.15	36.8	3.2		28600	503	1110	1.2

of water at the explosion by a factor of 2 reduces the value of ratio (B) for the same experiments to 1.4. In pure oxygen therefore the simple mechanism appears adequate to predict the onset of an explosion over the whole temperature and pressure ranges of the present study.

8.3.2 ADDED HYDROGEN, WATER AND METHANE

In the presence of hydrogen, equation (A) and ratio (B) were modified as follows:

(D) $$\frac{[H]}{[O]} = \frac{k_4[H_2O] + k_5[H_2] + k_7 + k_8[CO][M]}{k_3[O_2]}$$

(E) $$\frac{[O]}{[H]}\left[\frac{k_4[H_2O] + k_5[H_2] + k_3\frac{[H]}{[O]}[O_2]}{k_7\frac{[O]}{[H]} + k_8\frac{[O]}{[H]}[CO][M] + k_9[O_2][M]}\right]$$

The values of (D) and (E) were calculated for all experiments with added hydrogen and are included in Tables 8.4 - 8.7. The values of ratio (E) were considerably greater than the values obtained in pure oxygen or in the presence of other additives. In other words, explosion occurred after the conversion of a greater amount of carbon and therefore after the formation of a greater amount of water than is predicted by the inclusion of the branching reaction (5). Water is less reactive as a chain branching agent than is hydrogen. Therefore, it seems likely that a substantial part of the hydrogen was converted to water before

explosion occurred so that the important branching reaction was (4) rather than (5). Making the assumption that at these temperatures all the added hydrogen was converted to water before the explosion, values of the rates of branching and termination reactions and of ratio (B) were recalculated for the experiment with added hydrogen. The new values are included in Tables 8.4 - 8.7 in brackets below the values obtained using the concentration of hydrogen added in the experiment. Since the new values are comparable to those obtained in all the other experiments, it is probably reasonable to conclude that water rather than hydrogen was the effective branching agent in these experiments. Attempts were made to test the extent of conversion of hydrogen to water by introducing mixtures of oxygen plus 0.1% hydrogen into the reaction vessel both with and without the carbon film present. Formation of water was observed although a quantitative estimation of conversion was complicated by losses of water. Nevertheless, the results clearly demonstrated that a large fraction of hydrogen was converted to water immediately after admission into the reaction vessel. In the original calculations the rate of the branching reaction was therefore over-estimated leading to large values for ratio (E). In a similar manner, ratio (E) was calculated for experiments with additions of water and the results are included in Tables 8.4 - 8.7.

Additions of methane were made to test qualitatively the effect of an additional hydrogen donor on the onset of explosion. Because reaction (6) introduces the new radical, CH_3, into the system the mechanism can no longer be represented by the small set given on p.130,

and ratio (B) would therefore not adequately describe the conditions for explosion. Quantitative assessment of the effect of methane was therefore not attempted.

8.3.3 ADDED INERT GAS

In the presence of inert gases, equation (A) and ratio (B) were modified as follows:

$$\frac{[H]}{[O]} = \frac{k_4[H_2O] + k_7 + \Sigma k_8[CO][M]}{k_3[O_2]} \qquad (F)$$

$$\frac{[O]}{[H]}\left[\frac{k_3\frac{[H]}{[O]}[O_2] + k_4[H_2O]}{k_7\frac{[O]}{[H]} + \frac{[O]}{[H]}\Sigma k_8'[CO][M] + \Sigma k_9[O_2][M]}\right] > 1 \qquad (G)$$

where $\Sigma k_8[CO][M] = k_8[CO]([O_2]+[CO]) + k_{8,He}[CO][He] + k_{8,CO_2}[CO][CO_2]$

and $\Sigma k_9[O_2][M] = k_9[O_2]([O_2]+[CO]) + k_{9,He}[O_2][He] + k_{9,CO_2}[O_2][CO_2]$

The constants $k_{8,He}$, k_{9,CO_2}, $k_{9,He}$ and k_{9,CO_2} take into account the different efficiencies of helium and carbon dioxide, compared to the usual mixture of oxygen and carbon monoxide, as stabilizing molecules in reactions (8) and (9). In accord with previous studies [80,97] the efficiencies of carbon dioxide and of helium relative to oxygen were taken as 1.8 and 0.7 respectively, so that $k_{8,He} = 0.7\ k_{8,CO_2} = 1.8\ k_8$, $k_{9,He} = 0.7\ k_9$ and $k_{9,CO_2} = 1.8\ k_9$. Adjustments were also made in the surface termination rate constant, k_7, to account for the variation

in the rate of diffusion in the presence of inert gases. It was assumed that the diffusion of oxygen atoms through helium is 4 times faster than through oxygen molecules and through carbon dioxide is slower by a factor of 1.5 [105]. Values of ratio (G) are included in Tables 8.4 - 8.7. In all cases, whether the effect of the inert gas was inhibiting (at 900 and 935 K) or accelerating (at 1048 K), explosion was predicted at the observed concentration of the reactants.

8.4 Relative values of branching and termination reactions

Tables 8.4 - 8.7 list the relative values calculated for each branching and termination reaction for each set of experimental conditions. Only relative values are given since neither [H] nor [O] could be obtained independently. The widest variation occurred in the relative importance of the heterogeneous termination reaction. Over the range of conditions explored, the ratio of the rate of surface termination to the total rate of gas phase termination ranged from 25 to 0.3. The two homogeneous termination reactions (8) and (9) were of similar magnitude over the whole range of temperature, concentration of reactants and inert gas pressures. Only in the presence of added hydrogen did reaction (9) become significantly greater than reaction (8). The rates of the two branching reactions (3) and (4) remained within a factor of 5 of each other except again during the experiments with added hydrogen, where reaction (3) became more important than (4). The validity of these increases in the importance of reactions (9) and (3) are questionable, however, in view of the probable conversion of hydrogen to water, as explained earlier.

In all experiments the ratio H/O remained below 10^{-2} and was often close to 10^{-3}. This result suggests that oxygen atoms are the important radical species and that their steady-state concentration will control the development of the explosive conditions. The importance of this conclusion is evident when an alternative calculation of the critical condition for explosion is considered. The ratio H/O given by equation (A) was obtained by assuming a steady-state concentration of oxygen atoms. This ratio may alternatively be obtained by assuming steady-state concentration of hydrogen atoms and of hydroxyl radicals, as follows:

$$\text{(H)} \qquad \frac{[H]}{[O]} = \frac{2k_4[H_2O]}{k_9[O_2][M]}$$

When the ratio H/O obtained by this equation is used for the calculation of ratio (B) (the critical condition for an explosion), the values obtained are greater than obtained using equation (A) for ratio H/O, particularly at temperatures 973 and 1048 K. For example, for experiments at 15 Torr at 1048 K, the value of ratio (B) changed from 1.4 to 10, when the above alternative equation (H) is used for the ratio H/O. It must be concluded that hydrogen atoms and hydroxyl radicals do not attain steady-state concentration in the system and the rates of the reactions are controlled by the concentration of oxygen atoms.

8.5 Comparison with the hydrogen-oxygen reaction

The mechanism of the explosion in the carbon monoxide-oxygen system as presented on p.130 has many similarities to the mechanism of the hydrogen-oxygen reaction, and may be regarded as a modified hydrogen-oxygen explosion reaction. In the latter system, reactions (3) and (5) are the branching reactions and reaction (9) is the predominant termination reaction at higher pressures. The contribution of carbon monoxide to the explosion condition, besides through the termination reaction (8), is through the conversion of OH to H by the chain propagation sequence, reactions (2) and (3). Although carbon monoxide itself is not involved in a branching reaction, the reduction of hydroxyl radicals to hydrogen atoms is equally important in providing the conditions for an explosion.

The most important factor leading to branching is the concentration of water in the reaction mixture. Reaction proceeds until sufficient water is present to allow the rate of branching to exceed the rate of termination. Other conditions of reactant concentration and total pressure must, of course, also be fulfilled. An interesting intermediate situation was observed in region III, where the yields of carbon monoxide remained low throughout the course of the reaction. It was concluded, from the results of experiments with additions of carbon monoxide and from the fact that carbon reacted at about the usual rate, that the yield of carbon monoxide represented a steady-state value, kept low because of a rapid reaction causing its removal. This suggests that in region III the total rate of branching is not sufficient to cause explosion but the concentration of hydroxyl radical is sufficient to cause rapid oxidation

of carbon monoxide by reaction (2). This delicate balance may be achieved over a range of pressures if the increase in the rate of reaction (4) as reaction proceeds is accompanied by a decrease in the rate of reaction (3) (through stabilization). At still higher pressures reaction (3) may not occur at all and the concentration of OH remains too low to cause effective oxidation by reaction (2).

There are some further differences between the hydrogen-oxygen reaction and the carbon monoxide-oxygen reaction which may be commented on at this point. The hydrogen-oxygen reaction is characterized by either a slow reaction or an ignition while the carbon monoxide-oxygen reaction shows two additional phenomenon viz. sustained chemiluminescence (or glow) and oscillatory luminiscence. Gray [106,107], Yang [100] and Bond, Gray, Griffiths and Scott [88] offered theoretical analyses of these modes of reaction on the basis of Liapunoff's stability theorem [108]. Depending on the value of the net branching factor, ϕ, which is the difference between rates of branching and termination, three kinds of behaviour are predicted by these analyses: (i) no reaction (or very slow reaction controlled by initiation)) when $\phi < 0$; (ii) damped oscillation or a sustained glow when $\phi > 0$ but less than some critical value, ϕ_r; and (iii) explosion when $\phi > \phi_r$. These analyses thus suggest a gradual transition within the region $0 < \phi < \phi_r$ in the carbon monoxide oxidation system, in contrast to a sharp transition from slow reaction to explosion at $\phi = 0$ in the hydrogen oxidation system. Recently, Gray and coworkers [79,85,88] provided experimental evidence for all four modes of reaction and showed that the occurrence of a particular mode of reaction depends critically on the temperature, pressure, the amount of hydrogen present

in the mixture and conditions of the surface. In fact, using a continuously fed, stirred-tank reactor (c.s.t.r.) and by an interplay of the parameters just mentioned, they were able to see all six types of transitions between different pairs of the four modes of reaction [85]. By comparison of these results with those of the present study, it seems plausible that the onset of explosion corresponds to a transition from slow (or dark) reaction to ignition and the behaviour in the region III corresponds to a transition from slow reaction to chemiluminescence. This study was, however, not accompanied by the measurement of emitted light and further interpretation of the reaction in this region is probably not warranted at this stage.

8.6 Effects of inert gases and the relation to the explosion limits

The fact that the simple mechanism proposed here can satisfactorily predict an explosive condition over the temperature interval 900-1048 K is indeed remarkable, taking into consideration the changes in the relative significance of the various reactions over this temperature interval. The most striking example of this change was the reversal in the effect of inert gases on the onset of an explosion, from inhibition to promotion. This change reflects an important shift in the relative contribution of gas phase termination to surface termination. The presence of inert gas increases the rate of homogeneous termination but reduces the rate of heterogeneous termination, where this is diffusion-controlled. The global effect of inert gas will therefore depend on the relative importance of the two termination reactions, which in turn depends on the total pressure. At high pressures, where homogeneous

termination dominates, inert gases will exert an inhibiting effect on the onset of explosion, whereas at low pressures, where heterogeneous termination dominates, inert gases will have a promoting effect.

These effects of inert gases are illustrated in Figure 8.1. The change in the amount of carbon consumption prior to the onset of explosion on addition of inert gas is shown at three temperatures. At each temperature a pressure in the middle of the range where explosion occurred is used for illustration. At 935 K in the presence of inert gas a large increase in the amount of carbon conversion, and hence in the concentration of water, was needed for the occurrence of an explosion, which implies a large inhibiting influence of these gases. At this temperature where explosion was observed at fairly high pressures, gas phase termination reactions (8) and (9) were important (Tables 8.4 and 8.5) and the main effect of the inert gas was to increase the rates of these reactions. To approach unity ratio (G) required a higher pressure of water vapour and therefore a higher conversion of carbon. Incidentally, it may be pointed out here that the fact that carbon dioxide was more effective than helium as an inhibitor is an important evidence in favour of the conclusion that explosion in the oxidation of carbon monoxide is the result of branched chain reactions and not thermal imbalance. In the latter case, helium would be a better inhibitor due to its higher thermal conductivity. At 973 K the effect of addition of inert gas was small but at 1048 K the effect was clearly promoting. At this temperature explosion was observed at low pressures and surface destruction (7) was the dominant termination reaction. The most

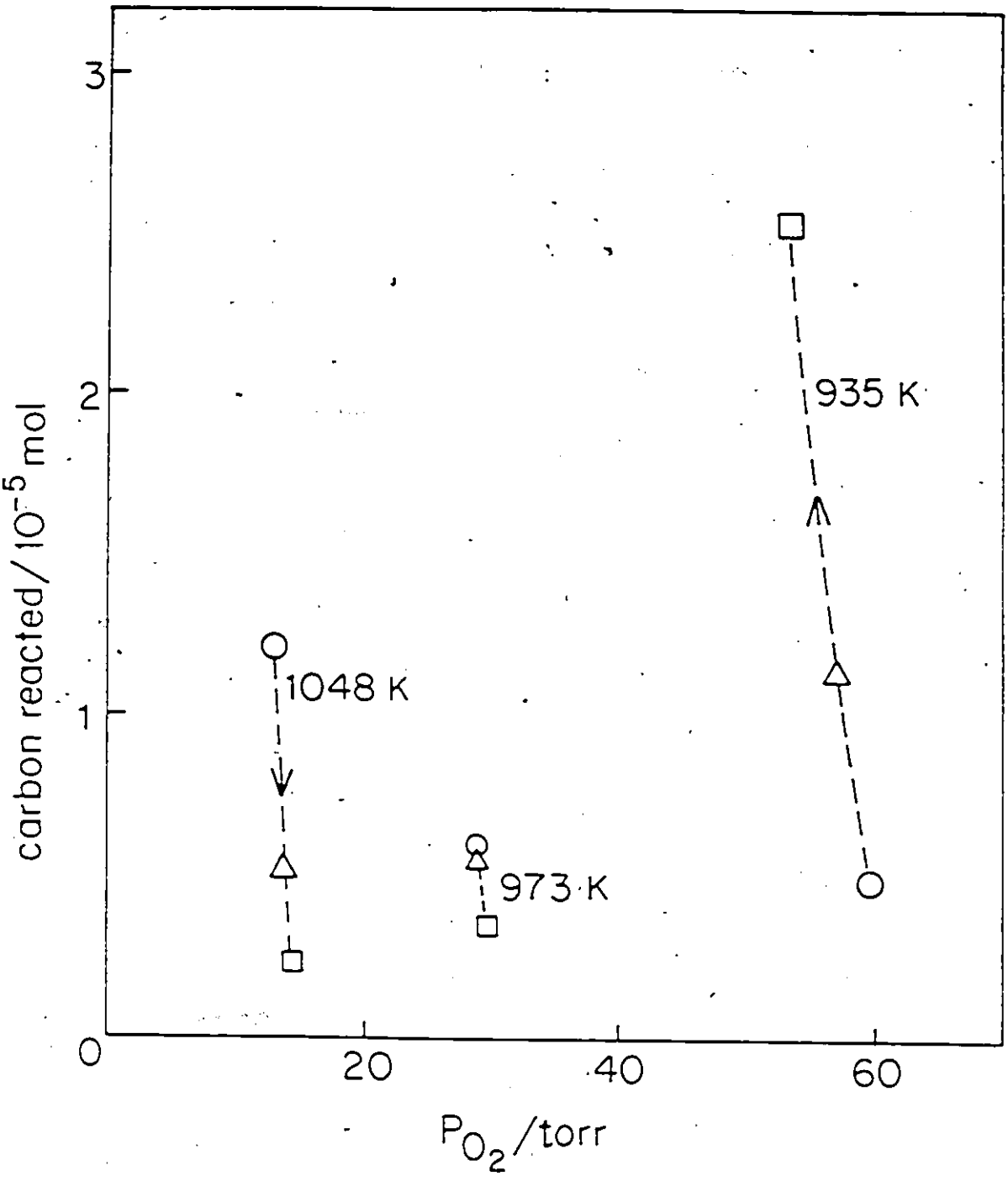


Figure 8.1. Reversal in the effect of inert gas on the onset of an explosion. Arrows indicate the trend towards higher conversion of carbon before an explosion at 935 K and towards lower conversion of carbon before an explosion at 1048 K.

○ : O_2; △ : O_2 + He; □ : O_2 + CO_2.

important effect of the inert gas was inhibition of this surface termination through reduction in the rate of diffusion to the surface. The value of ratio (G) thus reached unity at a lower extent of reaction.

The effect of inert gases is also illustrated in Figure 8.2 which shows some of the results of a series of reactions with a constant partial pressure of oxygen (30 Torr) and increasing pressures of carbon dioxide (10,30,90,120,150 and 180 Torr) at 973 K. Explosion was observed with pure oxygen and with the mixture containing 10 Torr of carbon dioxide, which promoted the explosion at a lower extent of reaction, as expected. With the mixtures containing 30 and 90 Torr of carbon dioxide the explosion was less clearly defined. A sudden drop in the pressure of carbon monoxide occurred, as illustrated for 90 Torr of carbon dioxide, and carbon monoxide no longer accumulated in the system during the rest of the reaction. With additions of 120, 150 and 180 Torr of carbon dioxide a very rapid secondary oxidation of carbon monoxide, which could no longer be described as an explosion, commenced at a later stage in the reaction. This rapid reaction began after an amount of carbon consumption much larger than the amount consumed before the onset of explosion with pure oxygen. With 180 Torr of carbon dioxide in the mixture it occurred after about 90% of the carbon had reacted and continued after the carbon had been completely consumed. These results are summarized in Figure 8.3, where the points show the amount of carbon consumed before the onset of an explosion, or of a secondary oxidation of carbon monoxide, as a function of increasing partial pressure of carbon dioxide in the mixtures. The figure clearly shows that the extent of

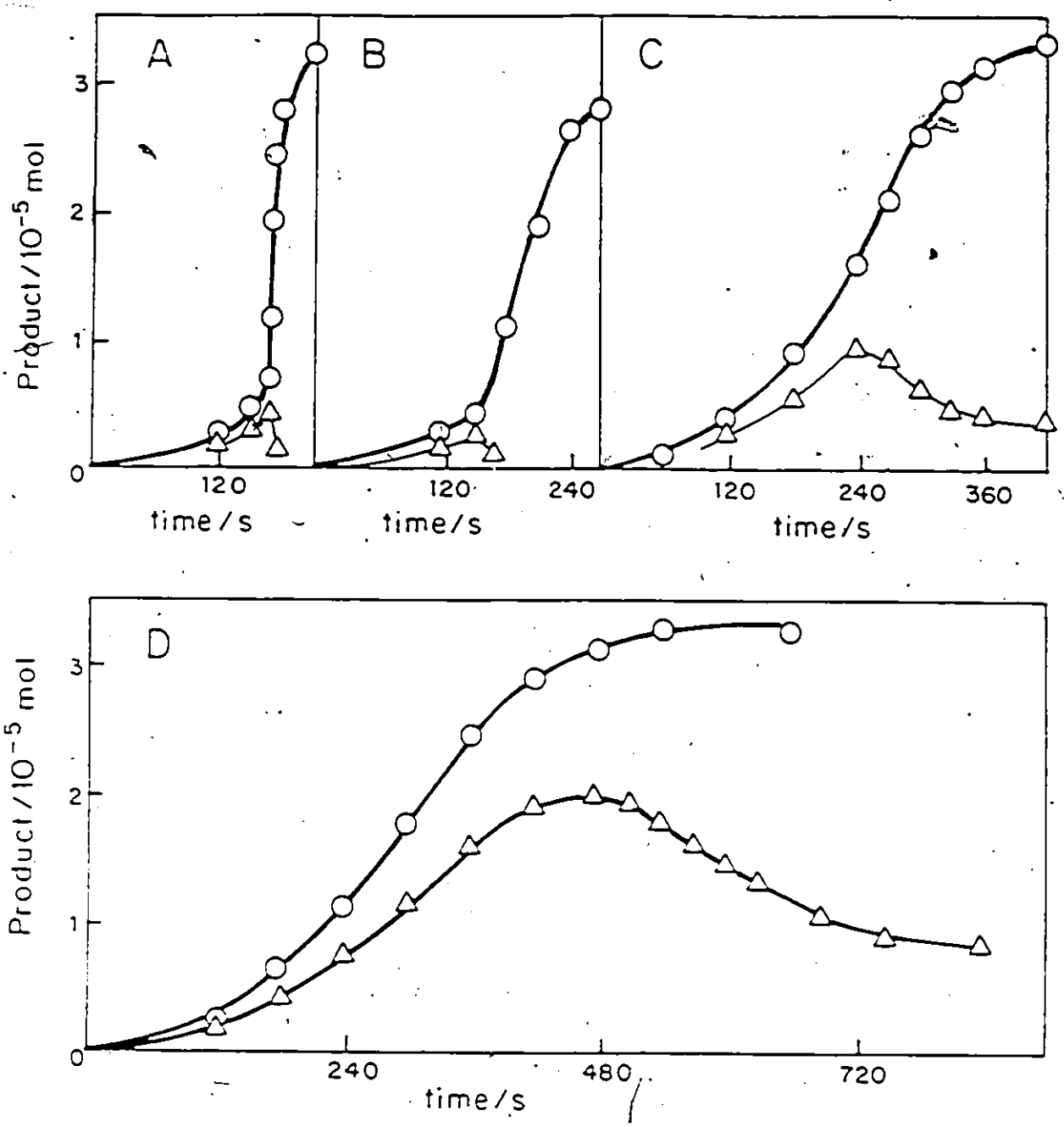


Figure 8.2. Illustration of the changes in the rate of oxidation of carbon monoxide on addition of carbon dioxide at 973 K. Initial pressure of oxygen: 30 Torr. Circles refer to carbon consumed and triangles to carbon monoxide formed.

A: O_2; B: $O_2 + CO_2$ (1:3); C: $O_2 + CO_2$ (1:5); D: $O_2 + CO_2$ (1:6).

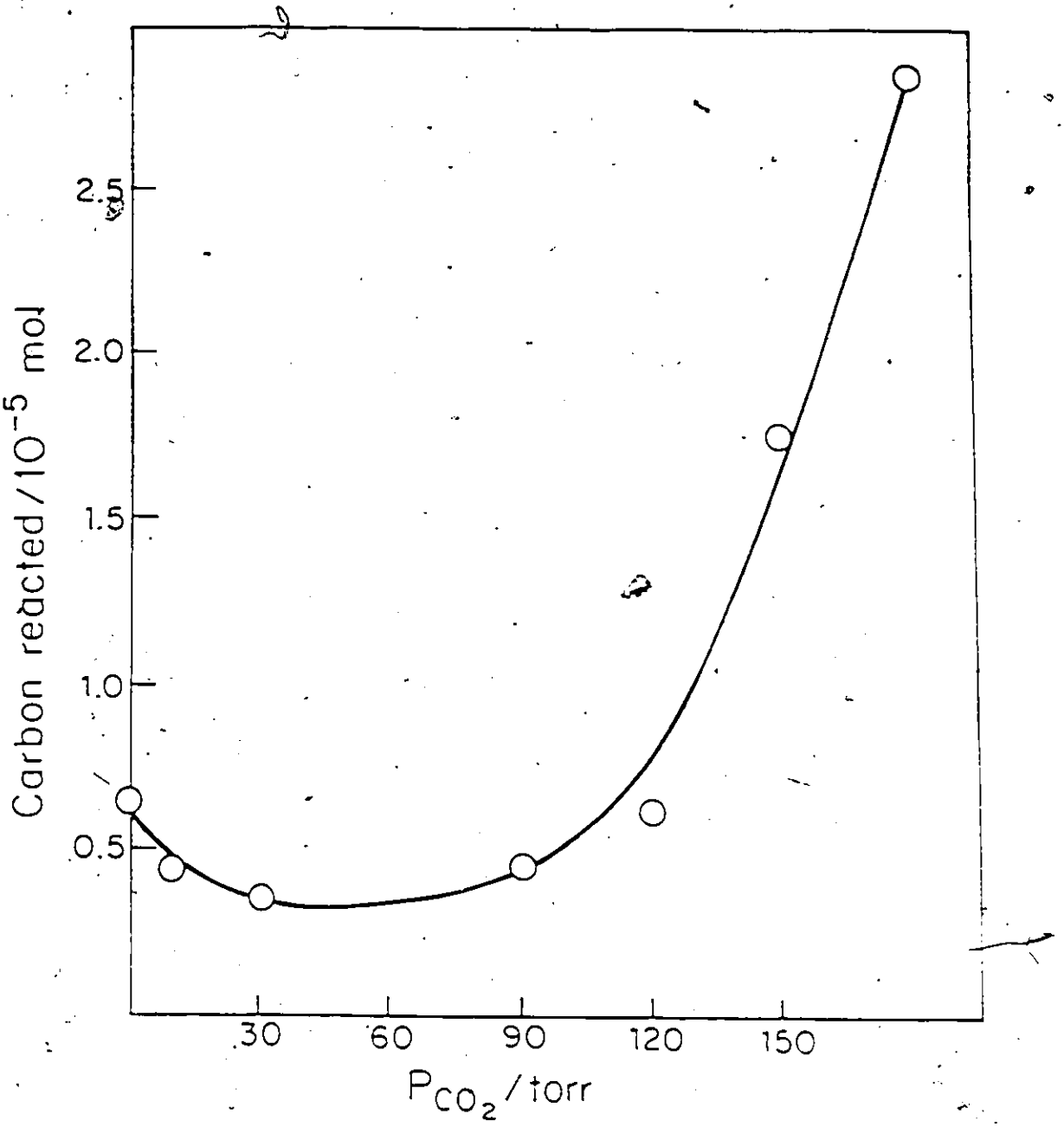


Figure 8.3. Effect of carbon dioxide on the extent of carbon consumption prior to the onset of an explosion or of a rapid oxidation of carbon monoxide at 973 K. Initial pressure of oxygen: 30 Torr.

carbon consumption prior to the onset of explosion or rapid oxidation passed through a minimum value as the pressure of carbon dioxide in the mixture was increased.

Two effects of inert gas are illustrated by this set of experiments: a transition from the region of the first explosion limit to the region of the second explosion limit and a gradual change in the rate of oxidation of carbon monoxide from an explosion to a rate comparable to the "normal" surface reaction with oxygen. The reversal in the trend describing the extent of carbon conversion with increasing pressure of carbon dioxide clearly indicates a change in the relative importance of surface and gas phase termination processes. At low pressures carbon dioxide promoted the explosion and thus acted primarily to lower the rate of the surface termination. At higher pressures carbon dioxide inhibited the explosion or rapid reaction of carbon monoxide and its main effect was therefore to increase the rate of the homogeneous termination, reactions (8) and (9). These results clearly show that a gradual transition from the region of the first explosion limit to the region of the second explosion limit can be attained simply by diluting the reactants with an inert gas. This set of experiments also shows how changes in the rate of oxidation of carbon monoxide over several orders of magnitude can be achieved simply by the addition of inert gas to the reaction mixture*. Again this emphasizes the complex balance between the rates of homogeneous and heterogeneous termination reactions and between

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* The net rate of oxidation of carbon monoxide is the rate of loss shown in Figure 8.2 plus the rate of removal of carbon.

the rates of chain branching and termination reactions, particularly reactions (3) and (9). The explosion and the rapid oxidation represent only slightly different rates of these various reactions. Both involve oxidation of carbon monoxide through reaction (2) but in the rapid oxidation the concentration of radicals remains just below the critical condition. The transition from slow to rapid oxidation is exactly analogous to the transition from slow reaction to ignition and both depend critically on the presence of water.

Figure 8.2 also illustrates the dependence of the rate of gasification on the concentration of radicals in the gas phase. When an explosion occurred, the rate of gasification also increased suddenly and dramatically. The onset of rapid oxidation of carbon monoxide, on the other hand, did not affect the rate of gasification (note experiments with 180 Torr CO_2). The concentration of radicals was sufficient to oxidize carbon monoxide but not sufficient to affect the rate of removal of carbon. It should be mentioned that until the onset of rapid secondary oxidation of carbon monoxide, the ratio of the products, CO/CO_2, remained practically constant, again suggesting that both the explosion and the secondary oxidation begin rather suddenly at a particular, crucial concentration of water vapour, and that up until this point the reaction is described by the series of heterogenous processes discussed in Part I. This point will be discussed further in Part III, Chapter 9.

From previous studies of ignition of mixtures of carbon monoxide and oxygen in the region of the second explosion limit, there is a general agreement that the addition of inert gases helium, argon, nitrogen or

carbon dioxide inhibits the explosion [80]. In the region of the first limit, however, variable effects have been reported. Hadman, Thompson and Hinshelwood [81] found that at 923 K argon and nitrogen lowered the partial pressure of the combustible mixture required to produce an explosion, while Linnett, Reuben and Wheatley [84] found no effect of additions of nitrogen, argon or carbon dioxide at 897 K. These apparently conflicting results reflect the large differences in reactivity and the unpredictable nature of quartz surfaces, which determine the rate of the termination process in this region. The carbon-coated surface, on the other hand, was entirely reproducible in controlling the rate of the termination process and therefore the results defined unambiguously the contribution of heterogeneous and homogeneous processes in the region of the first explosion limit. In fact, a carbon-coated surface could perhaps be useful in providing definition of the first explosion limit in other reactions leading to explosion.

8.7 Explosion on exposure of quartz surface

The occurrence of an explosion immediately after the complete consumption of carbon (Figure 7.13) clearly illustrates the striking difference in the efficiency of the surface termination process between the carbon-coated surface and the bare quartz surface. As soon as the quartz surface is exposed the destruction of oxygen atoms becomes much less efficient, the rate of termination drops and the conditions for explosion are fulfilled. It appears that the carbon-coated surface retained its efficiency in preventing explosion until at least 98% of the

carbon was removed. The small amount of carbon remaining would be barely sufficient to cover the surface with a monolayer. Although previous studies [38] have indicated that the carbon film, similar to that used in the present study, forms a uniform layer, it hardly seems plausible that the uniformity extends to a monolayer thickness. Rather it seems likely that rapid removal by carbon is maintained, even if the surface is only partly covered, because of a high degree of mobility of the oxygen atoms on the surface. In all cases where explosion was observed on bare quartz a reduction in efficiency of the surface termination by a factor of about 50 was sufficient to bring the system to an explosive situation. Explosions under these conditions were not observed at 935 K or below because, for similar pressures, the rates of branching are considerably lower.

This phenomenon of the occurrence of an explosion in the presence of the quartz surface under conditions where explosion did not occur when the surface was covered by carbon, undoubtedly indicates that the carbon coating displaces the lower explosion limit to higher pressures. The fact that at a temperature of 1048 K explosions did not take place below a total pressure of the reactant of 10 Torr is a convincing demonstration of the high efficiency of the carbon surface for removal of chain carriers. With a bare quartz reaction vessel at this temperature explosions should occur at pressures down to about 0.1 Torr, although no direct measurements have been made. Other coatings on a quartz surface have also been shown to raise the pressure of the first explosion limit. Aleksandrov and Azatyan [109] studied reactions in a vessel coated with magnesium oxide and Linnett et al. [84] used a vessel with an alumina

surface. The magnitude of these changes in the explosion limit can not be quantitatively compared because of differences in the systems, but qualitatively the effect shows the importance of the efficiency of the surface in destroying chain carriers in defining the first explosion limit.

8.8 Dependence of criticality for explosion on temperature and pressure of oxygen

The attainment of explosive conditions depends in a complex way on the temperature, total pressure and concentration of reactants, oxygen, carbon monoxide and water. Figure 8.4, where the points represent the onset of an explosion, illustrates how these conditions alter at five temperatures, in terms of the amount of carbon reacted, which is proportional to the concentration of water in the gas phase, and the pressure of oxygen. The trends may be understood from an examination of the factors which affect ratio (B).

At the three highest temperatures explosive conditions are fulfilled with smaller consumption of carbon as the pressure of oxygen increases. The rates of the two branching reactions in the numerator thus roughly balance each other. The dependence becomes very strong at low pressures, as the surface termination assumes increasing importance and becomes the dominant term in the denominator, requiring large concentrations of water for ratio (B) to approach unity. As the pressure of oxygen increases branching by reaction (3) begins to dominate. Only small quantities of water are required for explosion. The ratio H/O is also a function of the pressure of oxygen and although changes in it will affect the relative magnitude of reactions (3) and (4), the qualitative

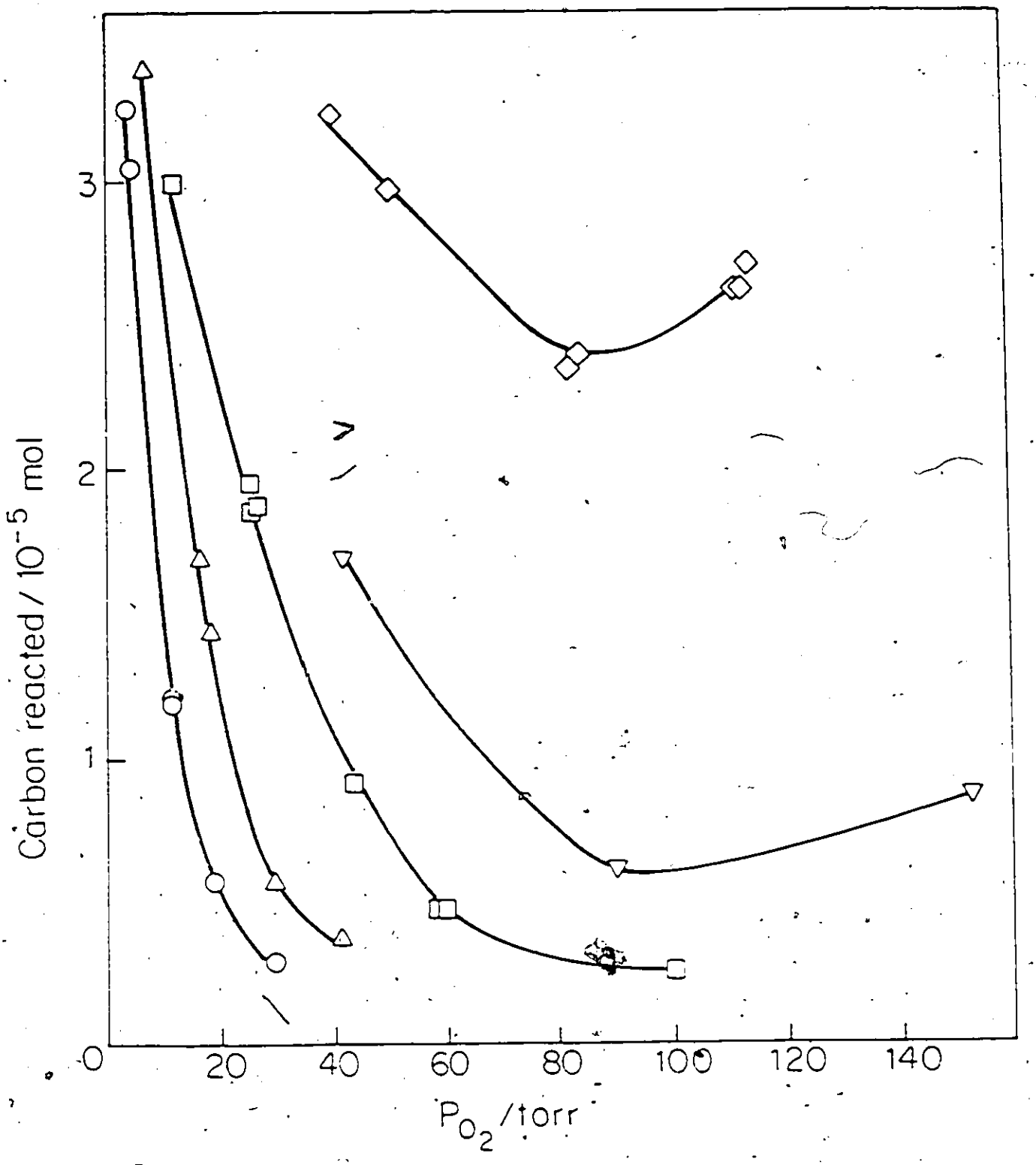

Figure 8.4. Effect of temperature and pressure of oxygen on the extent of carbon consumption prior to the explosion.

◇ : 900 K; ▽ : 918 K; □ : 935 K; △ : 973 K; ○ : 1048 K.

significance of the curves is not changed. Finally, in addition to these changes, the yield of carbon monoxide becomes too small to provide a sufficient rate of reduction of hydroxyl radicals and the system passes into region III. Because of the variable and non-reproducible behaviour of quartz surfaces for radical termination, relatively few studies of the reaction have been made to determine the first explosion limit [78,81,84, 109,110], particularly at temperatures above 900 K. With the carbon surface, oxygen atoms react so rapidly that the surface termination was diffusion-controlled at all temperatures and as a result, these limits were entirely reproducible in the present study.

The dependence of criticality for explosion on temperature is complex. The rate constants most strongly dependent on temperature are k_3 and k_4, while k_7, k_8 and k_9 are almost independent of temperature. The ratio H/O will probably not alter substantially with temperature since the temperature coefficients of k_3 and k_4 are similar and their changes will largely compensate each other. The value of ratio (B), on the other hand, will depend strongly on the temperature since both the temperature-dependent rate constants, k_3 and k_4, appear in the numerator and the denominator involves only termination reactions. As the temperature is raised explosions take place with lower concentration of water and lower pressures of oxygen. It is clearly seen from the figure that with increasing temperature, for a constant pressure of oxygen explosions occur at progressively lower consumption of carbon or for a constant consumption of carbon at progressively lower pressure of oxygen. This indicates the contribution of both branching reactions to the development of explosive conditions.

The slope of the curves decreased as the temperature decreased as a result, among others, of the changes in the ratio H/O and of the lessening importance of the surface termination at higher pressures. At 900 K the curve passed through a minimum value. This is explained by the increasing importance of reactions (8) and (9) in the termination processes. In the range of pressure where these homogeneous terminations are not important, the rates of the branching reactions in the numerator roughly compensate each other as the pressure of oxygen is increased. Beyond a pressure of about 80 Torr, gas phase termination reactions cause sufficient reduction in ratio (B) to require more water to reach the explosive condition. The effect was also observed, but not as definite, at 918 K. At higher temperatures the system passed out of the explosion region before passing the minimum. At 883 K no explosions were observed under any conditions. The attainment of explosive conditions is thus seen as a complex balance between the rates of the branching and termination reactions, each of which has its own dependence on temperature, total pressure and concentration of reactants.

PART III

RELATION OF THE GAS PHASE REACTIONS TO THE GASIFICATION OF CARBON

In the last four chapters, the phenomenon of gas phase explosions between carbon monoxide and oxygen during the gasification of thin films of pyrolytic carbon was described. As illustrated in several figures (e.g. Figures 6.1, 7.1B, 7.2), the explosion caused a dramatic increase in the rate of gasification of carbon. For example, under the conditions of the reaction described in Figure 6.1, there was approximately a 70-fold increase in the rate of gasification at the onset of explosion.

These results clearly show that the atomic and radical reactions occurring during the explosion affect the rate of the gasification process. In Part III (Chapters 9 and 10), the relation between the gas phase reactions and the gas-solid reactions will be examined with regard to both qualitative and quantitative aspects. In Chapter 9 qualitative effects of the presence of water and of inert gases in the reactants on the gasification process under conditions where explosions were observed will be discussed. As a comparison, the effect of various additives on the reaction will also be examined under conditions outside the regions where explosions occur. In Chapter 10 the rates of gasification observed during a gas phase explosion will be quantitatively related to the concentration of various reactants. The results are interpreted to indicate that gasification under these conditions occurs largely by reaction of oxygen atoms.

CHAPTER 9

THE EFFECT OF WATER VAPOUR AND OF INERT GASES ON THE CARBON-OXYGEN REACTION

9.1 Effect of water vapour

The results described in the earlier chapters showed that the formation of a small quantity of water vapour played a key role in the development of explosive conditions. The source of water in the products of the oxidation was the presence of traces of hydrogen in the carbon film. The film was prepared by pyrolysis of methane at 1223 K. Pyrolytic carbons and carbon blacks prepared in this manner by decomposition of hydrocarbon gases and vapours and subject to heat-treatment up to 1000 K usually retain some hydrogen, not as adsorbed or occluded hydrogen (since these carbons are usually of low porosity), but as C-H bonds. During the reaction with a large excess of oxygen, this hydrogen is released into the system as water in the gas phase and in the present system was produced continuously throughout the course of the reaction. From the effect of added water vapour on the onset of explosion (described in Section 8.3), it was concluded that the carbon films used in the present study contained approximately 0.35% hydrogen by weight which, after complete gasification of the film, gave a pressure of water of about 0.2 Torr.

Since the source of water in the present system was the hydrogen present in the carbon, it may be useful to mention the H-content of some other varieties of carbon which are often used for the oxidation studies. Marsh, Taylor and Lander [111] reported that the graphitizable carbons

prepared from polyvinyl acetate retain 0.45%, 0.12% and 0.07% of hydrogen after heat-treatment to 1200, 1500, and 1800 K respectively; the carbons prepared from polyfurfuryl alcohol and acenaphthylene heat-treated to 1200 K retain 0.71% and 0.65% hydrogen respectively. Millet, Millet and Vivares [112] reported a hydrogen content of carbonized polyacrylonitrile of about 0.1% after heat-treatment to 1800 K. Mason and Owen [113] reported a value of about 50 ppm (by weight) as a typical hydrogen content for a U.K. nuclear graphite (PGA) heat-treated to 3000 K and Redmond and Walker [114] reported a value of about 7 ppm for an American nuclear graphite (TSP) heat-treated to about 2300 K. Gonzalez-Vilchez, Linares-Solano, Lopez-Gonzalez and Rodriguez-Reinoso [115] reported that the activated carbons prepared from almond shells and olive stones have a H-content of about 0.65% and 0.63% respectively. Recently, Deitz [116] reported the elemental analysis of some commercial activated carbons which showed that some of the samples, particularly those prepared from coconut shell and lignite, may retain about 0.2% hydrogen. Thus it is quite possible that investigations on the gasification of carbon were often made with carbons containing sufficient hydrogen to generate an amount of water in the gas phase comparable to that of the present study.

The effects of minute quantities of water vapour, hydrogen and other hydrogeneous substances on the gasification rates of the carbon-oxygen reaction have received attention from time to time. Most authors [40,117-122] observed an inhibiting action of water vapour on the oxidation of graphite. Lang, Magnier, Gilles, Pollet and Brie [119] examined the pore structure of an oxidized electrode graphite and

observed that when oxidation was made with dry air all pores were attacked, but with moist air only the large pores were attacked. Lang, Blanchard and Magnier [120], and Lang, Blanchard and Fessler [121] also obtained similar results with pure nuclear graphite. These results suggested that in dry air oxidation proceeded uniformly on pores of all sizes, but in moist air oxidation was inhibited on micropores. About 10 years ago, Tyler et al. [40] carefully examined the effects of hydrogeneous impurities in the gas phase on the kinetics of the oxidation of spectroscopic grade polycrystalline graphite. From the effects of cooling the oxygen supply to 90 K and 195 K before admission to the reaction vessel, of previous "soaking" of the graphite samples in nitrogen, and of additions of small, discrete amounts of water vapour, hydrogen or hydrocarbon vapour to the gas-steam on the specific rate of carbon loss on gasification, these authors concluded that the presence of these substances in oxygen inhibit the oxidation reaction. It should be emphasized that the carbons used in the studies described above were all porous. On the other hand, during the oxidation of single-crystals of graphite, which provide examples of non-porous carbon, contrary to the inhibiting influence a catalytic influence of water vapour on the rate of gasification was observed [123-125]. Noting that the inhibition occurred with polycrystalline graphites but not apparently with isolated crystals, Tyler et al. [40] suggested that the inhibition is due to fast, diffusion-controlled chemisorption of these substances (or -COOH groups derived from these substances) on the entrances of micropores of atomic dimensions thereby blocking the approach of oxygen molecules to the surface within. A somewhat similar explanation was given earlier by Lang

and Magnier [122]. As for the catalytic effect, Laprov [126] suggested that it is due to the dissociation of water into hydrogen and oxygen atoms and hydroxyl radicals which interferes with the normal reaction involving dissociation of oxygen molecules at the surface.

These interpretations emphasize that the action of water on the kinetics of the oxidation of carbon arises mainly from its adsorption on the surface, which is in turn related to the porous structure of the carbon. These interpretations all disregard any influence of water through gas phase reactions of reactant and products. Recently, Sundaresan and Amundson [127] investigated, by model calculations, the effect of a modest amount of water vapour on the combustion of a carbon particle. Their calculations suggested that steam participates in the combustion by accelerating homogeneous oxidation of carbon monoxide (by the set of reactions described in Chapter 8) and through the carbon-steam reaction (thereby enhancing the rate of carbon combustion). In their analysis of the combustion of carbon, Adomeit, Mohiuddin and Peters [128] have shown that there is negligible oxidation of carbon monoxide in dry air, while at relative humidities of 10% or higher it is enhanced by a factor of 5000 compared to the dry air reaction rate. These analyses, however, neglected the combustion of carbon by reaction with oxygen atoms generated during homogeneous oxidation of carbon monoxide.

The present results have clearly demonstrated how severely the kinetics of the carbon-oxygen reaction may be affected by the presence of a very small pressure of water in the gas phase. In particular, water initiates a series of radical reactions which cause the conversion of carbon monoxide to carbon dioxide. When this oxidation occurs by an

explosion the concentration of radicals, and particularly oxygen atoms, increases by many orders of magnitude, causing the dramatic increase observed in the rate of gasification. For example, an increase of 10^3 was observed for a thick film at 900 K with 30 Torr of oxygen. The product distribution was, of course, drastically altered by the explosion but in addition, although the explosion lasted for less than a second, the effect on the rate of gasification and on the product ratio, CO/CO_2 persisted during the complete course of the reaction. This is illustrated in Figure 9.1. Apart from illustrating the dramatic increase in the rate of carbon removal and the reversal in the product distribution at the onset of explosion, the figure shows that during the period following the explosion carbon continues to react at rates appreciably higher than the rate preceding the onset of explosion and that carbon monoxide no longer builds up in the system, despite the fact that nearly 70% of the initial amount of carbon in the film reacted during this period. This behaviour after the explosion was analogous to that observed in region III described in Section 7.1.

The effect of water vapour in region III was also interesting. It was described that in this region the yield of carbon monoxide remained low throughout the course of the reaction because of rapid secondary oxidation to carbon dioxide. Under the conditions of the reaction described in Figure 7.1C, the rapid oxidation of carbon monoxide began when less than 25 ppm of water (0.0025%) had been formed (estimated from the carbon consumed). In many systems an amount of this magnitude may readily accumulate from various sources such as outgassing from reaction vessels, apart from the oxidation of hydrogen present in the carbon.

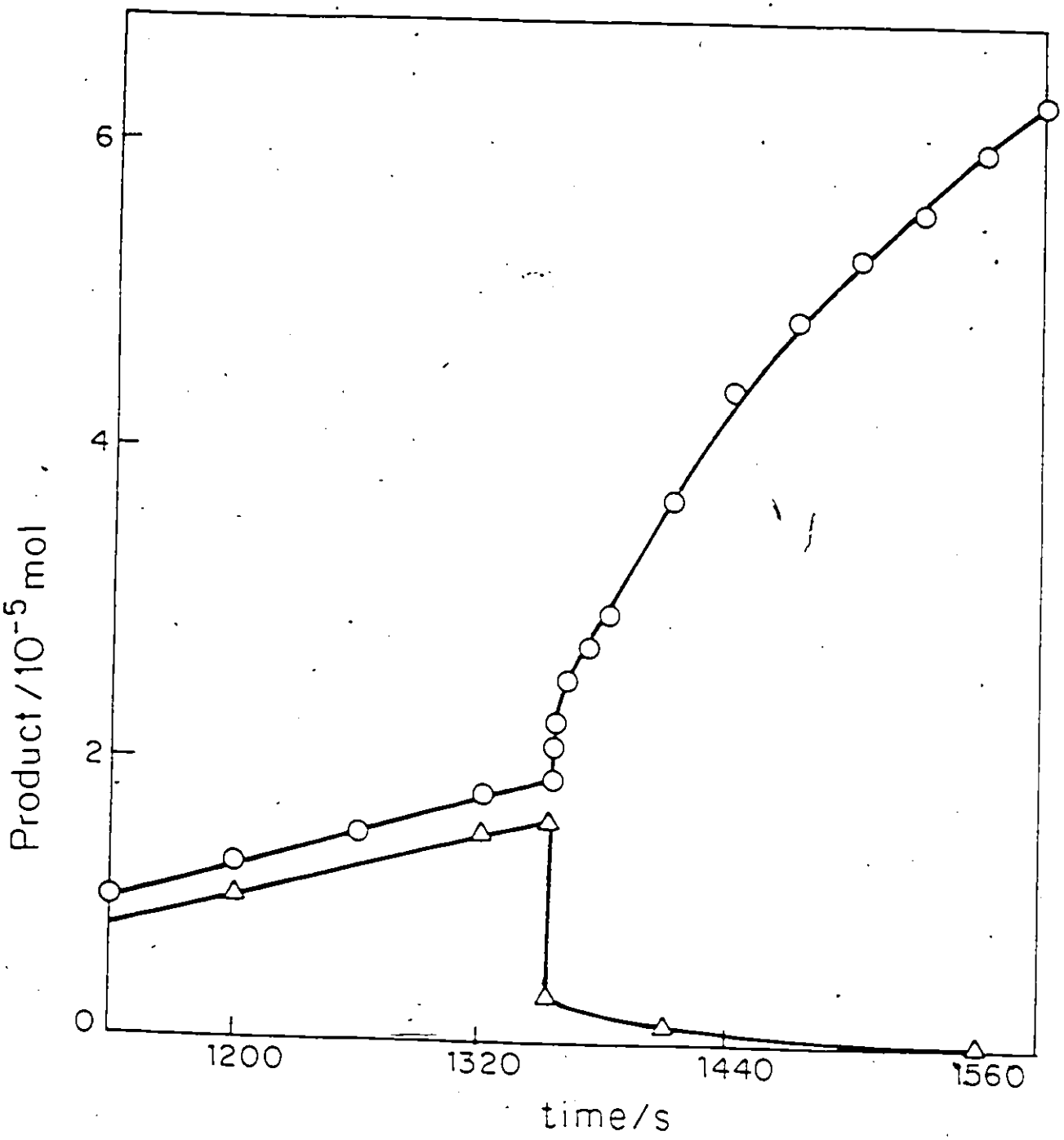

Figure 9.1. Effect of explosion on the rate of gasification and on the product distribution during the course of the reaction. The experiment was performed on a thick film at 900 K with 45 Torr of oxygen.

○ : carbon consumed; △ : CO.

9.2 Effect of inert gases

In the mid 1970s it was reported that the rates of a number of heterogeneous and catalytic reactions were influenced by the presence of inert, diluent gases [129-131] and this was called the diluent gas effect (DGE). In the case of carbon gasification, the only study reporting a diluent gas effect was by Walker, Pentz, Biederman and Vastola [132]. They measured the rates of oxidation at a total pressure of 0.1 atm and at temperatures between 823 and 889 K with mixtures of oxygen with nitrogen, argon and helium at three ratios of O_2: inert gas (1:3,1:1,3:1). The weight decrease of the carbon during gasification was followed by a quartz beam microbalance. They observed that the gasification rates varied in the order $N_2 > Ar > He$ at 889 and 871 K. They did not, however, compare these rates with those observed with pure oxygen. The authors critically examined the applicability of various models proposed by Hudgins and Silveston [129] concerning the DGE in catalytic surface reactions, to the effects observed in the carbon-oxygen reaction. Briefly, these models include: (1) increased rates of desorption of products carbon monoxide and carbon dioxide due to collisions between the intermediate oxygen surface complexes and inert gas molecules; (2) changes in the efficiency of removal of heat (note the carbon-oxygen reaction is exothermic) from the carbon surface site by collisions with inert molecules; (3) changes in the mobility of reactant and/or products on the surface due to the adsorption of inert gases on the surfaces; (4) physical (van der Waals) adsorption of inert gas at an activated complex which weakens the bonds with the carbon surface, with the consequence that the desorption is facilitated in the presence of

diluent gases. The degree of effectiveness of each of these processes will depend upon the nature of the diluent gas and in each case an order of reactivity in the rate of gasification in the presence of diluent may be predicted. Because their observed order was not consistent with any of these models, Walker et al. [132] proposed an additional model for the diluent gas effect. This model was based on the idea of formation of nascent or highly reactive sp^3 sites by gasification with subsequent rehybridization to less reactive s^2p^2 sites. The inert gas enters into the picture by influencing the rate of this rehybridization process.

In the present study, several interesting effects of inert gases on the kinetics of the carbon-oxygen reaction in regions II and III were observed. These were not due to the surface processes proposed by Hudgins and Silveston [129] but were due to gas phase reactions, including stabilization of radicals and to retardation of the diffusion of oxygen atoms to the surface. It was shown in Chapter 7 that below 973 K, inert gases delayed the onset of explosion and with sufficiently large amounts explosion did not occur at all. At 973 and 1048 K inert gases caused the explosion to occur at a lower extent of carbon conversion than observed with pure oxygen. In region III at all temperatures, the rapid secondary oxidation of carbon monoxide was avoided by addition of sufficient inert gas. Inert gases therefore caused significant effects on both the rate of gasification and the ratio of CO/CO_2, solely by effects on the gas phase reactions.

The effects on the rate of gasification are illustrated in Figure 9.2 where the rate, defined as the maximum rate of gasification as

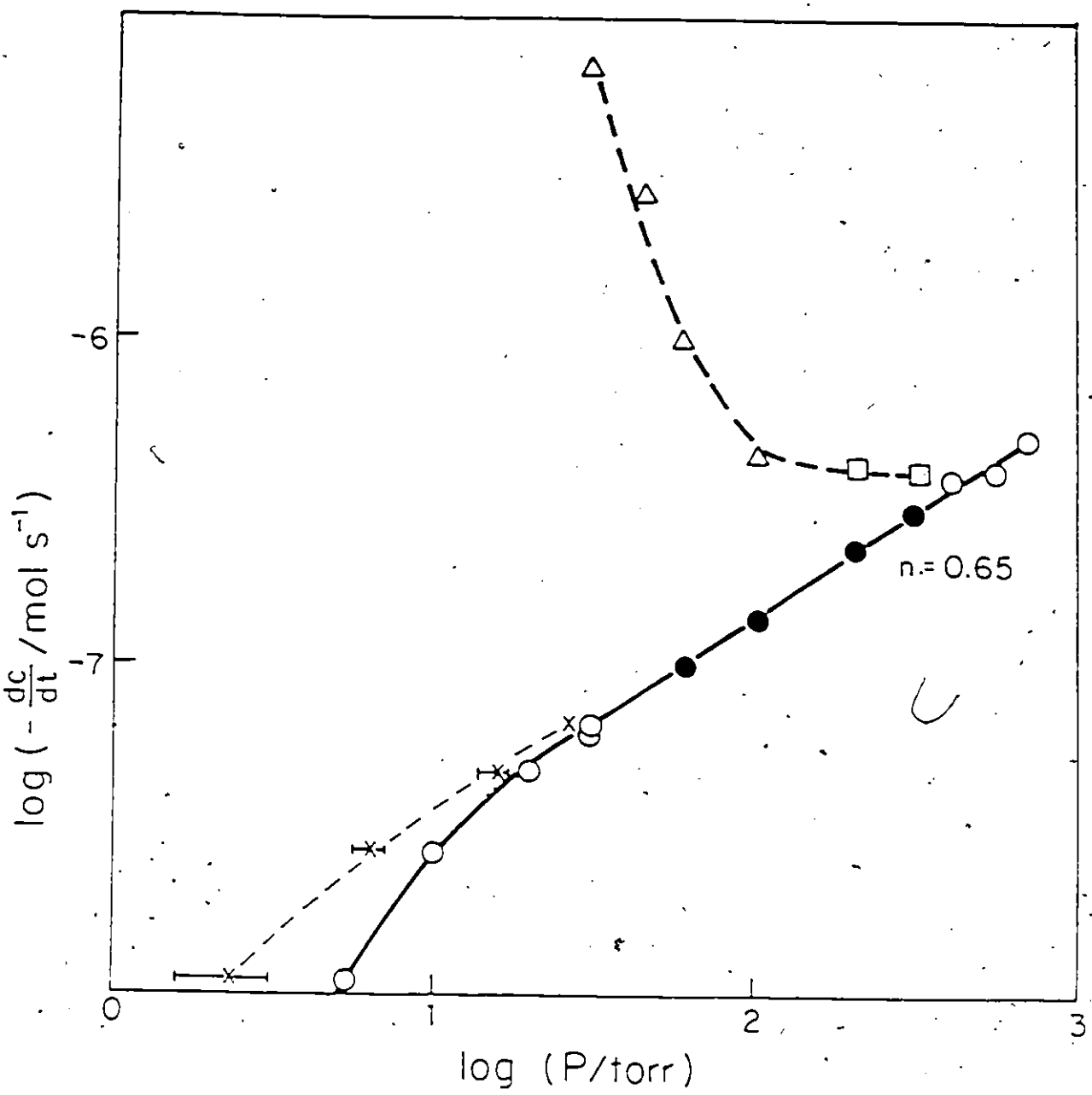

Figure 9.2. Maximum rates of carbon removal as a function of pressure of oxygen.

○ : pure O_2 (pressures of oxygen correspond to initial pressure);
X : pure O_2 (pressures of oxygen correspond to those at the instant of maximum rate of reaction);
□ : pure O_2 in region III; △ : pure oxygen at explosion;
● : O_2 - CO_2 mixtures.

illustrated in Figure 7.1, is shown as a function of pressure of oxygen. This figure shows the large increases in the rate of gasification induced by the explosions as well as the effect on the rate of the presence of inert gases. The open symbols represent the rate with pure oxygen as reactant in regions I-IV described earlier. The circles refer to regions I and IV where explosions did not occur. The triangles indicate region II and the squares, region III. Pressures below 30 Torr correspond to region I where rates were easily measured. In this region the rates increased with increasing pressure of oxygen, with an order of about 0.65. Between 40 and 100 Torr the rate was dramatically increased, but decreased with increasing pressure of oxygen, levelling off at about 200 Torr as the system entered region III. At higher pressures, in region IV, the rate continued the dependence on pressure of oxygen observed in region I with values corresponding to an extrapolation of the rates from region I. Dilution with inert gas in region II or III shifted the reaction into region IV, and the maximum rates are shown as filled circles. These correspond exactly to the values expected by interpolation of the rates between region I and IV. Inert gas therefore prevented the explosion and allowed the "normal" oxidation of carbon to proceed. Since many studies of the gasification of carbon were made in the presence of inert gas explosions may often have been avoided. The figure also shows that the rates of gasification in region III were appreciably higher than the interpolated values. As discussed in Section 8.5, the concentration of radicals in this region is sufficient to cause the increase in rate, but not sufficient to cause an explosion.

9.3 Effects outside the explosion region

The effects of the additives, water, hydrogen, inert gases and carbon monoxide on the rate of gasification and on the product ratio in region IV were investigated at 935 K, and an example is given in Figure 9.3. It is clear that addition of water vapour or carbon dioxide did not have any notable effect on the kinetics of the gasification in region IV. Addition of hydrogen and carbon monoxide slightly reduced the induction period but the maximum rate was not appreciably affected. Similar ratios of CO/CO_2 (0.8-1.0), were observed with oxygen and with the mixtures with carbon dioxide, with water and with hydrogen, but with the mixture with carbon monoxide the ratio was somewhat lower, 0.6-0.7. This suggests that some secondary oxidation of carbon monoxide may have occurred in the presence of added carbon monoxide, but this did not appreciably influence the over-all rate of gasification of carbon. It should be pointed out that the additions of carbon monoxide, carbon dioxide and water vapour in this series of experiments were at least 5, 50 and 6 times larger respectively than the amounts produced from the reaction.

This series of experiments clearly illustrated that in the absence of explosion or of rapid oxidation of carbon monoxide, these additives had little influence on the kinetics of the oxidation of carbon. It may be concluded that in regions I and IV and in region II (before the occurrence of explosion), the gas phase oxidation of carbon monoxide is slow and oxidation of carbon proceeds primarily as described in Part I. Indeed, many studies in the literature suggested that secondary oxidation of carbon monoxide was unimportant under most conditions

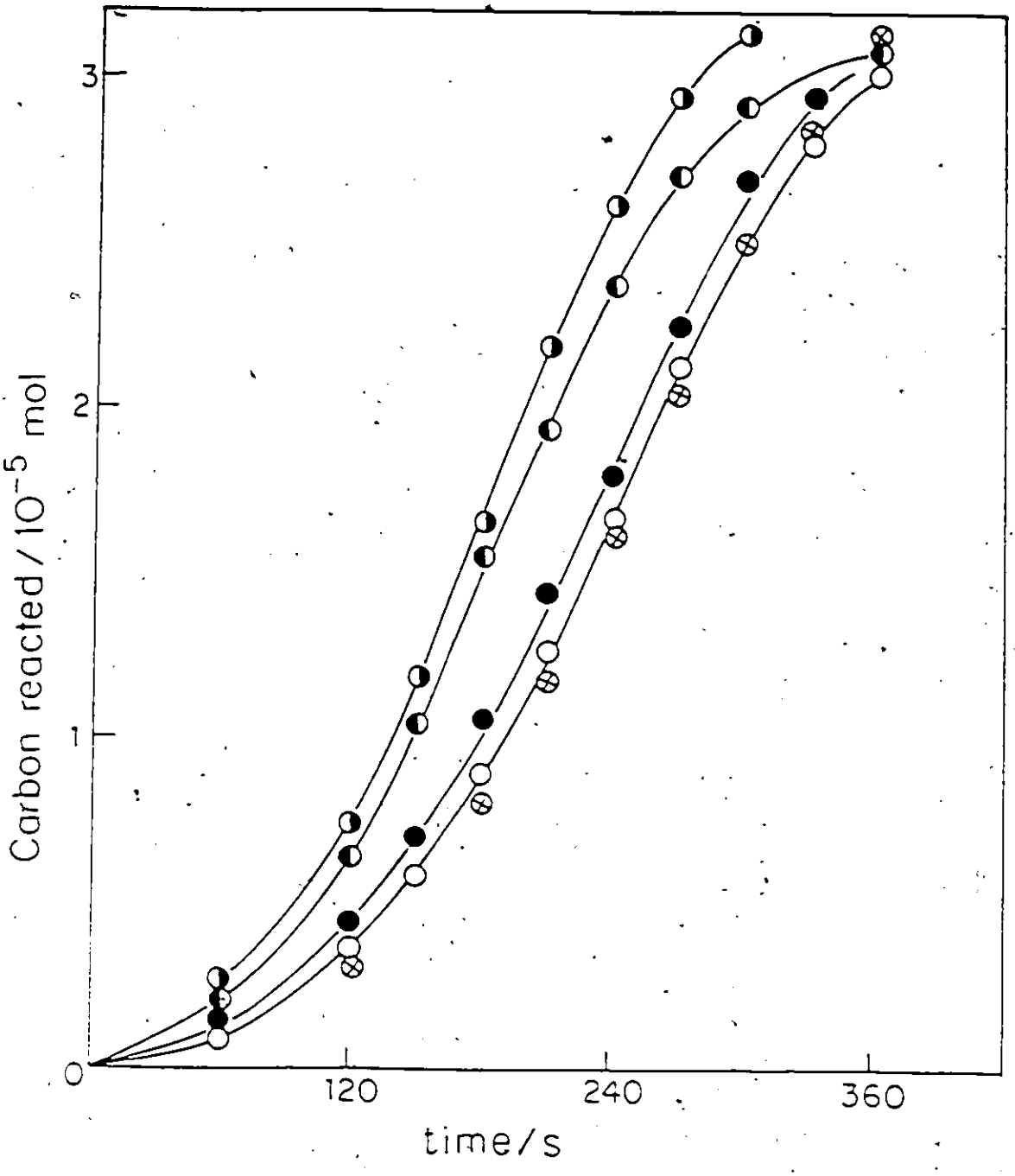

Figure 9.3. Effect of additives, hydrogen, water, carbon monoxide and inert gas, in region IV at 935 K. Initial pressure of oxygen: 400 Torr. All curves represent removal of carbon.

○ : O_2; ⊗ : O_2 + 0.2% H_2O; ◑ : O_2 + 0.1% H_2;
◐ : O_2 + 4.0% CO; ● : O_2 + CO_2 (2:1).

[36,37,43-48,133,134]. For example, Lewis, Dix and Murdoch [134] observed that addition of 6000 ppm of water to oxygen-nitrogen mixtures at 1 atm (partial pressure of oxygen ranging from 20 to 150 Torr) had no effect on the rates and on the activation energies of reaction of British PGA nuclear graphite at 848 and 898 K. Although this partial pressure of oxygen was inside region II, dilution with nitrogen caused a shift into region IV and therefore no unusual behaviour was noticed. A similar shift from region II to region IV at 900 K was described in Section 7.2. Also the results in Figure 9.3 represent a situation comparable to that of Lewis et al. [134], where addition of 2000 ppm water vapour to 400 Torr of oxygen (Region IV) had no appreciable influence on the rate, on the induction period or on the product distribution.

9.4 Conclusion

From this discussion, it is clear that interpretation of the effects of water and of inert gases on the kinetics of the carbon-oxygen reaction should not be confined to effects on the surface. Under certain conditions, radical reactions in the gas phase may drastically alter the rate of gasification as well as the ratio of products, CO/CO_2.

CHAPTER 10

RELATION OF THE RATES OF CARBON GASIFICATION AT THE ONSET OF EXPLOSION TO THE CONCENTRATION OF VARIOUS REACTANTS

The purpose of this chapter is to examine the order of the rate of gasification at the explosion with respect to the concentration of carbon monoxide, water, oxygen and total pressure, and to interpret the results in terms of the mechanism of gasification during the explosion. From traces such as shown in Figure 6.1, the rate of gasification at the instant of explosion was measured under conditions described in Chapter 7, covering a wide range of temperature, total pressure, concentrations of carbon monoxide, oxygen and water. A summary of the measurements showing the rate at and just before the explosion is given in Tables 10.1 - 10.4.

The approximate order of the rate with respect to each reactant was first estimated by choosing experiments for which the concentration of only one reactant was altered while the others remained constant. For example, in the series of experiments with pure oxygen at 900 K (Table 10.1A) the concentration of water vapour at the explosion was almost the same and the concentrations of carbon monoxide in the 2nd and 3rd experiments or in the 1st and 4th experiments were also similar. Comparison of the rates of reaction between the experiments in each of these pairs provided the dependence of the rate on the total pressure.

In this manner, a function was found at each temperature which represented the dependence of the rate on the concentration of carbon monoxide, water and total pressure and, where possible, oxygen. These

Table 10.1. Effect of explosion on the rate of gasification at 900 K

Pressure at explosion/Torr					$(-dC/dt)/10^{-8}$ mol s^{-1}	
CO	O_2	H_2O	CO_2	He	At explosion	Just before explosion
A. Reactions with O_2						
3.7	56.3	0.14	3.4	-	790	5.1
3.1	85.2	0.12	2.8	-	320	4.7
3.2	112.2	0.14	3.5	-	190	5.9
4.0	144.8	0.15	3.8	-	160	7.8
B. Reactions with O_2 + CO mixtures						
5.7	84.1	0.14	3.8	-	1250	5.1
8.3	83.7	0.17	4.9	-	1600	5.4
6.9	117.9	0.16	4.0	-	600	5.7
10.7	116.2	0.19	5.0	-	900	4.3
C. Reactions with O_2 + H_2O mixtures						
1.5	41.8	0.21	2.3	-	190	3.8
0.9	86.6	0.12	0.5	-	45	2.8
D. Reactions on thick films with O_2						
9.0	20.6	0.58	5.4	-	3600	3.0
5.0	36.4	0.23	1.0	-	1600	4.6
2.9	58.9	0.12	0	-	520	2.8
2.3	90.5	0.10	0	-	130	3.6

Table 10.2. Effect of explosion on the rate of gasification at 935 K

Pressure at explosion/Torr					$(-dC/dt)/10^{-8}$ mol s^{-1}	
CO	O_2	H_2O	CO_2	He	At explosion	Just before explosion
A. Reactions with O_2						
2.9	25.9	0.12	3.1	-	700	6.4
1.5	43.0	0.060	1.4	-	290	5.8
0.9	58.9	0.032	0.7	-	100	5.1
0.6	100.0	0.016	0.3	-	45	4.3
B. Reactions with O_2 + CO mixtures						
3.5	25.0	0.12	3.2	-	1020	6.3
4.1	25.5	0.11	3.0	-	1800	5.7
1.6	58.5	0.045	1.4	-	280	6.9
2.3	52.2	0.045	1.5	-	500	6.0
C. Reaction with O_2 + H_2O mixture						
1.2	29.7	0.032	0.5	-	180	3.0
D. Reactions with O_2 + Inert gas mixtures						
3.8	25.2	0.13	33	-	470	6.5
4.5	53.2	0.16	64	-	120	9.5
3.5	24.2	0.15	3.9	30	560	5.8
1.6	57.0	0.074	2.1	60	190	7.3
1.1	96.3	0.045	1.1	100	60	7.3
E. Reactions on thick films with O_2						
2.3	29.9	0.045	0	-	490	3.5
0.6	60.1	0.013	0	-	47	1.5
F. Reactions on thick films with O_2 + inert gas mixtures						
3.7	29.4	0.061	60	-	310	3.6
3.6	58.5	0.066	120	-	630	6.2

Table 10.3. Effect of explosion on the rate of gasification at 973 K

Pressure at explosion/Torr					$(-dC/dt)/10^{-8}$ mol s^{-1}	
CO	O_2	H_2O	CO_2	He	At explosion	Just before explosion
A. Reactions with O_2						
2.8	17.7	0.10	2.0	-	480	11
1.2	27.8	0.043	1.0	-	330	7.7
0.7	40.9	0.023	0.5	-	250	5.8
B. Reactions with O_2 + CO mixtures						
4.0	16.7	0.090	2.1	-	690	10
5.4	17.6	0.073	1.6	-	1080	10
C. Reactions with O_2 + Inert gas mixtures						
0.9	29.1	0.030	10	-	200	6.5
0.7	29.7	0.022	30	-	94	4.7
0.9	29.2	0.030	91	-	25	5.3
1.4	28.7	0.040	121	-	19*	6.1
3.2	25.5	0.12	153	-	16*	11.2
6.3	23.9	0.19	185	-	10.8*	10.8
2.7	17.0	0.090	1.8	20	420	8.5
0.9	28.2	0.037	0.9	30	250	6.0

* Corresponds to the onset of a rapid oxidation of carbon monoxide, rather than of an explosion, as explained in Section 8.6.

Table 10.4. Effect of explosion on the rate of gasification at 1048 K

Pressure at explosion/Torr					$(-dC/dt)/10^{-8}$ mol s^{-1}	
CO	O_2	H_2O	CO_2	He	At explosion	Just before explosion
A. Reactions with O_2						
2.7	12.3	0.083	1.5	-	670	37
1.5	18.4	0.048	1.1	-	121	27
0.9	29.0	0.034	0.9	-	115	24
B. Reactions with O_2 + CO mixtures						
4.0	12.2	0.062	1.4	-	100	30
7.0	15.0	0.034	1.1	-	290	38
2.3	18.5	0.041	1.3	-	185	20
3.6	19.0	0.031	1.0	-	260	35
C. Reactions with O_2 + Inert gas mixtures						
1.4	10.8	0.041	12	-	440	14
0.6	11.3	0.021	36	-	240	4
0.9	15.0	0.034	15	-	560	35
0.4	14.5	0.014	45	-	250	8

functions are as follows:

$$900\ K: \qquad -\frac{dC}{dt} \propto \frac{[CO]^2}{[M]^2[H_2O]} \tag{10.1}$$

$$935\ K: \qquad -\frac{dC}{dt} \propto \frac{[CO]^2}{[M]^{3/2}[H_2O]} \tag{10.2}$$

$$973\ K: \qquad -\frac{dC}{dt} \propto \frac{[CO]}{[M][H_2O]} \tag{10.3}$$

$$1048\ K: \qquad -\frac{dC}{dt} \propto \frac{[O_2][CO]^{1/2}}{[M][H_2O]} \tag{10.4}$$

The functions are represented graphically in Figures 10.1 - 10.4. The rates represented in these figures include results from experiments with pure oxygen and with additions of water, carbon monoxide, carbon dioxide and helium, and with both thin and thick films. Except for experiments with added inert gases, the contribution of gases other than oxygen to the total pressure was negligible. For mixtures of oxygen and inert gases, it was assumed that carbon dioxide is 1.5 times as effective as oxygen both as a quencher in a three-body collision and as a retarder to the diffusion of oxygen atoms to the surface. Helium was assumed to be 0.25 times as effective as oxygen in slowing down the diffusion of oxygen atoms to the surface and to be 0.7 times as efficient as oxygen as a third body. The term involving M in the function (10.2) was separated

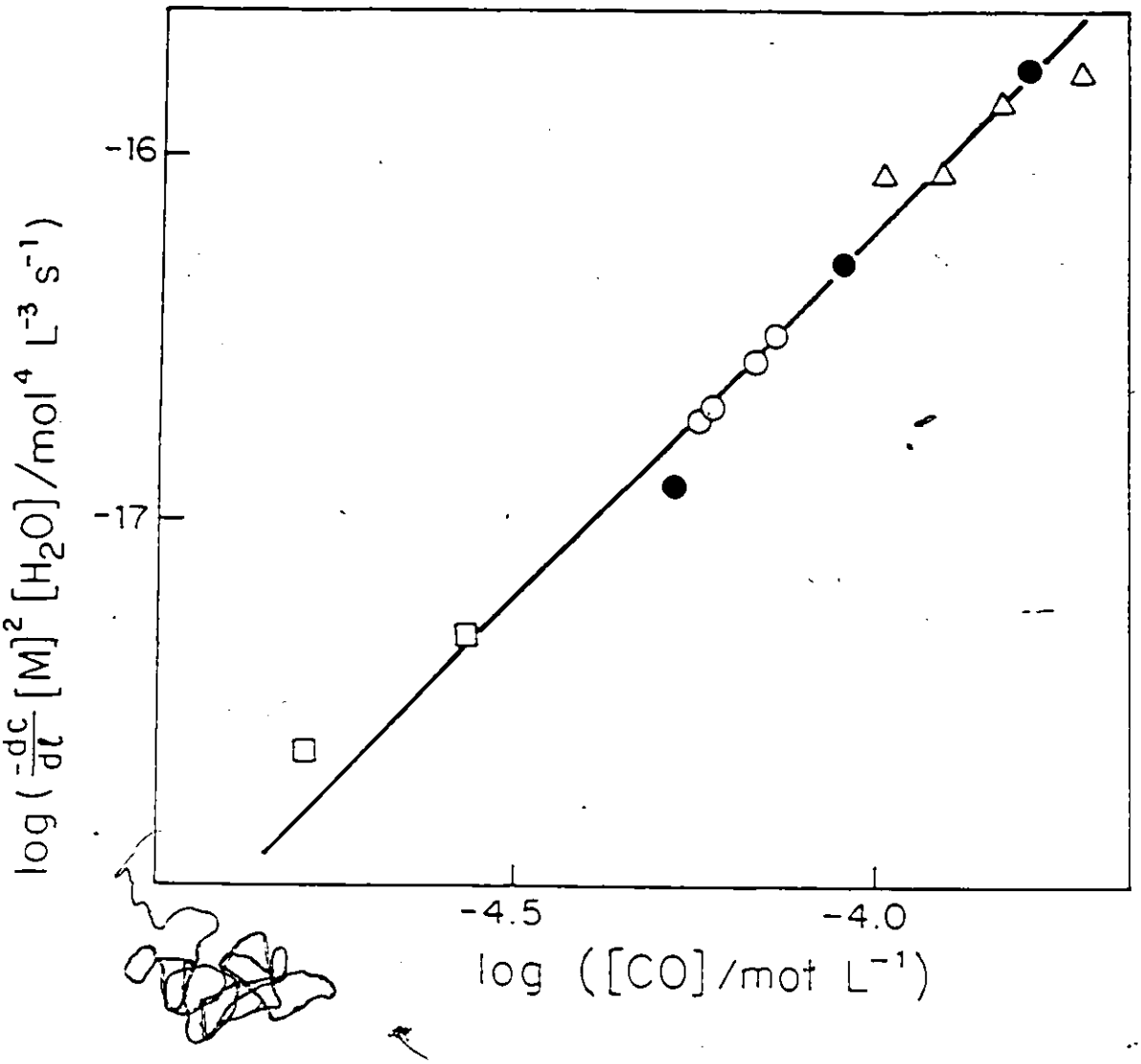

Figure 10.1. Dependence of the rate of gasification at the onset of explosion on the concentration of CO, H_2O and total pressure at 900 K. Symbols correspond to reactions with pure oxygen and with mixtures of oxygen with different additives.

○ : O_2; △ : O_2 + CO;

□ : O_2 + H_2O; ● : O_2 (thick films).

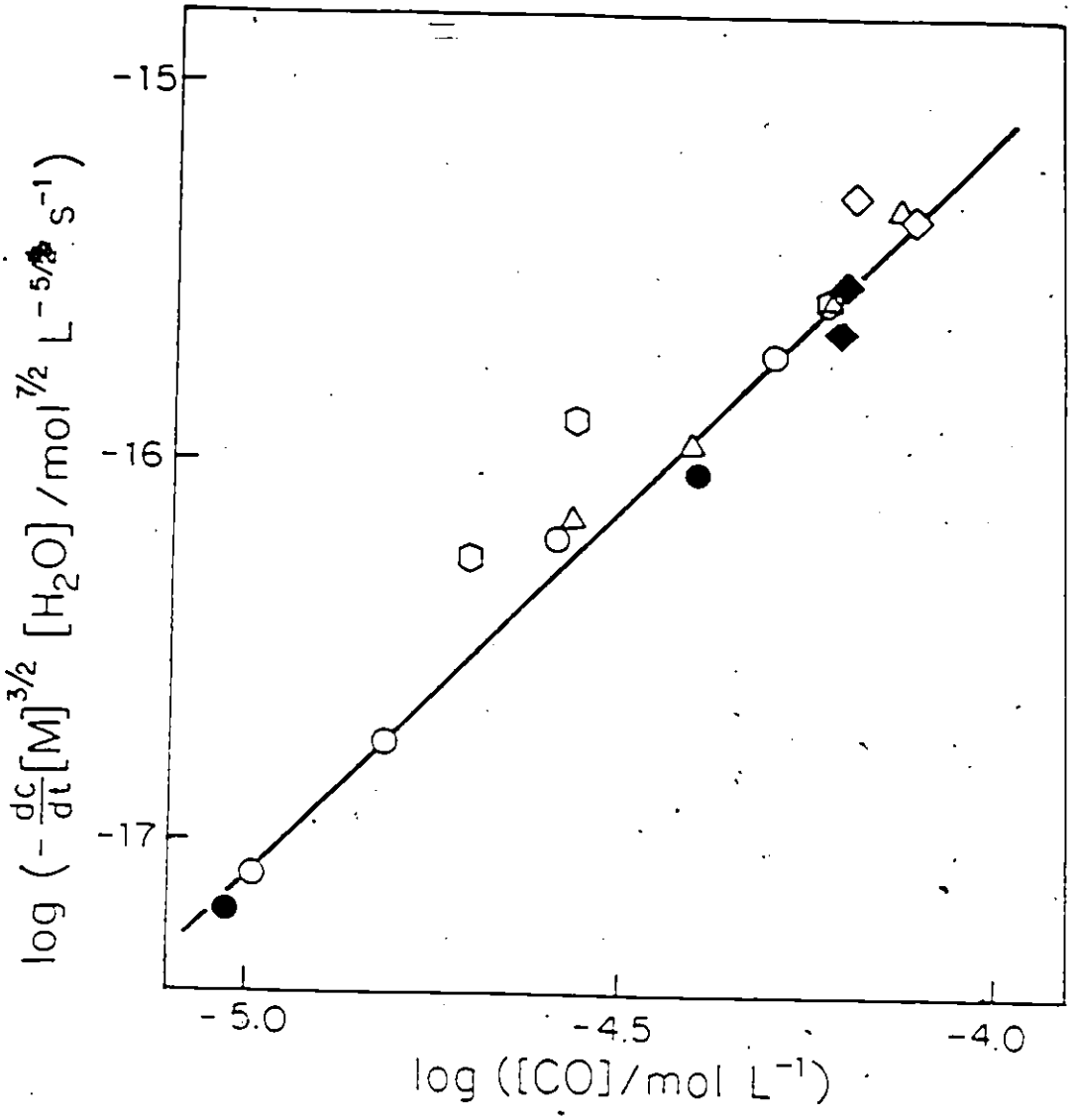

Figure 10.2. Dependence of the rate of gasification at the onset of explosion on the concentration of CO, H_2O and total pressure at 935 K. Symbols correspond to reactions with pure oxygen and with mixtures of oxygen with different additives.

○ : O_2; △ : O_2 + CO; ◇ : O_2 + CO_2
⬡ : O_2 + He; ● : O_2 (thick films); ◆ : O_2 + CO_2 (thick films).

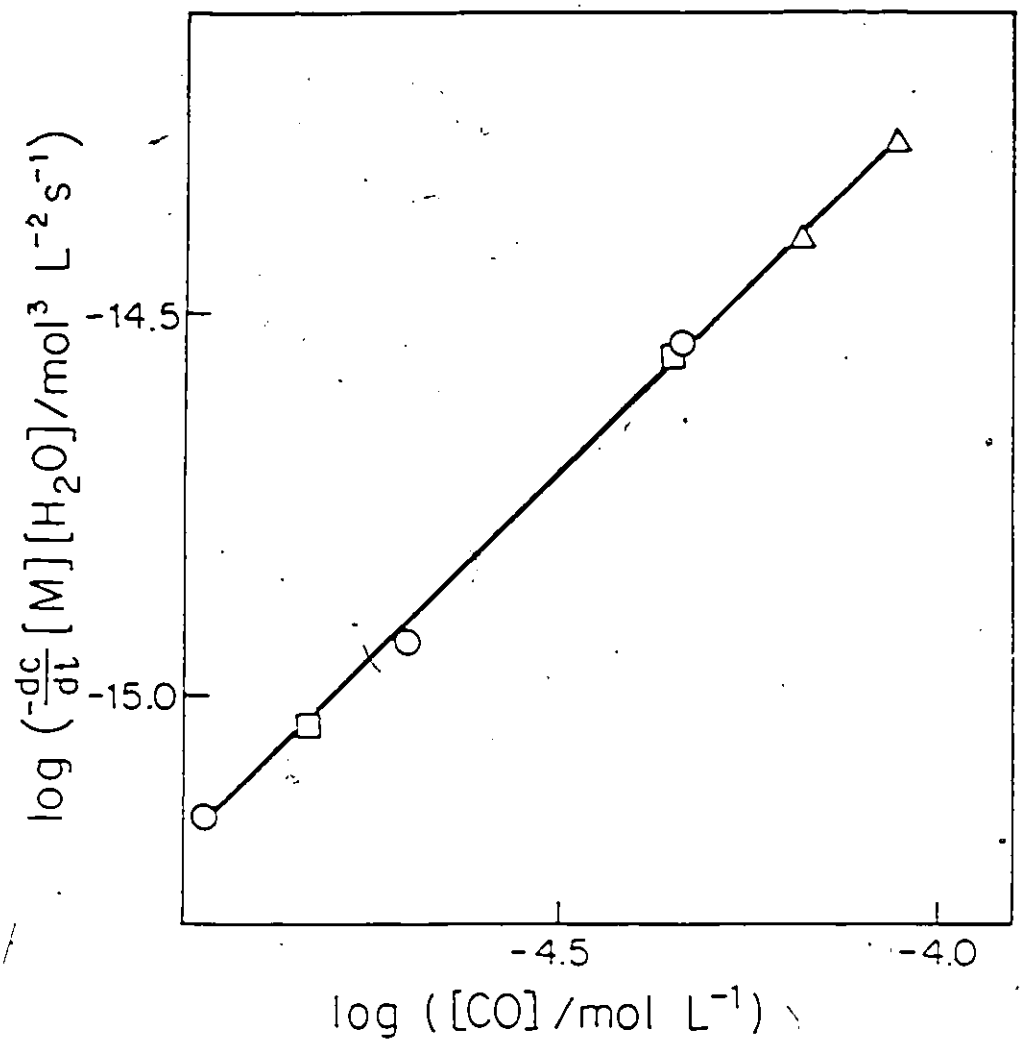

Figure 10.3. Dependence of the rate of gasification at the onset of explosion on the concentration of CO, H_2O and total pressure at 973 K. Symbols correspond to reactions with pure oxygen and with mixtures of oxygen with different additives.

○ : O_2; △ : O_2 + CO; □ : O_2 + He

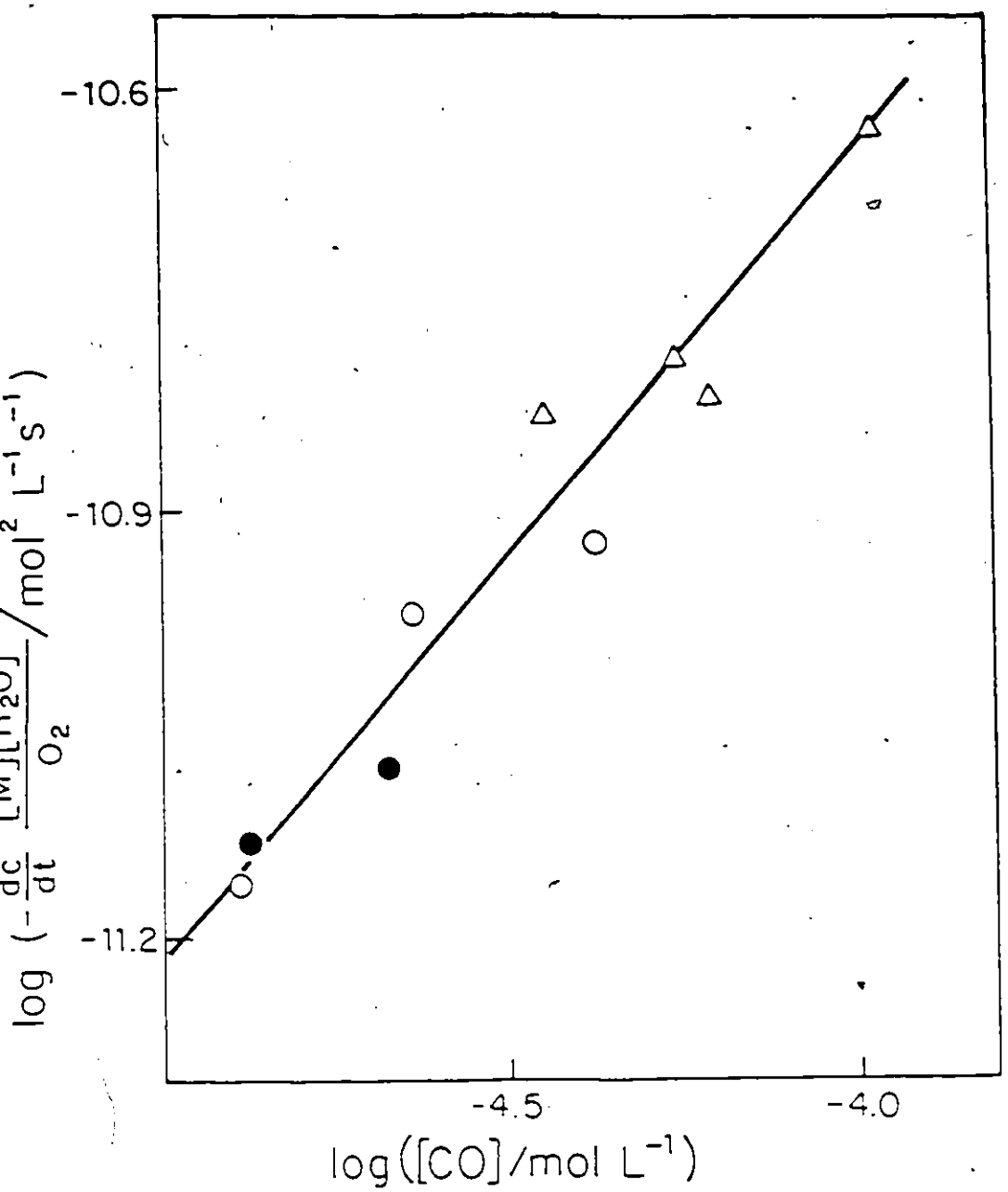

Figure 10.4. Dependence of the rate of gasification at the onset of explosion on the concentration of CO, H_2O and total pressure at 1048 K. Symbols correspond to reactions with pure oxygen and with mixtures of oxygen with different additives.

○ : O_2; △ : O_2 + CO; ● : O_2 + CO_2

into two parts

$$[M]^{3/2} = [M] \times [M]^{1/2}$$

The linear dependence on [M] was attributed to diffusion of oxygen atoms to the surface and the square root dependence to a three body stabilization. In functions (10.3) and (10.4), only the diffusional effect was important. The results may be summarized as follows:

1. Carbon monoxide accelerates the rate of gasification and the order of the rate changes with temperature from +2 at 900 K to +1/2 at 1048 K.
2. Water vapour retards the rate and the order is approximately 1 over the whole range of temperature of the present study.
3. Inert gas slows down the rate through its contribution to the total pressure and the order rises with temperature from -2 at 900 K to -1 at 1048 K.
4. Oxygen affects the rate of gasification in two ways. At lower temperatures (e.g. 900 K) where explosion occurs at relatively higher pressures, oxygen primarily slows down the gasification process through its contribution as a third body, whereas at higher temperatures (e.g. 1048 K) where explosion takes place at relatively low pressures, it is also important as a reactant.

According to reaction (7) in Chapter 8, the rate of disappearance of carbon by reaction with oxygen atoms is given by,

$$-dC/dt = k_7[O]_g$$

where $[O]_g$ represents the concentration of oxygen atoms in the gas phase and k_7 the diffusion-controlled surface termination rate constant.

It is not possible to derive an explicit expression for oxygen atoms independent of other radicals or atoms from the steady-state treatment of the reaction scheme described in Chapter 8. Nevertheless, expressions for the ratios O/H and H/OH may be derived as follows:

$$\frac{[O]}{[H]} = \frac{k_3[O_2]}{k_4[H_2O] + k_7 + k_8[CO][M]}$$

$$\frac{[H]}{[OH]} = \frac{k_2[CO]}{k_3[O_2] + k_9[O_2][M]}$$

Therefore,

$$-\frac{dC}{dt} = \frac{k_7}{k_4[H_2O] + k_7 + k_9[CO][M]} \cdot \frac{k_3[O_2]}{k_3[O_2] + k_9[O_2][M]} \cdot k_2[CO][OH]$$

or

$$-\frac{dC}{dt} \propto \frac{1}{[M]} \cdot \frac{1}{k_4[H_2O] + k_7 + k_8[CO][M]} \cdot \frac{k_3[O_2]}{k_3[O_2] + k_9[O_2][M]} \cdot k_2[CO][OH]$$

This adequately explains the observed dependence of the rate on total pressure (i.e. M) and water, but does not give a dependence on carbon monoxide higher than one nor does it predict the dependence on oxygen. Probably, the main weakness is the unknown dependence of [OH]. It should

also be pointed out that the steady-state approximations for oxygen and hydrogen atoms and hydroxyl radicals may be legitimate only under conditions removed from those of an explosion. An explosion occurs when the concentration of the chain carriers suddenly increases by several orders of magnitude, causing breakdown of the steady-state approximations. Although the steady-state solutions may be useful in assessing the contribution of reaction of oxygen atoms (generated by the gas phase reactions) to the over-all gasification process under the conditions of a normal reaction, they are probably of doubtful significance in estimating oxygen atom concentrations during an actual explosion.

Within these limitations, it may be concluded that the rate of gasification during an explosion is adequately accounted for by a rapid reaction with oxygen atoms generated by the gas phase chain branching reactions described in Part II.

CLAIMS TO ORIGINAL RESEARCH

1. The kinetic study of the oxidation of carbon has led to a definite characterization of the role of the strongly-bound complex formed on the surface of the carbon in the gasification process. The simultaneous measurement of both the rate of formation of the complex on the surface and the rate of gasification revealed that the formation of the complex precedes the gasification process. Comparison of the kinetics of the reaction in the presence and absence of the complex at the start of the reaction showed that the presence of the complex shortened the induction period of the gasification. These results were interpreted to indicate that the complex was an intermediate in the series of surface reactions leading to formation of the final products, carbon monoxide and carbon dioxide.

2. The role of the complex as an intermediate was further illustrated through the measurements of the yields of the complex and the products as a function of time over a wide range of temperature and pressure of oxygen. These measurements gave an improved definition of the rate of product formation and hence of the activation energies for the processes of adsorption and formation of carbon monoxide and carbon dioxide. The activation energy for formation of carbon monoxide was similar to that measured for the desorption of the complex by TPD measurements. A small drop in the activation energy for formation of carbon monoxide at high temperature was shown to be caused by depletion of the saturation concentration of complex on the surface.

3. A mechanism for the oxidation was proposed involving steps for the interaction of oxygen, either gaseous or adsorbed, with the surface complex. This new type of surface process was shown to account for the kinetics of the reaction, including the activation energy for the formation of the products, and for results obtained by other authors.

4. Because the complex achieves a low steady-state concentration on the surface through continuous formation and reaction, it was suggested that the active sites on the carbon surface may be compared to those of a catalyst in a heterogeneous reaction. Thus a turnover number for the oxidation may be defined as follows:

$$\text{Rate of gasification, } -dC/dt = \frac{\text{Rate of formation of product}}{\text{Concentration of active site on the surface}}$$

Both terms in the ratio may be expressed in terms of mol of carbon and hence the TON has the usual units of s^{-1}.

5. A new method, with distinct advantages over conventional methods, has been developed for the study of ignitions in mixtures of carbon monoxide and oxygen. The method involves the generation of an explosive mixture of carbon monoxide, oxygen and a small quantity of water by the reaction of oxygen with carbon. In the static system the rate of formation of the products was monitored continuously and the concentration of the reactants at the moment of ignition was known with good accuracy.

6. Measurements on ignitions in mixtures of carbon monoxide and oxygen were extended to a realm of composition not previously studied, illustrating that an explosion could occur at a ratio of CO/O_2 as low as 5×10^{-3} or with less than 1 Torr of carbon monoxide.

7. A simple mechanism consisting of branching and homogeneous termination reactions suggested in previous studies, together with heterogeneous termination at the carbon surface, was shown to account quantitatively for the occurrence of explosions under all conditions of temperature, pressure and concentrations of reactants, chain-branching additives and inert gases.

8. A reversal in the effect of inert gas on the onset of an explosion, from an inhibiting effect at temperatures below 935 K to a promoting effect at temperatures above 1000 K illustrated the transition from the first explosion limit to the second explosion limit.

9. It was shown that the high efficiency of carbon surface as a terminating agent for oxygen atoms made the system well suited to a study of conditions for explosion near the first limit at temperatures above 900 K. With the carbon surface, the first limit was considerably shifted to higher pressures. The poor efficiency of quartz surface compared to carbon surface as a heterogeneous chain terminating agent was also eloquently demonstrated.

10. The rate of carbon consumption as well as the product distribution of the carbon-oxygen reaction were severely affected by homogeneous reactions induced by the presence of small quantities of water vapour. Previous interpretations of the effect of water vapour on the oxidation had been confined to surface effects, such as preferential adsorption.

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