HETEROGENEOUS AND HOMOGENEOUS ISOMERIZATIONS OF THE n-BUTENES

by

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TO

MY MOTHER

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ABSTRACT

The odd electron content and chemical activity of carbons produced by the pyrolyses of allyl bromide, cis-butene-2, ethyl bromide, and 3-chloro-2-methylpropene have been examined. The odd electron concentration and other physical properties of pyrolytic carbons have been related to their chemical reactivity. Reactions studied were cis→trans and cis→butene-1, trans→cis and trans→butene-1 isomerisations of butene-2, and butene-1→cis- and trans-butene-2 isomerisations, all of which are catalysed by pyrolytic carbons. It was shown that catalysed reaction takes place at or near the surface of the carbons. In each case the surface reaction was first-order. Also studied were the effects of oxygen, olefins, and halogen-containing substances on the chemical activity and odd electron concentration of the carbons.

The equilibrium constant, free energy, and entropy for cis- and trans-butene-2 have been determined by measuring the initial rates of their heterogeneous isomerisations catalysed by pyrolytic carbon over the temperature range 202-451°C. The results agree well with thermodynamic data and with recent data from equilibrium studies of the homogeneous iodine-catalysed isomerisations of the n-butenes.

The homogeneous halogen acid catalysed isomerisations of the n-butenes were studied. The hydrogen chloride catalysed reactions were found to be kinetically complex. Both the hydrogen chloride and bromide catalysed isomerisations of cis-butene-2 can be inhibited by cyclohexene. It is suggested that the

reaction possibly, at least partially, involves free-radical reactions.

The significance of the results to the study of gas-phase reaction kinetics has been discussed.

CHAPTER 1

INTRODUCTION AND HISTORICAL REVIEW

I. Isomerization of the n-butenes

(A) Thermal isomerization

The first quantitative study of the cis→trans isomerization of butene-2 was that of Kistiakowsky and Smith(1) who analysed the mixed isomers by the melting point depression method. The first-order Arrhenius parameters were $A = 2\ sec^{-1}$, $E_a = 18\ Kcal\ mole^{-1}$. The data were hard to reconcile with collision theory and with the theoretical interpretation offered by Magee, Shand and Eyring (2) based upon a postulated triplet state of an ethylenic molecule; Kistiakowsky proposed a chain mechanism for the reaction. Since then, infrared spectroscopy has become available and it was used to reinvestigate the cis→trans isomerization of butene-2 by Anderson, et al.(3). They found the Arrhenius parameters $A = 10^{11}\ sec^{-1}$, $E_a = 52\ Kcal\ mole^{-1}$ and this value was noted to approach that for the singlet isomerization of trans-dideutero-ethylene(4).

Rabinovitch and Michel(5) found that the unimolecular thermal cis→trans isomerization of butene-2 obeyed first-order kinetics; the first-order rate coefficient began to fall off at pressures below 2 mm. The reaction was found to be complicated by side reactions due to the presence of free radicals at pressures greater than 10 mm, but which were believed to be negligible below 5 mm. The observed unimolecular behaviour was considered with respect to Slater's theory. From the plot of

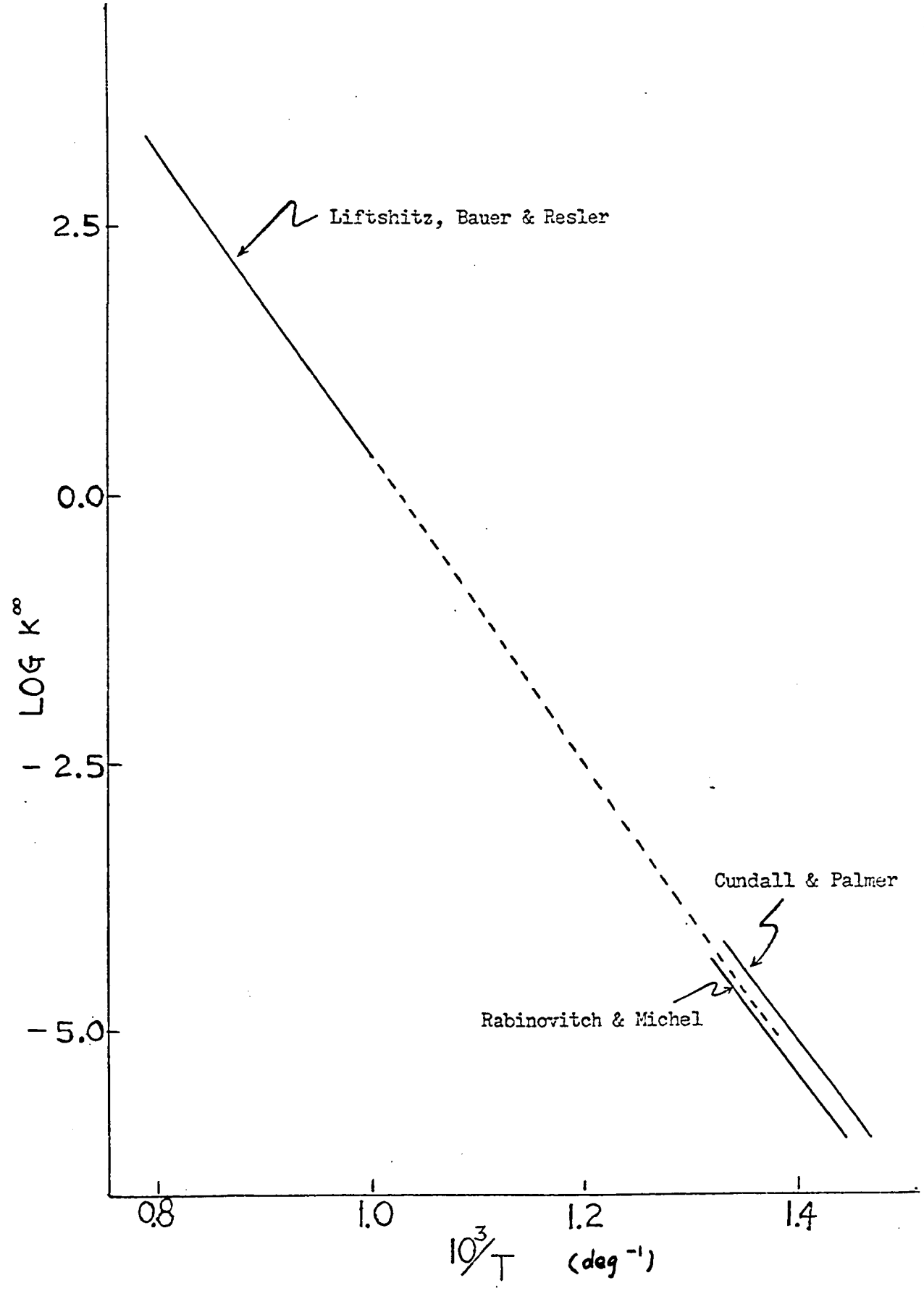
k^{-1} versus $P^{-\frac{1}{2}}$, a limiting high pressure rate constant was determined, $k_\infty = 6.1 \times 10^{13} e^{-62,800/RT}$ sec^{-1}.

In 1961 Cundall and Palmer(6) confirmed the conclusions of Rabinovitch and Michel(5), that the isomerization of cis-butene-2 is not a pure unimolecular process over the whole range investigated. They found that below 10 mm, the behaviour is that of a true unimolecular reaction with a pronounced fall-off below 4 mm. Above 10 mm, side reactions and surface catalysis seriously affect the rate of isomerization. Both of these investigators declared that catalysis or cracking could be brought about by the presence of metallic oxides or acid sites on the clean glass surface and ageing of the vessel was brought about by forming a covalent covering. They believed that over-ageing and increased autocatalysis at high pressures in packed vessels might be due to hydrogen abstraction from the surface by free radicals leaving unpaired electron sites and thus some autocatalysis could be due to the effect of these sites upon colliding or adsorbed molecules. The first order rate constant was obtained as $k_\infty = 1.0 \times 10^{14} e^{-62,400/RT}$ sec^{-1}.

Liftshitz, Bauer and Resler(7) investigated the reaction by the shock wave method in the temperature range 1000° — 1250° K; concentrations 1% and 6% of the butene in argon were used. The first-order rate constants obtained fell slightly above the extrapolated Arrhenius lines of the low-temperature studies(5,6). An activation energy of 65, rather than 62.8 Kcal $mole^{-1}$, was obtained when a straight line was drawn between the high and the low temperature data. The expression for Bauer's rate

Figure 1

Arrhenius plots of the results from Liftshitz, Bauer and Resler(7), Rabinovitch and Michel(5), and Cundall and Palmer(6)


Liftshitz, Bauer & Resler
Cundall & Palmer
Rabinovitch & Michel
2.5
0.0
- 2.5
- 5.0
- LOG K^8
0.8
1.0
1.2
1.4
10^3/T (deg^-1)

constant was $k_\infty = 3.5 \times 10^{14} e^{-65,000/RT}$ sec^{-1} (see Figure 1). Recently, Lin and Laidler(8) have considered some theoretical aspects of the thermal isomerization reactions and they concluded that if account is taken of the reverse reaction, in which the highly energized product molecule is reconverted into a reactant molecule, good agreement would be achieved with experiment results of the cis-butene-2 isomerization. They also estimated(9) a "best" value of $k = 1.3 \times 10^{14} e^{-(63,400 \pm 1,000)/RT}$ sec^{-1} by averaging the results from Rabinovitch(5), Cundall(6), and Liftshitz(7).

(B) Catalysed isomerization

Many kinetic investigations of catalysed isomerizations of the n-butenes have been made. Paramagnetic substances were reported(10) to be particularly effective in catalysing the cis→ trans isomerization; polarization affecting the π electrons of the double bond was a possible explanation. Harman and Eyring (11) pointed out that paramagnetic substances, free radicals, and atoms would catalyse the triplet mechanism by providing a non-homogeneous magnetic field which will act differently on each of the two magnetic dipoles arising from the spin of the two electrons of the double bond. An activated complex is formed with the paramagnetic substances involving the state with the spins the same, as well as the state with the spins opposed.

Rabinovitch and Looney(12) found that nitric oxide displays a very marked catalytic effect on the isomerization of trans-dideuteroethylene. A similar result was obtained by Cundall and Palmer(13) with cis- or trans-butene-2 and nitric oxide. The reaction was second-order and free from any appreciable side

products. The Arrhenius parameters $A = 4 \times 10^{10}$ cc mole^{-1} sec^{-1}, $E = 26.2$ Kcal mole^{-1} and $A = 3 \times 10^{10}$ cc mole^{-1} sec^{-1}, $E = 26.1$ Kcal mole^{-1} were found for the cis- and trans-butene-2 isomerizations, respectively. They concluded that the effect of nitric oxide is not due to physical catalysis since the activation energy is lower than the triplet state energy expected on photochemical grounds. Terao, Hirokami, Sato and Cvetanovic(14) have estimated that the potential-energy difference between the twisted singlet and twisted triplet states is about 18 Kcal mole^{-1}. This leads to a value of about 45 Kcal mole^{-1} for the triplet barriers(Fig.2). They concluded that the reaction must involve

$$NO + C_4H_8\text{-}2 \text{ (cis- or trans-)} \rightleftharpoons CH_3\text{-}\dot{C}H\text{-}CH(NO)\text{-}CH_3 ,$$

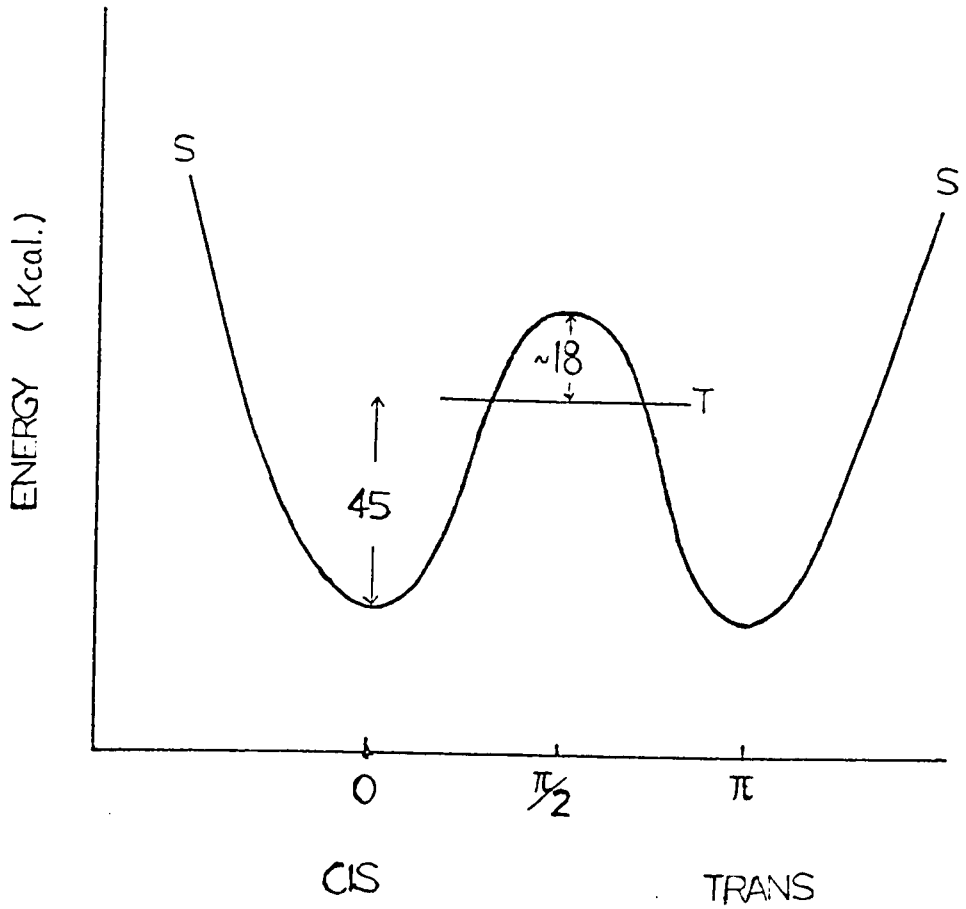
with the forward step rate determining. It is possible that the reaction involves a π complex which may decompose without isomerization or rearrange to produce the above radical which may, after time for rotation, breakdown without an opportunity to participate in any other reaction. The formation of propene and butene-1 which was produced from pure butene-2 isomerization is completely suppressed in the nitric oxide catalysed isomerization.

Bromine and iodine in trace amounts bring about the cis $\rightarrow$trans isomerization. The effect of bromine was used as evidence for the participation of atoms and free radicals in organic reactions(15). The question of halogen atom catalysis raises the issue of the role of π complex formation. Abell and Piette(16) have evidence for complex formation between olefins

Figure 2

Schematic potential-energy diagram for a cis→trans isomerization

S : singlet, T: triplet


ENERGY (Kcal.)
S
S
~18
T
45
0
π/2
π
CIS
TRANS
ANGLE OF TWIST

and bromine atoms from electron spin resonance results. It is possible that the reactions involve

$$X^{\cdot} + \text{Olefin} \longrightarrow \pi \text{ complex} \longrightarrow \sigma \text{ complex},$$

where a π-complex is the interaction complex of the X atom with the double bond in such a way that the rigidity of the double bond is preserved. A σ-complex is the transfer of one electron from X atom to a double bond carbon atom yielding the C—C bond free to rotate. The σ-complex could be formed by direct addition or by rearrangement of π-complex. The reaction of iodine atoms with cis-butene-2 was studied at 65 °C by Beck(17). At constant iodine pressure the rate of isomerization approached a limiting value as the butene pressure was increased, which suggested that the butene was acting as a very efficient third body for the recombination of iodine atoms and to interpret the fact that the quantum yield approached a limiting value much less than 1 (0.1). In other words the reaction of an iodine atom with butene does not always form a radical in which rotation about the C—C bond may occur.

$$\text{cis-}C_4H_8 + I \longrightarrow C_4H_8{:}I \quad (\pi\text{-complex})$$

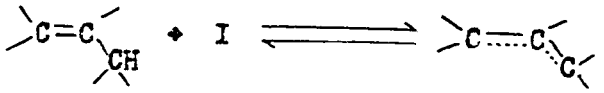
$$C_4H_8{:}I \longrightarrow \text{cis-}C_4H_8 + I$$

$$C_4H_8{:}I + I \longrightarrow \text{cis-}C_4H_8 + I_2 .$$

They reported that butene can bring about recombination of iodine atoms without undergoing isomerization itself and it may involve a π complex. The formation of a C_4H_8I free radical (a σ complex)

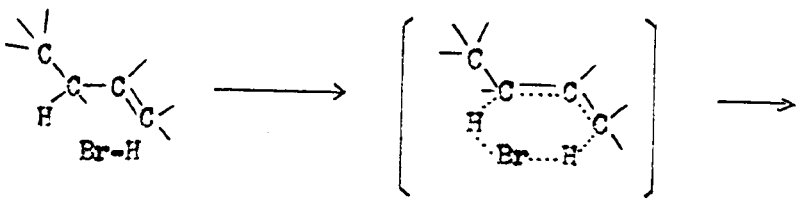
is required for the isomerization.

In 1963, Benson and Bose (18) used small amounts of I_2 to bring about the rapid isomerizations of the n-butenes, both positional and geometrical. They proposed that as a result of allylic resonance, olefins with α-H atoms can be in labile equilibrium with allylic radicals when exposed to I_2 vapour, i.e.



The reverse reaction would lead to the formation of a mixture of all possible isomers. Geometrical isomerization occurred at a much faster rate than positional isomerization which was presumed to take place via the direct addition of I to the double bond. Golden, Egger and Benson(19) repeated the iodine catalysed isomerization in order to determine equilibrium data for the three butenes. The results for the geometrical isomerization gave thermodynamic data in good agreement with A. P. I. values(20).

Maccoll and Ross(21) investigated the hydrogen bromide catalysed isomerizations of the n-butenes. The equilibria among the n-butenes and the kinetics of the butene-1 isomerization were studied in the temperature range 286° - 386° C. They declared that the reaction is predominantly homogeneous and molecular with the kinetic form :- rate of isomerization of butene-1 = k_2[butene-1][HBr]. They suggested a reaction path through a six-centered transition state, favouring trans-butene-2 formation.



Abell(22) found that butene-1 was very rapidly converted to cis- and trans-butene-2 in the presence of photodissociated hydrogen bromide. He proposed that the isomerization was via hydrogen abstraction by bromine atoms with replacement of the hydrogen largely at the terminal carbon atom. He used deuterium bromide in the reaction mixture and observed the position and extent of deuteration in the isomerised olefins. After separation by gas chromatography the n. m. r. spectra of the butenes were examined. Substantial reductions of the integrated areas of the methyl group absorptions were found showing that the vast bulk of the hydrogen abstraction by the allylic radicals was from hydrogen (or deuterium) bromide and not the allylic hydrogen from another olefin molecule.

$$CH_3CH_2CH=CH_2 + Br^{\cdot} \longrightarrow CH_3\dot{C}HCH=CH_2 + HBr$$

$$CH_3\dot{C}HCH=CH_2 \rightleftharpoons CH_3CH=CH\dot{C}H_2$$

$$CH_3CH=CH\dot{C}H_2 + HBr \longrightarrow CH_3CH=CHCH_3 + Br^{\cdot}$$

Values of ΔH, ΔG, and ΔS for geometrical isomerizations were also reported; they did not agree with the results of Maccoll and Ross(21) and were closer to the values obtained by Golden, Egger and Benson(19).

(C) Mercury photosensitized isomerization

The quenching cross sections of olefins for triplet Hg6 $^3P_1$ are very large(23). To conform with the conservation rule for spin angular momentum the excited olefins produced by Hg6 $^3P_1$ must be in the triplet state. A large number of investigations of the breakdown of excited olefins have been made but relatively little has been done on the rearrangement. Gunning and Steacie (24) examined the mercury photosensitized reactions of butene-1 which gave the butenes-2 and a liquid polymer as products. Cvetanović, Gunning and Steacie(25) stated that the primary step in the mercury photosensitized reactions of olefins is the formation of a vibrationally excited triplet state, by showing that butene-2 undergoes a ready isomerization. It was also found that butene-1 did not isomerize to butene-2 but later work has shown that both cis- and trans-butene-2 are products of prolonged irradiation of butene-1(26,27).

Cundall and Palmer(26) examined the cis- and trans-butene-2 isomerizations in more detail and the reactions are explained by the participation of vibrationally excited triplet states which can decompose or lose their vibrational energy by collision. The reaction scheme involves the following steps:-

$$Hg6\ ^1S_0 + h\nu \longrightarrow Hg6\ ^3P_1$$

$$Hg6\ ^3P_1 \longrightarrow Hg6\ ^1S_0 + h\nu$$

$$Hg6\ ^3P_1 + \text{cis-}C_4H_8\text{-}2 \longrightarrow C_4H_8\text{-}2^{**} + Hg6\ ^1S_0$$

$$Hg6\ ^3P_1 + \text{trans-}C_4H_8\text{-}2 \longrightarrow C_4H_8\text{-}2^{**} + Hg6\ ^1S_0$$

$$C_4H_8\text{-}2^{**} + M \longrightarrow C_4H_8\text{-}2^{*} + M$$

$$C_4H_8\text{-}2^{*} \longrightarrow cis\text{-}C_4H_8\text{-}2$$

$$\text{or} \longrightarrow trans\text{-}C_4H_8\text{-}2$$

$$C_4H_8\text{-}2^{**} \longrightarrow C_4H_7^{\cdot} + H^{\cdot}$$

where $C_4H_8^{**}$ —— vibrationally excited 1st triplet state,

$C_4H_8^{*}$ —— ground state of 1st triplet state.

At lower pressure (below 30 mm) the reaction became more complex, both butene-1 and iso-butene were produced together with butene, propylene, methane, hydrogen, etc., these presumably arise from free radical reactions such as:

$$CH_3\text{-}CH=CH\text{-}CH_3^{**} \longrightarrow CH_3\text{-}CH=CH\text{-}\dot{C}H_2 + H^{\cdot} ,$$

$CH_3\text{-}CH=CH\text{-}\dot{C}H_2$ by hydrogen atom abstraction $\longrightarrow$ butene-2 or butene-1,

$$H^{\cdot} + CH_3\text{-}CH=CH\text{-}CH_3 \longrightarrow CH_3\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3$$

$$CH_3\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3 + H^{\cdot} \longrightarrow CH_3CH_2CH_2CH_3$$

$$CH_3\text{-}CH_2\text{-}\dot{C}H\text{-}CH_3 \longrightarrow CH_3^{\cdot} + CH_3\text{-}CH=CH_2$$

isobutene can be produced by radical rearrangement or by secondary reactions. The rate of isomerization became constant above 30 mm at low conversions where decomposition was negligible. Prolonged irradiation produced a photostationary state with respect to the cis-/trans- ratio (47:53) which did not correspond to the 50:50 mixture suggested by Cvetanović, Cunning and Steacie(25) and this equilibrium was maintained, even though some decomposition occurred. They suggested that the small displacement

of the fraction from 50/50 to 47:53 could perhaps be due to slightly dissimilar quenching efficiencies of the two butene-2 isomers,(the trans- form having the larger cross section) and the probability of degradation of the excited butene-2 to cis- and trans- form, respectively, is equal.

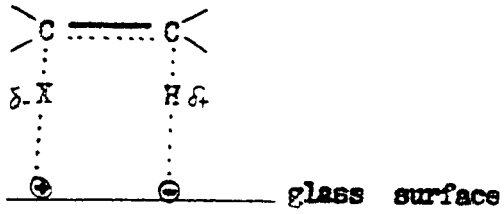
II. Surface effects in gas phase reactions

The usual test for the homogeneity of a gas phase reaction is to increase the surface : volume ratio of the reaction vessel. The rate will usually be increased when all or part of the reaction occurs on the surface.

The two most commonly used reaction vessel surfaces in gas phase kinetic studies are so-called "clean" Pyrex glass or silica and the carbonaceous films or coatings either deliberately deposited by the pyrolysis of olefins and halogen containing compounds, or produced by prolonged "seasoning" by the substance whose pyrolysis is being studied.

Silica displays polar characteristics which are most in evidence in the pyrolysis of polar compounds, particularly alkyl halides in which halogen acid is unimolecularly eliminated(28,29). The pyrolytic sensitivity towards "clean" glass surfaces is what one would expect in terms of heterolytic bond dissociation energies, $D(R^{+}Y^{-})$ of the carbon—halogen bond, i.e. $RI \geqslant RBr > RCl$. Shapiro and Swinbourne(30) have examined the kinetics of the catalysis of alkyl chloride pyrolyses due to the Pyrex surface. They believe that the polar glass surface assists charge separation in the reactant molecule. The physical picture was that of a simple attachment of the electronegative chlorine atom to a positive surface site.

Heterogeneity in halide pyrolyses increases from primary to tertiary compounds(30). The sensitivities of alkyl iodides towards a polar "clean" glass surface, ethyl < isopropyl < t-butyl, is similar to that observed by Shapiro, et al.(30) for alkyl chlorides and is in keeping with the decrease of heterolytic carbon—halogen bond dissociation energies in the sequence ethyl to t-butyl(31).



The "seasoned" or coated reaction vessel surface was believed to eliminate the wall effect and give reproducible and homogeneous rates. The thin carbonaceous films produced in reaction vessel "seasoning" act as a non-polar skin on the polar glass surface of the reaction vessel and this has been used as an inert surface in gas phase reactions(28,32,33,34). As a generalization, at a high enough temperature (above 600 °C) all organic compounds will deposit pyrolytic carbon on glass or silica surfaces. Allylic compounds are particularly useful in this respect since these compounds readily produce uniform carbon films at temperatures as low as 300 °C and have been frequently used for reaction vessel "seasoning". The absence of heterogeneous reactions on the carbon coating is usually tested by increasing the surface : volume ratio of the reaction vessel by packing it with glass tubes.

Alkyl chlorides and bromides have been shown to pyrolyse by two mechanisms; molecular elimination of halogen acid alone, or by molecular elimination together with a free radical chain reaction(33c, 35). Wojciechowski and Laidler(36) suggested that the carbon produced in reaction vessel "seasoning" might be catalytically active if it contained free radical sites, and could then act as both initiator and terminator in a radical chain reaction.

In 1964, Holbrook(37) reported that he had observed a strong electron spin resonance signal from allyl bromide carbon. He suggested that those supposedly inert surfaces catalysed some gas phase reactions. Holbrook and Rooney(38) found that both the rate of pyrolysis of 2-chlorobutane and the distribution of butene isomers in the products were dependent on the origin and the treatment of carbon surfaces. They showed that carbon derived from the ethyl chloride pyrolysis was less active towards the 2-chlorobutane pyrolysis than those derived from the pyrolyses of cis-butene-2 and allyl bromide.

Purnell and Quinn(39) studied the role of surface in the n-butane pyrolysis. They reported that the irreproducibility of the n-butane pyrolysis observed at high conversions can be explained, as due to conditioning of the reaction vessel wall by the deposition of carbon. During the conditioning, progessive reductions in reaction rate would be expected, until the wall of the vessel was completely covered with a fine layer of carbon, whereafter further deposition would not effect the rate of the reaction. No effect was observed when surface : volume ratio changes were studied with observed "clean Pyrex" vessels.

"Clean Pyrex", "KCl-coated", and "etched" vessels, gave identical rates. These results are compatible with a free-radical chain mechanism initiated and terminated homogeneously. They therefore conclude that the pyrolysis of n-butane in those three vessels is most probably entirely homogeneous. When a "clean Pyrex" surface is replaced by a magnesium perchlorate surface the rates of the uninhibited pyrolyses of the lower paraffins are depressed; this may well result from the introduction of a heterogeneous mode of termination of the free-radical chains. The authors also claimed to have identified the heterogeneous chain-termination at the surface of carbon-conditioned vessels. They suggested that the pyrolyses were best carried out at low conversions in clean reaction vessels where reactions may be considered to be completely homogeneous in character.

III. Object of present investigation

The mechanism of the gas phase isomerization of cis-butene-2 has long been a subject of discussion. In recent years there has been general agreement that the isomerization of butene-2 is unimolecular and proceeds through a singlet-singlet mechanism ($A \doteq 10^{14} sec^{-1}$ and $E \doteq 63$ Kcal $mole^{-1}$). This is not a chain reaction although at higher pressures side reactions occur.

Holbrook(37) described electron spin resonance measurements made on the carbon deposited during the gas phase pyrolyses of allyl bromide, cis-butene-2, and ethyl chloride. His observation of the strong e. s. r. signal in allyl bromide carbon provided

some evidence in support of Laidler's(36) speculations. Maccoll and Stone(40) found that the cis→trans isomerization of cis-butene-2 was very rapid in the presence of the carbon coating derived from allyl bromide. The isomerization of n-butenes in the gas phase is catalysed by weakly reactive free radicals such as nitric oxide(13) and iodine(18,19). Surfaces possessing unpaired electrons or electron acceptors may exert a similar effect; the reaction should therefore be a good test for free radical type reactivity in pyrolytic carbon.

In this work we describe the use of the kinetics of the surface catalysed isomerizations of the n-butenes as measures of the chemical activity of pyrolytic carbons and correlate the results with observations of other physical properties of the carbons. The equilibrium between cis- $\rightleftharpoons$ trans-butene-2 was studied because there is poor agreement between published thermodynamic equilibrium data obtained by various methods.

The homogeneous halogen acid catalysed isomerizations of the n-butenes were also studied in order to try to clarify the mechanisms of these reactions.

CHAPTER 2

APPARATUS AND EXPERIMENTAL

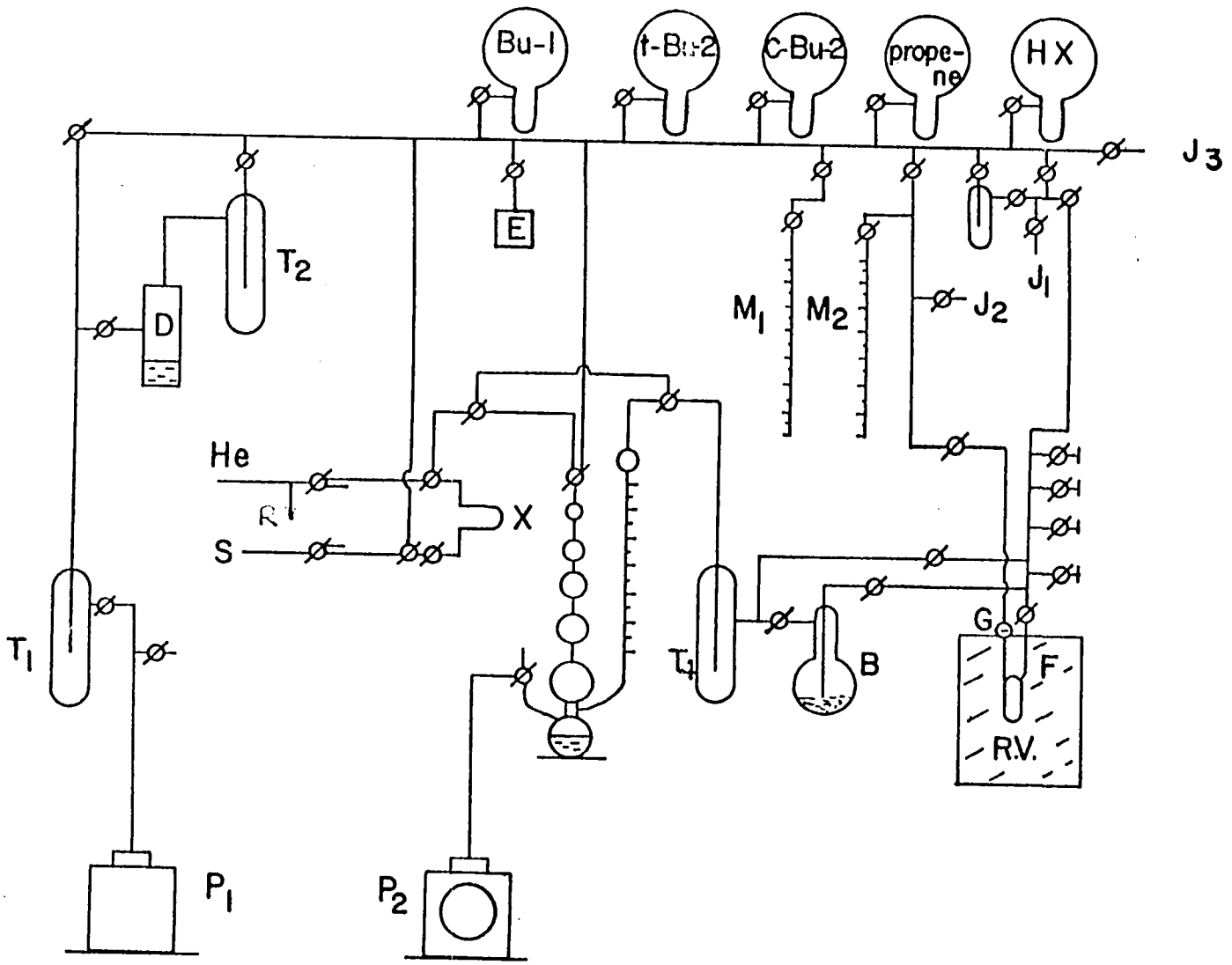
I. Apparatus

The experiments were carried out in a conventional static vacuum system, shown in the schematic diagram Figure 3. Silicone high vacuum grease was used for all taps and traps. A single manifold connected all parts of the apparatus. The entire system could be evacuated to less than 10^{-4} mm Hg by means of a mercury diffusion pump D, which was in series with a liquid nitrogen trap T_1 and Duo Seal vacuum pump P_1. The pressure was read on a Edwards Vacustat gauge E. A "sticky" vacuum indicated by the gaure was considered to be sufficiently low (10^{-4} — 10^{-5} mm Hg) for the experiments.

Five 3-litre bulbs were used for storing the three isomers of n-butene, propene and hydrogen halide. Two mercury manometers M_1 and M_2 and an Edwards Vacustat gauge were joined to the main manifold. Liquid samples, such as cyclohexene, n-propyl bromide, allyl bromide, ethyl bromide and bromine were stored in tubes which were separated from the system by taps. The outlets such as J_1, J_2, J_3 were used to admit air or to transfer the substances to and from the system. A finger tube F was joined to the system by means of a capillary tube between the reaction vessel and the tap. The side arm F was used for condensing the reactants before an experiment when such a procedure was appropriate. The glass tubing between the reaction vessel and its' tap was electrically heated by means of nichrome heating

Figure 3

Schematic diagram of the vacuum system


Bu-1
t-Bu-2
C-Bu-2
propene
HX
J3
E
T2
D
M1
M2
J2
J1
He
R
S
X
T1
T4
B
G
F
R.V.
P1
P2

ribbon lagged with asbestos. The temperature was controlled by a variable powerstat. The side arm was heated by covering it with a removable glass tube also wound with nichrome ribbon.

Except where otherwise stated the cylindrical reaction vessel was made of Pyrex glass with volume 150 ml., and packed with five concentric Pyrex glass tubes giving a surface : volume ratio of 5.2 cm^{-1}. The reaction vessel had two capillary tube outlets and a thermocouple well in its center. One outlet of the vessel was joined to the vacuum line and the other was joined to a diaphragm gauge G which consisted of two chambers separated by a thin glass membrane.

The reaction vessel was fitted evenly in a thermostat which was wound with three divided circuits in order to minimize the temperature gradient along the whole length of the reaction vessel. Each winding was connected to a powerstat and the voltage of each powerstat was adjusted. The temperature gradient along the reaction vessel was less than 0.2°C.

The temperature was controlled by means of a thermoelectronic temperature regulator which employed a chromel-alumel thermocouple. The thermocouple was placed near the bottom of the reaction vessel. A mercury plunger electronic relay was connected to the thermoelectronic regulator and through the powerstat to the center heating circuit of the thermostat.

Temperatures were measured by means of a chromel-alumel thermocouple connected with a Tinsley portable potentiometer, type 3184 D. The temperature was read against the standard reference at 0°C.

For the experiments involving hydrogen halides a five-litre removable glass bulb B was used for the expansion of the products; this contained a powdered basic absorbent to absorb the halogen acid from the mixtures of butene and hydrogen halide. Trap T_4 was used to condense the products and excess reactant from the reaction vessel. It was connected to a gas burette from which the sample was introduced to a by-pass in the gas chromatography apparatus. A rotary oil pump P_2 was employed for the gas burette.

Pressure measurement was accomplished by means of either the mercury manometer M_1 or the diaphragm gauge which was used as a null instrument against the mercury manometer M_2. The instrument was used as follows: Both sides of the membrane of the diaphragm gauge were thoroughly evacuated. The light was adjusted to focus on the membrane and the reflected image of a demarcation line was marked on a ground glass screen as zero pressure difference across the membrane. The reactant was admitted to the reaction vessel while the other side of the membrane was still evacuated. This caused a deflection of the image on the screen. Then air was admitted to the reference side of the membrane so as to bring the image back to the demarcation line. The pressure reading on the manometer attached to the gauge corresponded to the pressure in the reaction vessel. The pressure change in the reaction vessel was measured by the same procedure.

The gas chromatographic apparatus consisted of four three-way taps, a capillary U tube, columns and a thermal conductivity cell. Helium was used as the carrier gas and always passed

through the by-pass to the main column, and through R to the reference column as shown in Figure 3. Four three-way taps were interconnected such that the resistance to flow remained the same when helium flowed through the U tube "X" in order to carry the sample into the main column. This ensured that the recorder base line remained steady. The columns, of length 50 ft. were packed with the same material and kept in the thermostat at 0°C. The columns were made of copper tubing of $\frac{1}{4}$ inch outer diameter and were packed with 29 % W/W dimethylsulfolane on 60-80 mesh non-acid washed chromosorb P. Kovar seals were used to join metal to glass. A Gowmac thermal conductivity cell in a standard Wheatstone bridge circuit was used as a detector.

Calibration for the n-butenes was performed by admitting a measured amount of pure olefin into the gas chromatography apparatus. Calibrations for butene-1, trans-butene-2 and cis-butene-2 showed that their relative sensitivities showed the same trend as the literature values(61), although the relative magnitudes were not quite the same, namely 1.161, 1.126 and 1.000 respectively. (literature 1.055, 1.023, 1.000)

II. Materials

Propene, butene-1, cis- and trans-butene-2, and hydrogen chloride of research grade were obtained from the Matheson Company. An appropriate amount of gas was introduced through joint J_1 and condensed into the proper storage bulb at -196°C. The inlet pressure was measured by means of manometer M_1. After complete condensation, the tap attached to J_1 was closed,

and the liquid nitrogen bath of the storage vessel was replaced by slushy n-propanol at -127 °C for the degassing of the four olefins as mentioned above. The degassing process was repeated several times. Hydrogen chloride was degassed at -196 °C. No impurities were detected by examining about 150 micromoles of the purified gases through the gas chromatograph column but a trace (~ 0.5%) of n-butane was observed in purified trans-butene-2.

Hydrogen bromide was prepared by adding bromine to tetralin(42). The crude product was purified by passing through a column of red phosphorus to eliminate excess free bromine, thence through a bubbler filled with a concentrated aqueous solution of hydrogen bromide to remove bromides of phosphorus, and finally dried over pure phosphorus pentoxide. Bulb-to-bulb distillations from -78 °C to -196 °C with rejection gave pure hydrogen bromide, which was stored at liquid nitrogen temperature and warmed to -78 °C when samples were required.

Allyl bromide(b.p. 70.8 °C), ethyl bromide(b.p. 38.4 °C), n-propyl bromide(b.p. 71 °C), 3-chloro-2-methyl propene(b.p. 71.5 °C), and cyclohexane(b.p. 83.2 °C) were obtained from Eastman Organic Chemicals. They were all dried over anhydrous $CaCl_2$ for several hours and fractionated. The middle fractions were collected and were introduced to the system. All samples were degassed and stored under vacuum, and degassed again before use. Bromine was obtained from British Drug Houses and was temporarily joined to the system before use. It was thoroughly degassed and was sealed off after use.

III. Treatment of reaction vessel

Different coatings(surfaces) were given to the reaction vessel in the following way:

1. Clean glass:

For these experiments a clean glass reaction vessel was either one that had been washed with chromic acid, thoroughly rinsed with distilled water and dried in vacuo or one that had had a carbon coating burnt off in a stream of oxygen at ~500 °C. In most cases the latter constituted the "clean glass" vessel.

2. Allyl bromide carbon:

About 130 mm Hg of pure allyl bromide vapour were decomposed at 400°C for 30 minutes. This was arbitrarily chosen as a "standard" pyrolysis; it produced a thin carbonaceous coating on the surface of the reaction vessel.

3. cis-Butene-2 carbon:

About 520 mm Hg of pure cis-butene-2 were decomposed at 480 °C for 15 hours. A light carbonaceous film was deposited on the reaction vessel surface.

4. Ethyl bromide carbon:

About 500 mm Hg of pure ethyl bromide vapour were decomposed at 490°C for about 20 hours.

5. 3-Chloro-2-methyl propene carbon:

About 110 mm Hg of pure 3-chloro-2-methyl propene vapour were decomposed at 400 °C or 490 °C for 30 minutes as one pyrolysis which produced a thin carbonaceous film.

IV. Procedure for a typical run

Before each experiment the system was evacuated to a pressure lower than 10^{-4} mm Hg. The reactant was admitted to the reaction vessel from its storage bulb and its pressure measured by manometer M_1.

After a suitable reaction time, products and excess reactant were condensed in trap T_1 at -196°C for ~5 minutes. The condensate was then warmed to room temperature and the contents were thoroughly mixed; a sample of the gas was measured in the gas burette and then trapped by condensation at -196°C in the U tube "X" of the gas chromatography apparatus. The sample was then admitted to the gas chromatography apparatus and product peak heights were measured.

Some isomerisation experiments of cis-butene-2 were performed in the presence of propene and cyclohexene. In these cases, inhibitor was admitted to the reaction vessel and its pressure was measured by manometer M_1; it was then condensed at -196°C in the small side arm of the reaction vessel. A known pressure of cis-butene-2 from a calibrated volume was then condensed with the inhibitor in the side arm. The run was started by rapidly heating the side arm and covering it with its heating coil. At the end of a run the products and excess reactant were separated from cyclohexene by collecting at -48°C (n-hexanol slush) at which temperature the cyclohexene vapour pressure was negligible.

In the case of the catalysed isomerization of the n-butenes by hydrogen halide, the butene was admitted to the reaction vessel first, its pressure measured by means of

manometer M_1 and it was then condensed in the side arm at -196°C while the apparatus was re-evacuated. Then the butene was warmed and hydrogen halide was expanded at a much higher pressure into the reaction vessel. There was no detectable reaction of the butene in the time during which the halogen acid was being expanded into the reaction vessel. At the end of a run the products and excess reactant were expanded into an evacuated 5-litre flask B containing about 20 gm of $Ba(OH)_2$ (43) and 10 gm of anhydrone, $Mg(ClO_4)_2$. Hydrogen halide was removed by this basic absorbent in about 30 minutes when the hydrogen halide pressure in the reaction vessel was ~50 mms and in about 90 minutes when the pressure was ~200 mms. The products and excess butene were then collected in the gas burette, and sampled for V.P.C. analysis. The products in the inhibition runs were separated from cyclohexene by collecting the products and excess reactant at -48°C as described previously.

V. E. S. R. measurements

The e. s. r. spectra were obtained with Varian V-4502 spectrometers with 100 Kc./sec modulation. Some spectra were measured at -196°C by using the V-4546 quartz Dewar accessory filled with liquid nitrogen. The strength of the magnetic field at resonance was measured on a Varian F-8A proton fluxmeter. The frequency of the n. m. r. marginal oscillator was counted with a Computer Measurements Company model 731 B frequency convertor and 707 B frequency-period counter. The measurement of the magnetic flux density was to within ±0.05 gauss. The microwave

frequency was measured to within ±0.1 Mc. sec^{-1} by using a Hewlett-Packard model 540 B transfer oscillator in conjunction with the C. M. C. model 732 B frequency converter and 707 B frequency-period counter. Some spectra were recorded using a Hilger 'microspin' spectrometer with 100 Kc. sec^{-1} modulation.

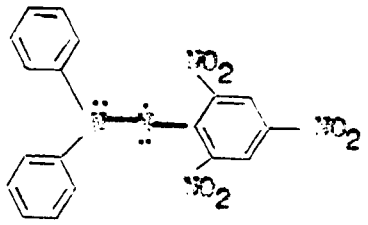
Coatings of pyrolytic carbon were prepared in 4 mm outside diameter Pyrex tubing which was sealed at one end and the other end of the tube was joined to the vacuum system. The tube was isolated by a tap and was placed in a well in a large thermostat. It was then thoroughly evacuated to a pressure of less than 10^{-4} mm Hg. The thermostat was adjusted to the desired pyrolysis temperature and a known pressure of reactant was admitted to the tube. At the end of the pyrolysis the tap was opened and the gaseous products and excess reactant were pumped away. Successive treatments for the same pyrolysis time were used to build up the thickness of the carbon coating. The tube was sealed off after the evacuation and was removed from the thermostat. It was then cooled by immersing the carbon-coated end in liquid nitrogen and was stored in liquid nitrogen until the e. s. r. measurement was made. It was found later that samples retained their spin content unchanged for at least several weeks at room temperature and the precaution of the immersion in liquid nitrogen was unnecessary and subsequent samples were kept at room temperature.

Spectra were recorded at -196°C and room temperature. A 1 cm length of the tube, just above the sealed end of the tube, was irradiated in the microwave cavity. After the e. s. r.

spectrum had been recorded the end few centimeters of the tube were cut off and the weight of carbon therein was determined by weighing the tube before and after buring out the carbon in a gas-air flame. The carbon deposit was assumed to be uniform and the weight of carbon irradiated in the cavity was calculated.

A typical e. s. r. signal for the samples showed only one absorption line and the first derivative e. s. r. spectra for allyl bromide, cis-butene-2 and isobutene carbons are shown in Figure 4. The e. s. r. spectra found in all the carbons have a characteristic shape and have been reviewed by Singer(44). Allyl bromide carbon has an unusally narrow absorption line(0.35 gauss) compared with the more commonly encountered width of 1 - 10 gauss. The smaller line-width may be due to exchange narrowing and it is believed to be typical of unpaired electrons delocalized in polyaromatic systems.

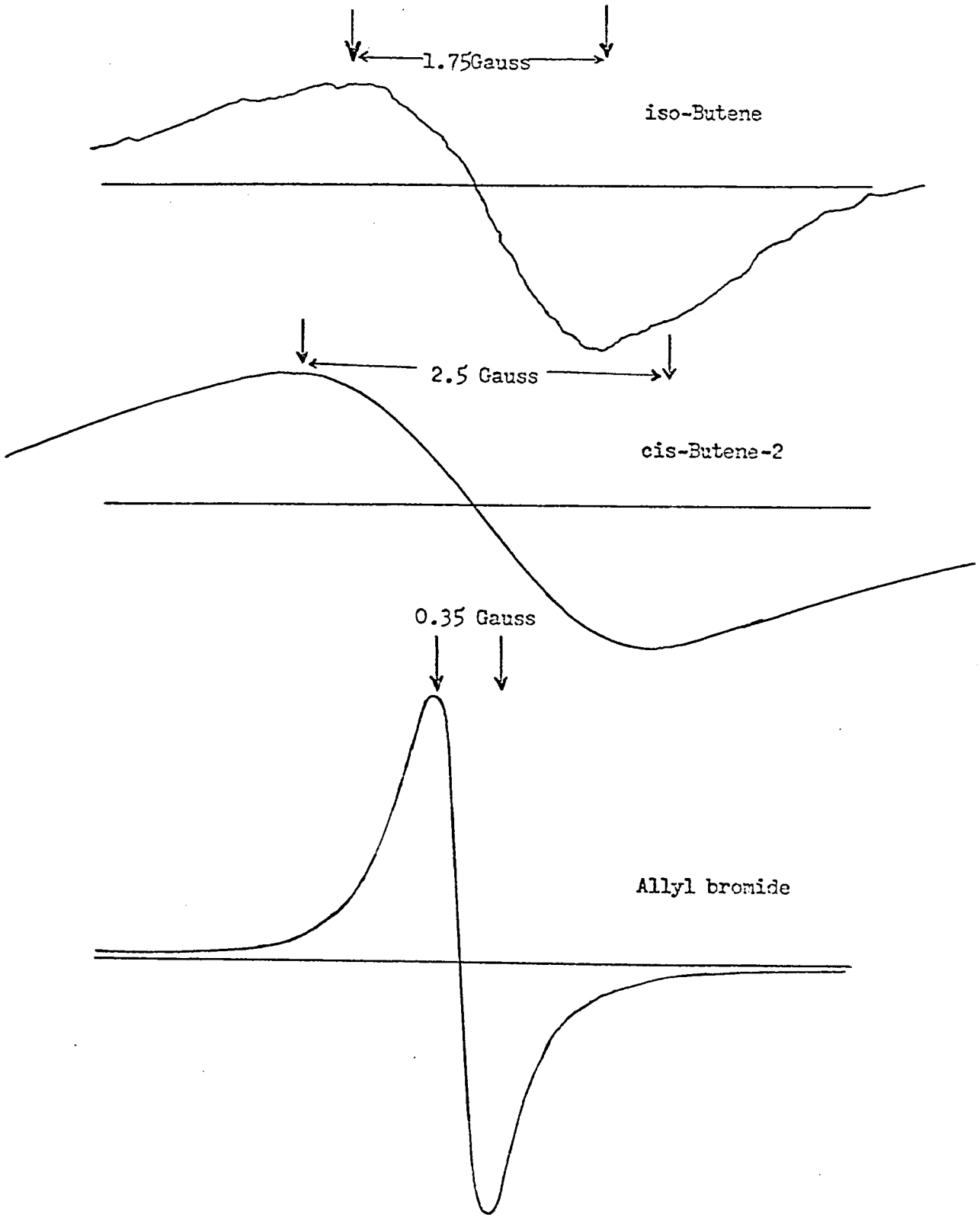
The spin content of the sample was estimated by comparison of the first derivative absorption curve with that for a standard sample of diphenylpicryl hydrazyl



The area under the normal absorption curve was found by double integration of the differential curve and was estimated by w^2h, where w was width and h was height of the first derivative absorption curve. This approximation is good provided that the curve is symmetrical and the width and height are large enough so as to minimize the uncertainty in the measurement.

Figure 4

First derivative e. s. r. spectra of pyrolytic carbons from isobutene, cis-butene, and allyl bromide


1.75Gauss
iso-Butene
2.5 Gauss
cis-Butene-2
0.35 Gauss
Allyl bromide

From the relation of $\Delta E = h\nu = g\beta H$, where $\beta = eh/4\pi mc$ is the Bohr magneton and H is the applied magnetic field, the g value can be evaluated. The g factor for allyl bromide carbon was measured as 2.0021 ± 0.00005. For the free electron g has the value of 2.0023.

The results for a number of organic compounds are summarised in Table 1. As in the case of allyl bromide carbon the spin content is proportional to sample size and the experiments are quite reproducible. It was found later that the spin content of allyl bromide carbon varies linearly with the number of pyrolyses performed as shown in Figure 5. Samples prepared in tubes packed with Pyrex fibres did not give reproducible results with allyl bromide. Holbrook(37) prepared his samples in tubes packed with silica fibres and found no signal in carbon deposited from cis-butene-2 and ethyl chloride, and approximately 10^{18} spins/gm in that from allyl bromide. The spin concentration of "standard" allyl bromide carbon was estimated to be 5.4×10^{20} spins/gm (45) in the present investigation and in the later result of Holbrook(46) the mean value of spin concentration was estimated as 1.4×10^{20} spins/gm.

The effect of various substances on the spin signal was also examined. If oxygen was admitted to the sample while in the cavity at room temperature, the signal collapsed instantly. Four successive allyl bromide pyrolyses in the presence of 0.2 mm oxygen produced the normal amount of carbon but only a very weak, broad e. s. r. spectrum was observed. The effect of oxygen was studied in more detail by storing oxygen in a micromanometer joined via a needle valve to the evacuated sample

Table 1 Free radical content of pyrolytic carbons

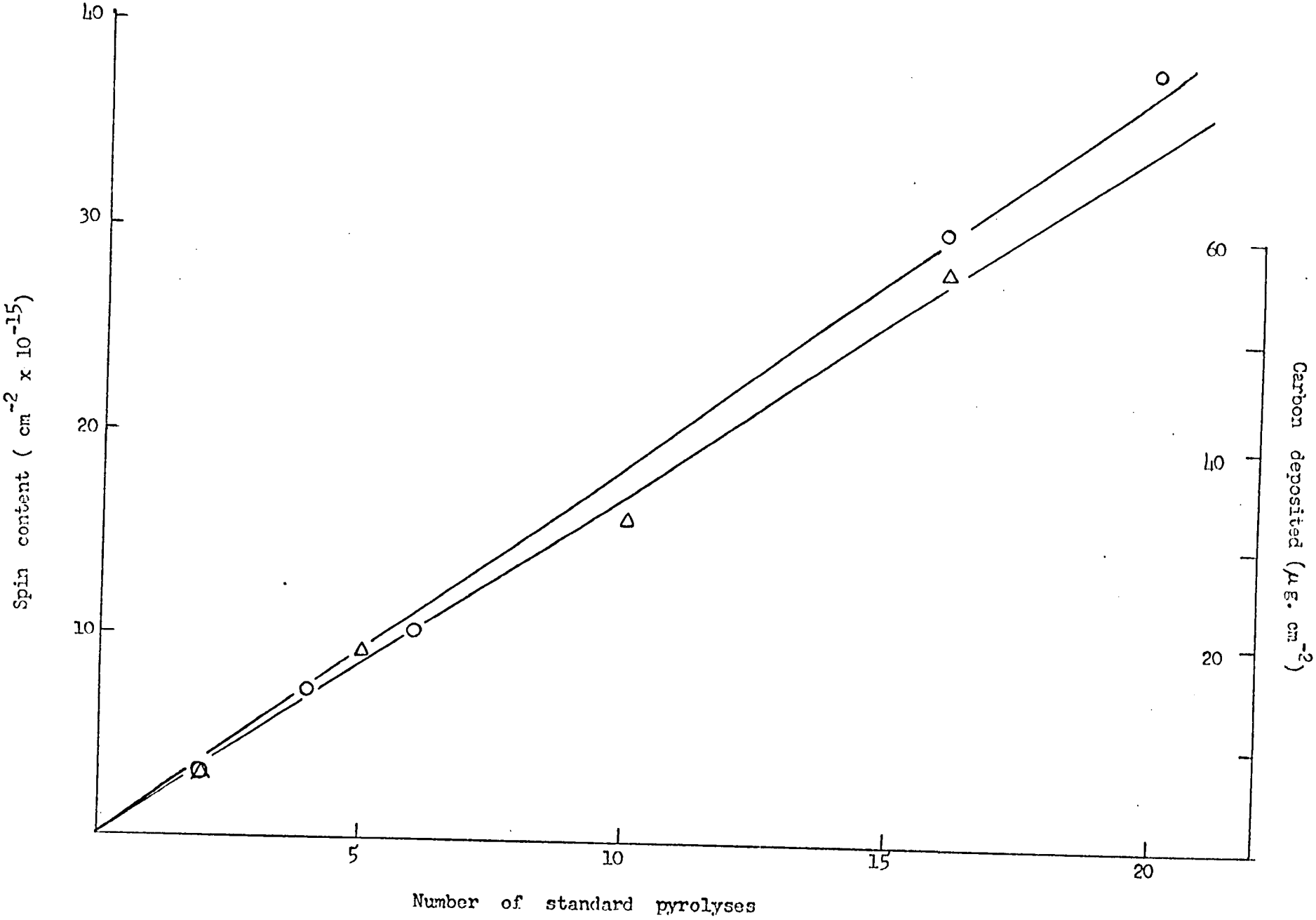
Compound	Pressure (mm.)	Pyrolysis temp.(°C)	Time (hr.)	Successive no. of pyrolyses	Wt. of C (μg.)	No. spins x 10^{-15}
Allyl bromide	150	400	0.5	2	-	3.3
Allyl bromide	150	400	0.5	4	24	5.0
Allyl bromide	150	400	0.5	8	45	10
Allyl bromide	150	405	0.5	12	-	16
Allyl bromide	150	400	0.5	16	85	20
Allyl bromide	150	400	0.5	4	22	5.1
Allyl bromide	150	490	0.5	4	15	6
Allyl bromide	150	522	0.25	8	43	3.1
Isobutene	680	490	34	1	~3	0.27
cis-Butene-2	650	490	34	1	40	6.1
Ethyl bromide	550	486	11	2	~2	~0.017
Ethyl bromide	550	522	7	3	10	0.06
3-Chloro-2-methyl propene*	150	490	0.5	2	-	3.5
3-Chloro-2-methyl propene*	150	490	0.5	4	-	5.9

* The result was obtained in this laboratory by Mr. P. Taillefer.

Figure 5

Spin concentration of " standard " allyl bromide carbon

o Spin content; Δ weight of carbon


40
30
20
10
Spin content (cm^{-2} x 10^{-15})
60
40
20
Carbon deposited (μg. cm^{-2})
5
10
15
20
Number of standard pyrolyses

tube so that small amount of oxygen could be admitted while the sample was in the spectrometer. The addition of oxygen reduced the height of the first derivative e. s. r. spectrum and increased the line width. It became difficult accurately to measure the latter and the result showed that the apparent collapse of signal when air was admitted was not an indication of complete removal of odd electrons but was mainly due to the line broadening. Bolbrook(46) has shown that oxygen does not irreversibly destroy the odd electrons since the e. s. r. signal can be partially recovered by prolonged evacuation of the sample.

A number of experiments were then performed in which tubes coated with four standard pyrolyses of allyl bromide carbon were treated with various substances at an elevated temperature to simulate the normal pyrolysis conditions of these additives. The spin content of the carbon was then determined after evacuation and the results are summarised in Table 2. The effect of cis-butene-2 on the spin content of allyl bromide was also examined. The result (Table 3) showed that no significant change was made by introducing gaseous cis-butene-2 into the tube which contained four-pyrolyses allyl bromide carbon.

Table 2 Effect of pyrolyses of various compounds on the spin content of allyl bromide carbon

Compound pyrolysed	Temp.(°C)	Pressure(mm Hg)	Time(min.)	Decomposition(%)	No. spins x 10^{-15}
Standard	-	-	-	-	5.0
Isopropyl bromide	400	200	0.4	26 (ref.47)	4.9
Isopropyl bromide	400	200	10	>90	4.0
Isopropyl bromide	400	200	10	>90	5.8
n-Butyl bromide	400	40	0.4	>1‡(ref.35a)	3.6
n-Butyl bromide	400	40	2	>5	4.9
Hydrogen iodide	400	10	1	-	3.4
Hydrogen iodide	350	10	5	-	4.2
Hydrogen iodide	250	10	5	-	4.4
Nitric oxide	400	6	5	-	3.7

* Decomposition calculated from refs. cited.

‡ Uninhibited pyrolysis.

Table 3 Effect of cis-butene-2 on the spin content of allyl bromide carbon

Experiment	No. spins x 10^{-15}
Carbon sample in vacuo	5.9
500 mm cis-butene-2 admitted	5.9
Butene condensed on carbon at -196 °C, then warmed to room temp.	4.9
Butene condensed in storage bulb(-196 °C)	5.0
Sample heated to 400 °C for 1 hour	6.0

CHAPTER 3

RESULTS

I. Isomerization of cis-butene-2 on allyl bromide carbon

The experimental techniques and procedures have been described in chapter 2. Standard allyl bromide pyrolyses were performed at 400°C as usual.

Some preliminary reactions were performed in the untreated clean reaction vessel. Initial pressures of cis-butene-2 of about 60 mm were decomposed at about 450°C and the first order rate constants for the trans-butene-2 production are shown in Table 4. These rate constants agree quite well with those calculated from the data of Rabinovitch(5).

The reaction vessel used for a series of experiments was coated with six successive standard allyl bromide pyrolyses at 400°C. The rates of the isomerization in the coated vessel were much faster than in the uncoated vessel. The major products of the cis-butene-2 isomerization were trans-butene-2 and butene-1. Typical percentage production against time plots for trans-butene-2 and butene-1 formations are given in Figures 6 and 7. The orders of the formations of trans-butene-2 and butene-1 were found to be close to unity as shown in Figure 8 and Figure 9, respectively. Some decomposition products appeared; at 430°C in addition to trans-butene-2 and butene-1, n-butane, ethane, ethylene and methane were observed. However, the latter four side products represented only 1% of the isomerization products at a total conversion of 8%. At 390°C only a trace of n-butane appeared representing less than 1% of the isomerization

Table 4 First order rate constants of cis→trans isomerization of cis-butene-2 in clean vessel

Temperature(°C)	$k_{et} \times 10^6$ (sec^{-1})	$k^1 \times 10^6$ (sec^{-1})*
450	5.6	6.1
457.6	11.0	9.7

* The rate constants evaluated from Rabinovitch and Michel's work (5).

Figure 6

Percentage production against time plot for trans-butene-2 formation in cis-butene-2 isomerization on allyl bromide carbon

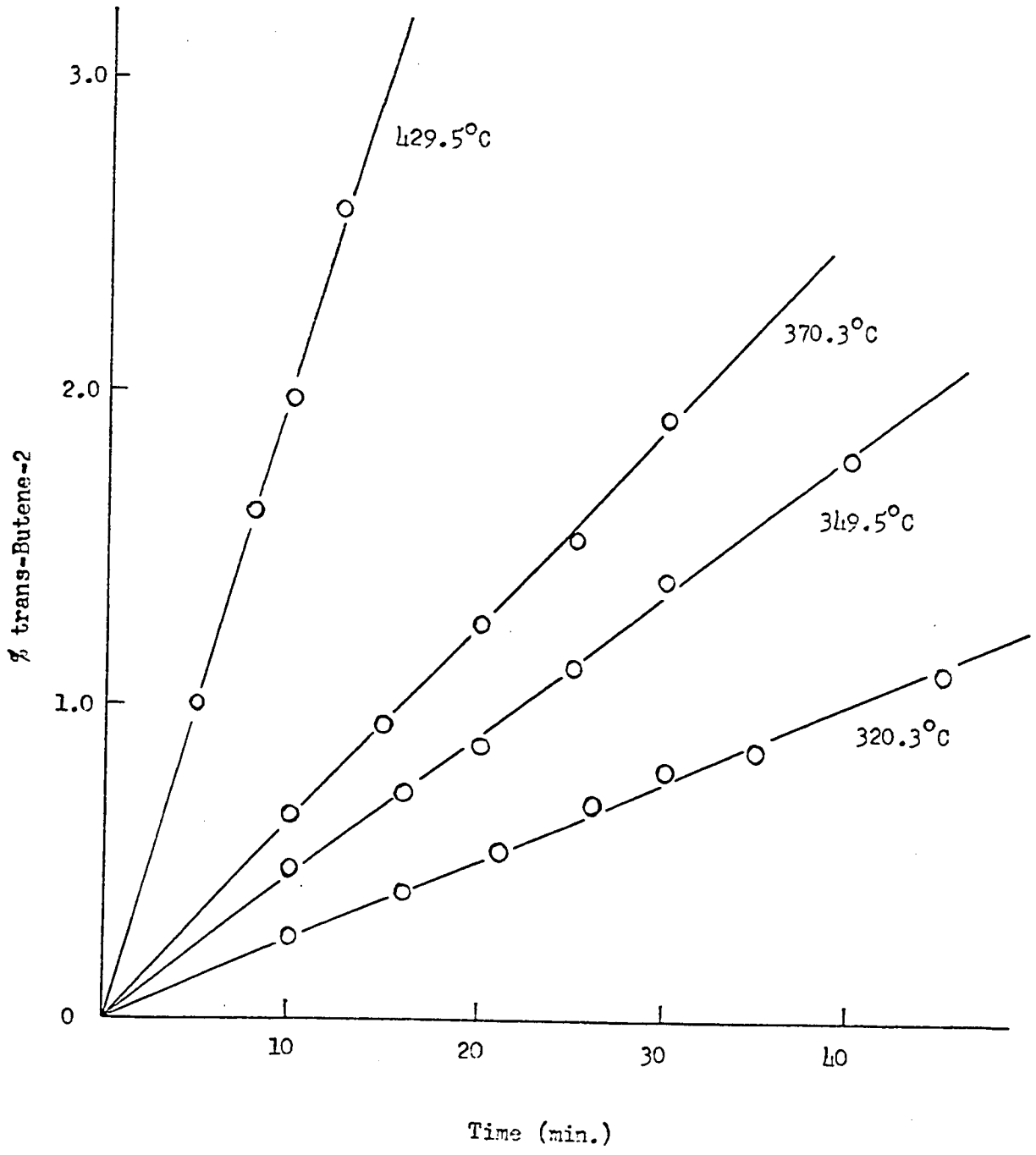

3.0
2.0
1.0
0
% trans-Butene-2
429.5°C
370.3°C
349.5°C
320.3°C
10
20
30
40
Time (min.)

Figure 7

Percentage production against time plot for butene-1 formation in cis-butene-2 isomerisation on allyl bromide carbon

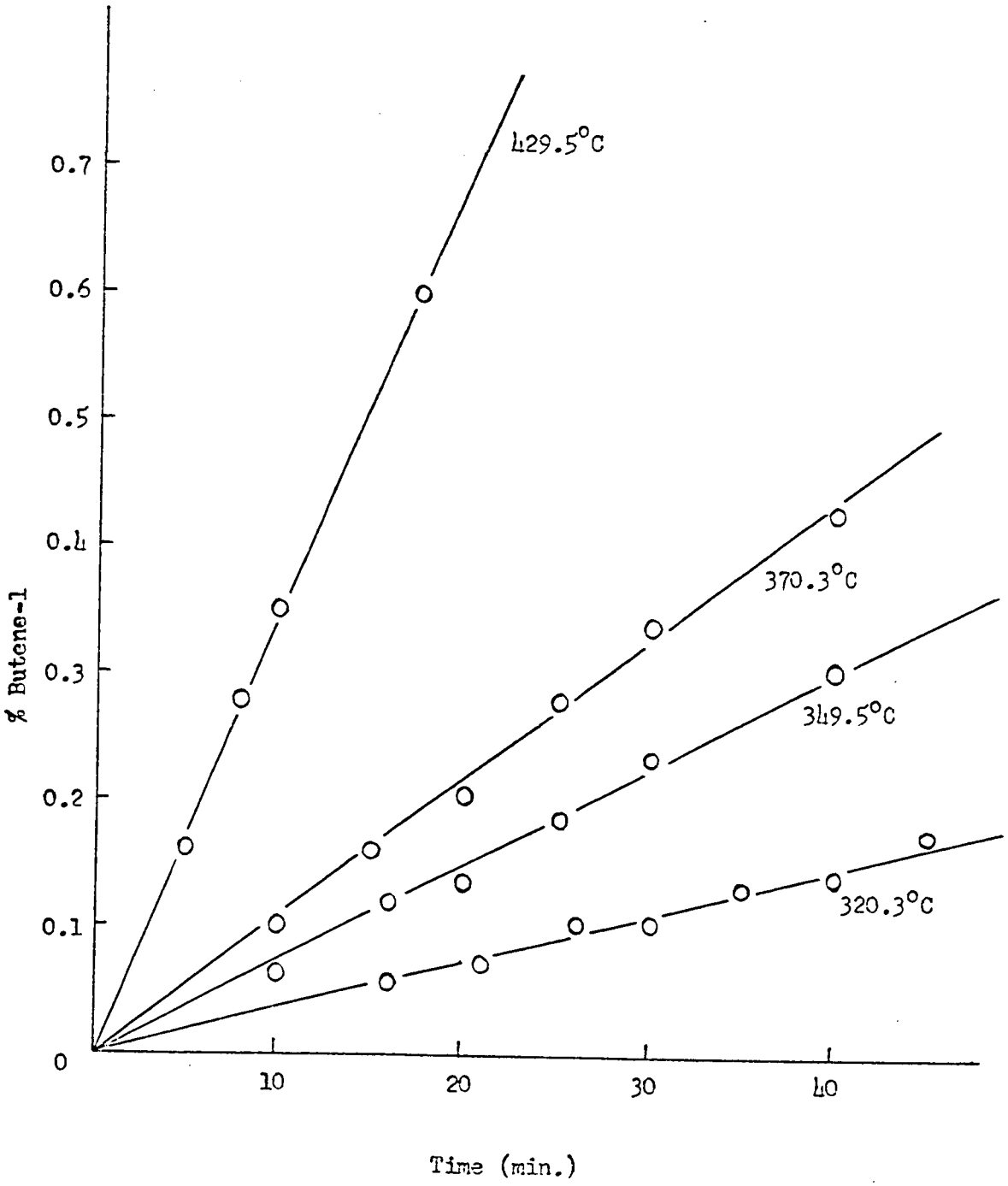

429.5°C
370.3°C
349.5°C
320.3°C
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
10
20
30
40
% Butene-1
Time (min.)

Figure 8

Order plot of cis→trans isomerization of butene-2 on allyl bromide carbon

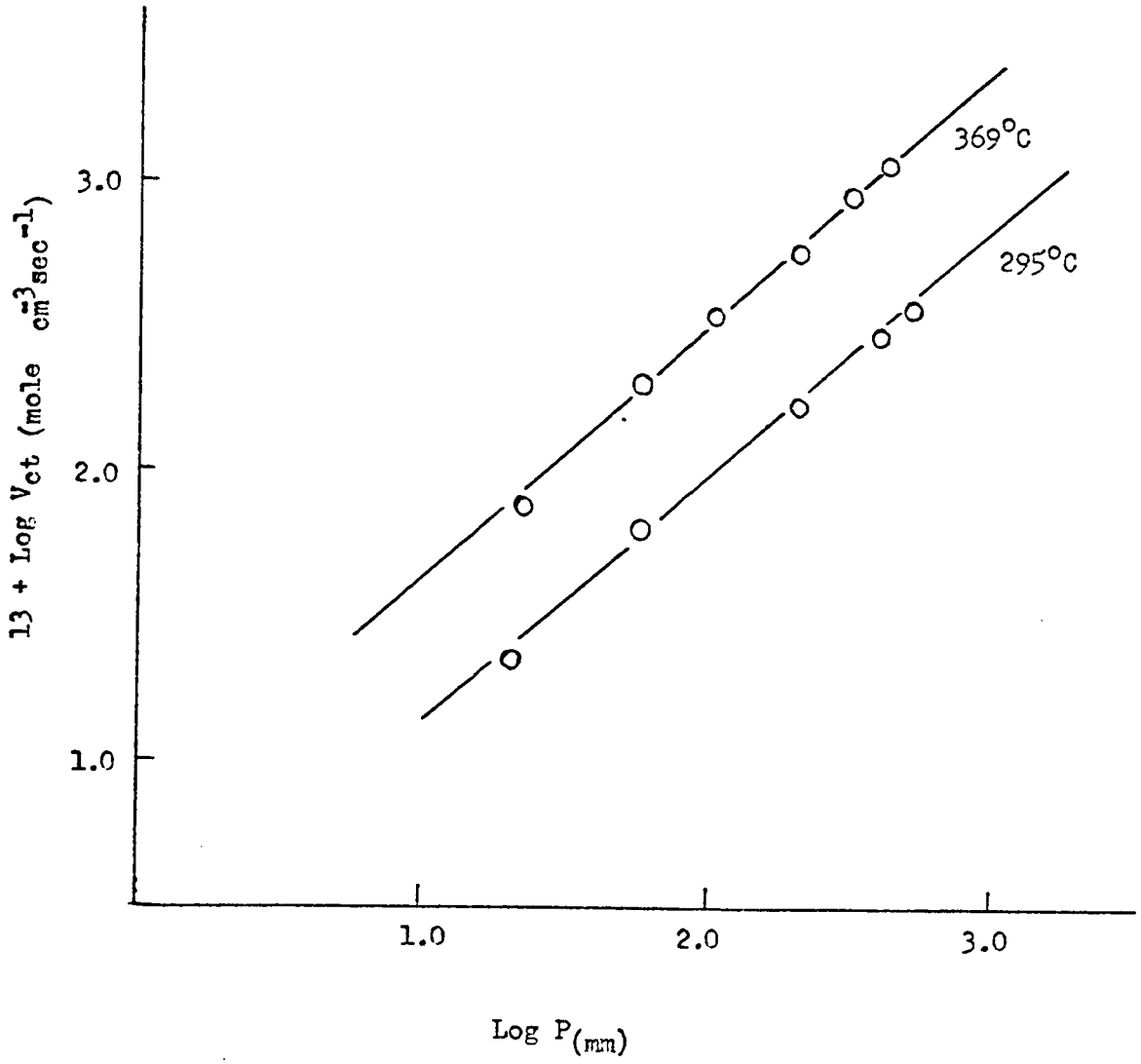
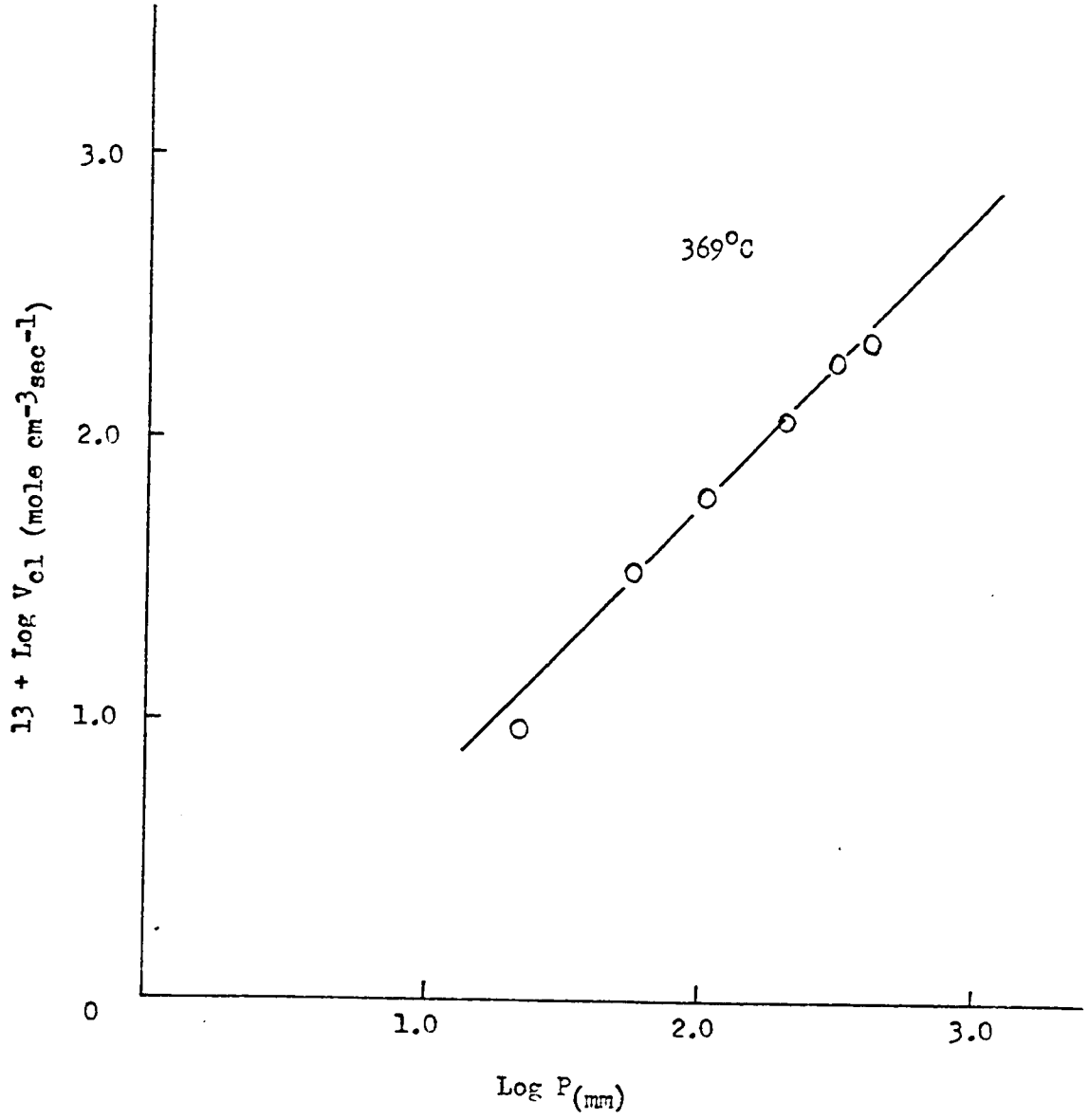

13 + Log V_{ct} (mole $cm^{-3}sec^{-1}$)
3.0
2.0
1.0
1.0
2.0
3.0
Log $P_{(mm)}$
369°C
295°C

Figure 9

Order plot of cis-butene-2 ⟶ butene-1 isomerization on allyl bromide carbon


3.0
2.0
1.0
0
13 + Log V_{cl} (mole $cm^{-3}sec^{-1}$)
369°C
1.0
2.0
3.0
Log $P_{(mm)}$

products at 6% conversion. At lower temperatures products other than the two isomers fell below the limit of detection of the apparatus and represented less than 0.1% of the products. Some results are summarised in Table 5 where the top six results refer to isomerizations performed using the fresh coating "(A)" and the remainder refer to "(B)", which was carbon (A) which had been heat treated at 460°C for ~ 16 hours.

A series of kinetic experiments were performed on carbon (A) at successively increasing temperatures from 350--430°C and then at decreasing temperatures in the same range. The rate constants so determined are summarised in Table 6. From the "temperature-rising" results, a curved Arrhenius line was obtained when log k_{cis} was plotted against 1/T as shown in Figure 10(H-K curved line). However the rate constants subsequently measured at successively lower temperatures gave a linear Arrhenius line K-L in Figure 10.

After completion of the above series of experiments on carbon (A) the reaction vessel was heated in vacuo to 460°C for ~16 hours and a new set of rate constants(Table 6) were obtained on this heat treated carbon (B). In Figure 10 the Arrhenius plot for carbon (B), line M-N, is almost parallel to Arrhenius line K-L obtained using carbon (A). The higher rate constants found with carbon B were interpreted as showing that the activity of the carbon could be enhanced by heat treatment. That heat treatment affected the odd electron content was then established when the spin content of a carbon produced from four standard allyl bromide pyrolyses was found to increase six fold after heating in vacuo at 510°C for 15 hours.

Table 5 Dependence of first order rate constants on initial pressure for the allyl bromide carbon catalysed isomerization of cis-butene-2 to trans-butene-2 and butene-1

Temperature(°C)	P_0 (mm)	k_{cis} x 10^6(sec^{-1})	k_{cis} x 10^6(sec^{-1})
350	30	4.03	-
350	60	4.28	-
350	120	4.79	-
403	30	14.0	-
403	60	13.8	-
403	120	14.9	-
295	20	3.90	-
295	60	3.85	-
295	210	2.90	-
295	420	2.60	-
295	525	2.45	-
369	22	13.6	2.1
369	60	13.6	2.9
369	105	12.9	2.6
369	210	11.8	2.4
369	310	11.5	2.6
369	422	10.9	2.2

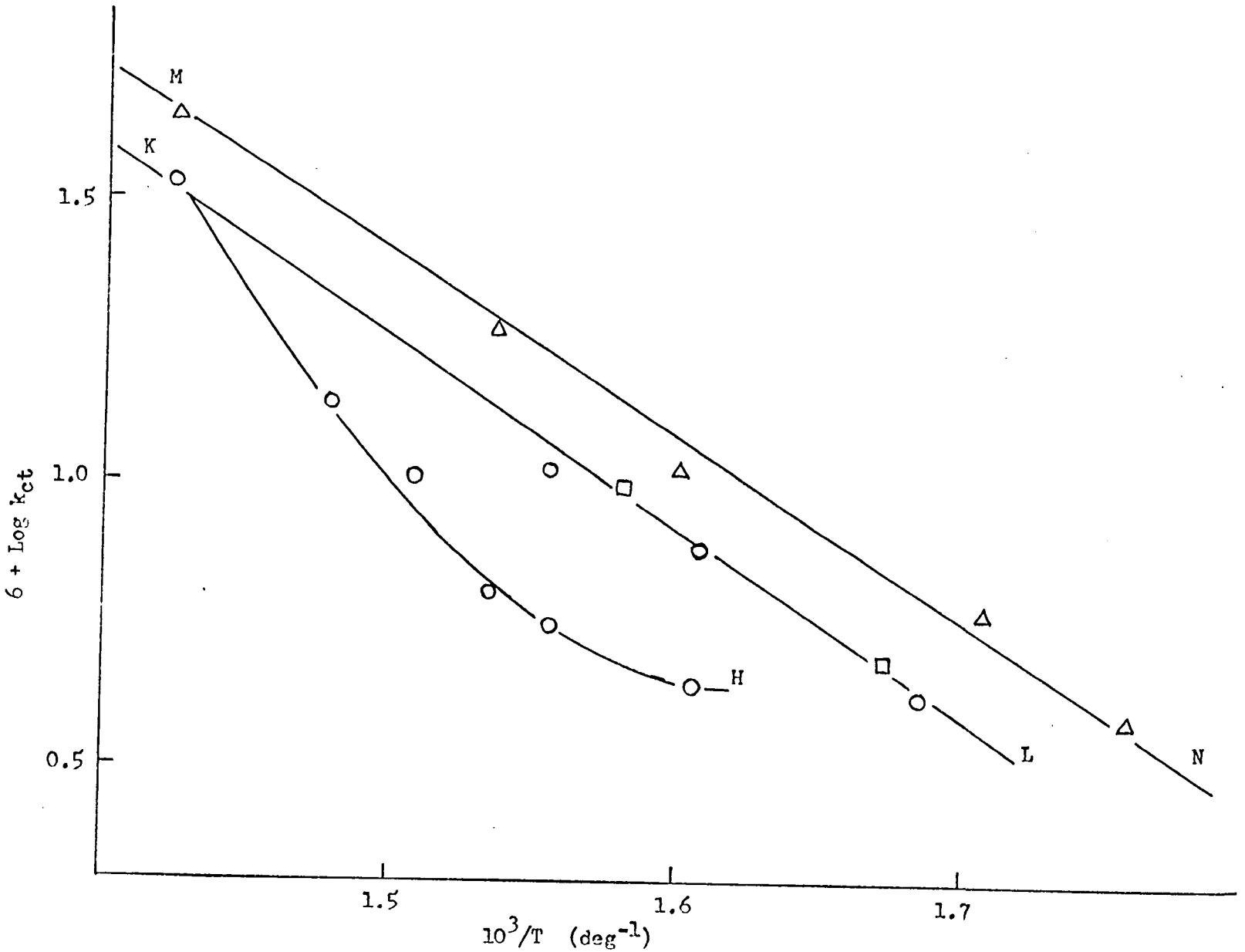
Note: The top six results were obtained on carbon [A] and the remainder on carbon [B] (see text).

Table 6 The rate constants of the isomerization of cis-butene-2 to trans-butene-2 and butene-1 on allyl bromide carbon

Carbon	Temperature(°C)	$k_{ct} \times 10^6 (sec^{-1})$	$k_{cl} \times 10^6 (sec^{-1})$
A	350.3	4.4	-
A	370.3	5.71	-
A	379.2	6.4	-
A	389.7	10.6	-
A	403.2	13.9	-
A	429.5	33.8	5.89
A	370.3	10.6	1.86
A	389.4	7.75	1.25
A	320.3	4.25	0.57
A	430.4	39.8	7.04
A	359.8	9.94	1.85
A	325.3	4.86	0.54
B	429.1	44.4	8.98
B	378.4	18.8	3.53
B	369	13.6	2.88
B	351.9	10.6	1.84
B	312.5	6.03	0.74
B	295	3.85	0.44

Figure 10

Arrhenius plots for cis→trans isomerization of butene-2 on allyl bromide carbon, showing effect of heat treatment


M
K
1.5
1.0
0.5
6 + Log k_{ct}
H
L
N
1.5
1.6
1.7
$10^3/T$ (deg^{-1})

The corresponding Arrhenius plots for the cis-butene-2 to butene-1 isomerization on the two carbons of different activity [A] and [B], are shown in Figure 11.

The Arrhenius activation energies for the cis-trans isomerization on the two carbons were 15.6 and 14.3 Kcal $mole^{-1}$, while those for the cis→1 isomerization were 17.6 and 17.9 Kcal $mole^{-1}$. The corresponding frequency factors are 2.4 and 1.3 sec^{-1} for cis→trans isomerization, while those for the cis→1 isomerization are 1.8 and 3.5 sec^{-1}.

Several carbons deposited from allyl bromide pyrolyses were examined and kinetic results were compared. Table 7 shows that the reproducibility of the rate constant is somewhat poor. The activity of the allyl bromide carbon depends significantly therefore on the heat treatment of the individual carbon.

A series of experiments were then designed to discover what was the effect of carbon deposit thickness on the rate of the isomerization. Allyl bromide carbon coatings of different thickness were deposited in the standard manner for various pyrolysis times. The reaction vessel was cleaned between coating experiments by burning off the carbon in a stream of oxygen at 500°C, a test isomerization was performed after each burn-off to check that the rate constant had fallen to the homogeneous value, thus indicating the complete removal of pyrolytic carbon. Each coating was heated to 450°C for 18 hours after deposition in an attempt to ensure uniformity. The first order rate constant for the cis-trans butene-2 isomerization was measured at 390°C for a given carbon; it was then burnt off and a new carbon deposit laid down. The results are summarised in Table 8

Figure 11

Arrhenius plots for cis-butene-2→butene-1 isomerization on allyl bromide carbon

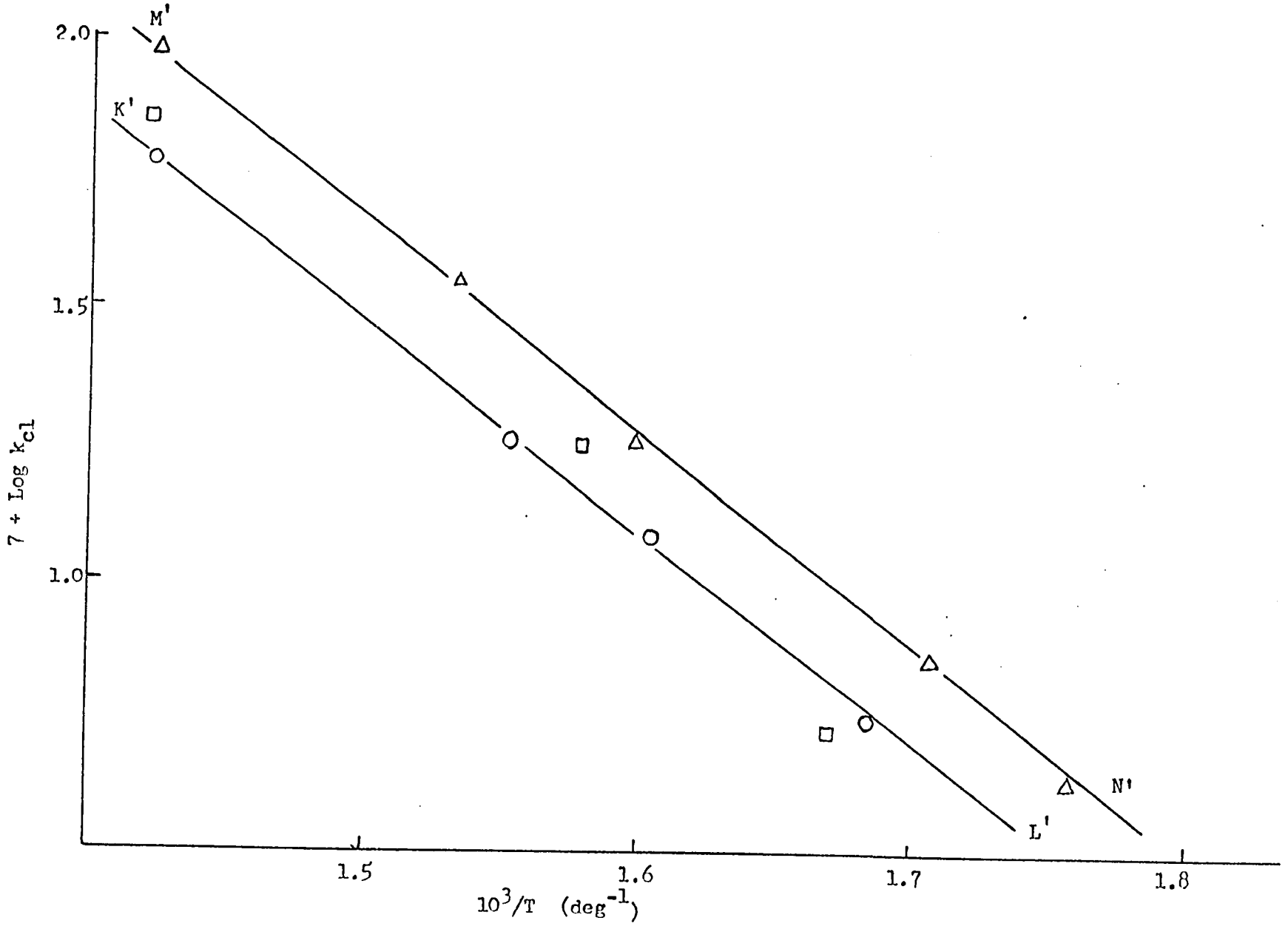

M'
K'
L'
N'
2.0
1.5
1.0
7 + Log k_{cl}
1.5
1.6
1.7
1.8
$10^3/T$ (deg^{-1})

Table 7 The effect of heat treatment of allyl bromide carbon on the rate of cis→trans isomerization of cis-butene-2 (Initial pressure of cis-butene-2 = 60mm)

Carbon	Heat treatment	Temp.(°C)	$k_{ct} \times 10^6 (sec^{-1})$
10 standard pyrolyses	450°C, 70 hrs.	380	13.8
3 standard pyrolyses	none	380	4.77
6 standard pyrolyses	none	380	5.99
6 standard pyrolyses	none	380	6.35
6 standard pyrolyses	none	380	6.37
6 standard pyrolyses	none	380	6.39
6 standard pyrolyses	460°C, 60 hrs.	380	10.4
6 standard pyrolyses	460°C, 60 hrs.	390	13.5
6 standard pyrolyses	460°C, 60 hrs.	390	13.4
6 standard pyrolyses	460°C, 60 hrs.	390	15.1
6 standard pyrolyses	460°C, 60 hrs. + 430°C, 7days	390	17.0

Table 8 The effect of the thickness of allyl bromide carbon on the rate of cis→trans isomerization of cis-butene-2 (Initial pressure of cis-butene-2 = 60 mm, Temp. = 390°C)

No. of successive pyrolysis	$k_{ct} \times 10^6$ (sec^{-1})
1/30	2.85
1/6	7.47
1/2	9.44
1	8.45
3	10.4
6	11.0
9	11.0

and also shown in Figure 12. Furthermore, to confirm the effect of the carbon thickness on the rate of isomerisation, the change of electrical conductivity was also measured at a frequent intervals during a 30 minute period of a standard allyl bromide pyrolysis. The conductivity sharply increased during the first minute and subsequently increased only slowly. This result shows a similar behaviour to the kinetic measurement of cis-butene-2 isomerization rate on the different thickness of the carbons in which the rate increases sharply in the first minute of deposition of allyl bromide carbon. The conductivity results are shown in Figure 13.

Some isomerizations were performed in the presence of propene and cyclohexene as possible homogeneous reaction inhibitors or, since they have a similar configuration to cis-butene-2, as possible competitors for active sites on the surface. The results are summarised in Table 9. Instead of inhibiting the isomerization, propene appeared to act as a deactivating agent of the carbon; the rate of the isomerization was appreciably decreased and the carbon had fallen from its original activity and the subsequent isomerizations of cis-butene-2 gave the results as summarised in Table 10. The result on this deactivated carbon showed that the rate was not so sensitive to temperature variation as that of the original carbon. The change of the carbon activity can be seen in Figure 14, where the activation energy of the cis-trans isomerization on the deactivated carbon was completely different from that on the original carbon. Accordingly, a carbon which gave $k_{ct} = 23.3 \times 10^{-6}$ sec^{-1} at 430°C was treated with 555 mm propene for 12 hours. At the end of

Figure 12

Effect of carbon thickness on the rate of the cis→trans butene-2 isomerization at 390°C

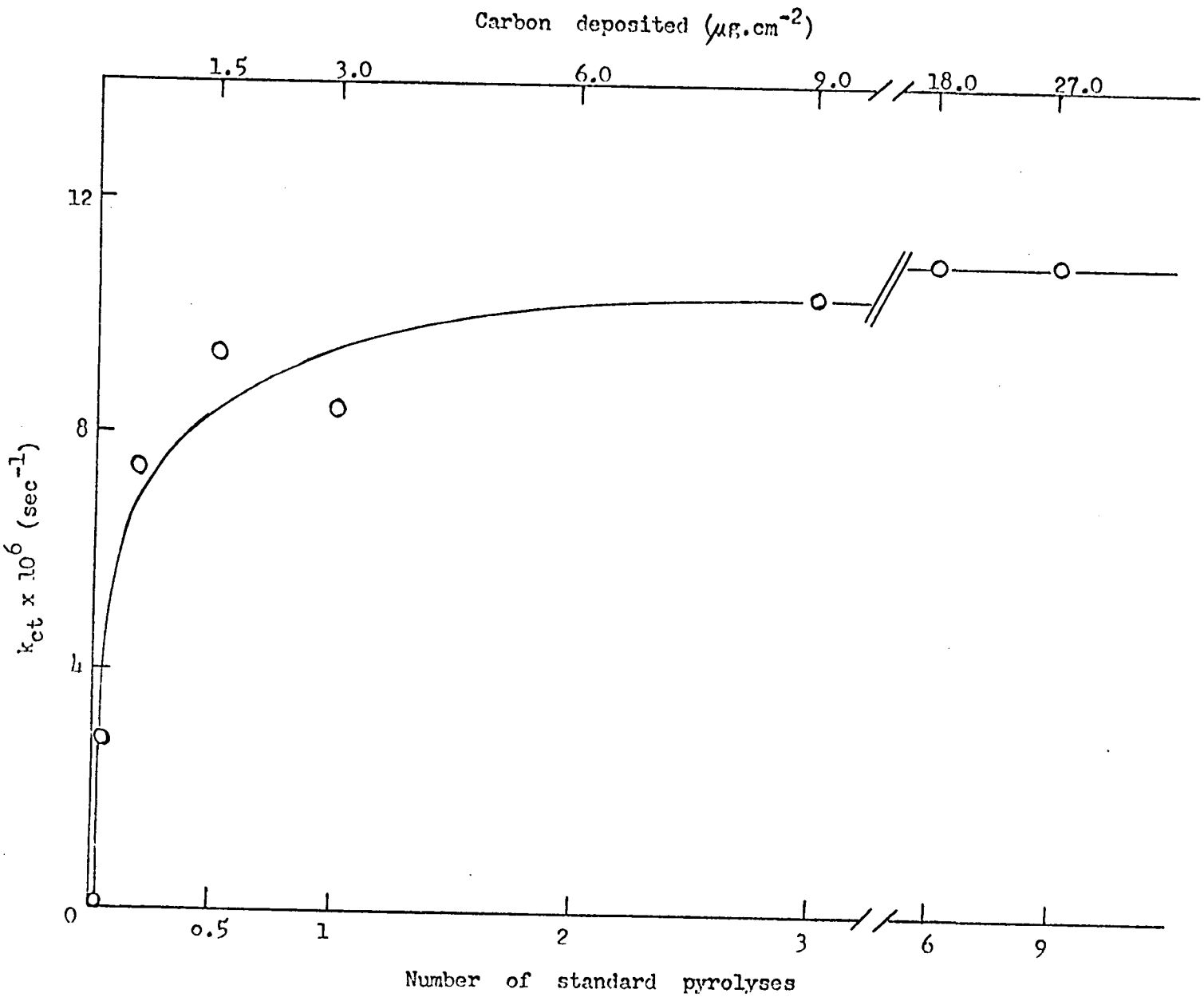

Carbon deposited ($\mu g.cm^{-2}$)
1.5
3.0
6.0
9.0
18.0
27.0
12
8
4
0
$k_{ct} \times 10^6$ (sec^{-1})
0.5
1
2
3
6
9
Number of standard pyrolyses

Figure 13

Electrical conductivity of allyl bromide carbon

○ First pyrolysis; △ sixth pyrolysis

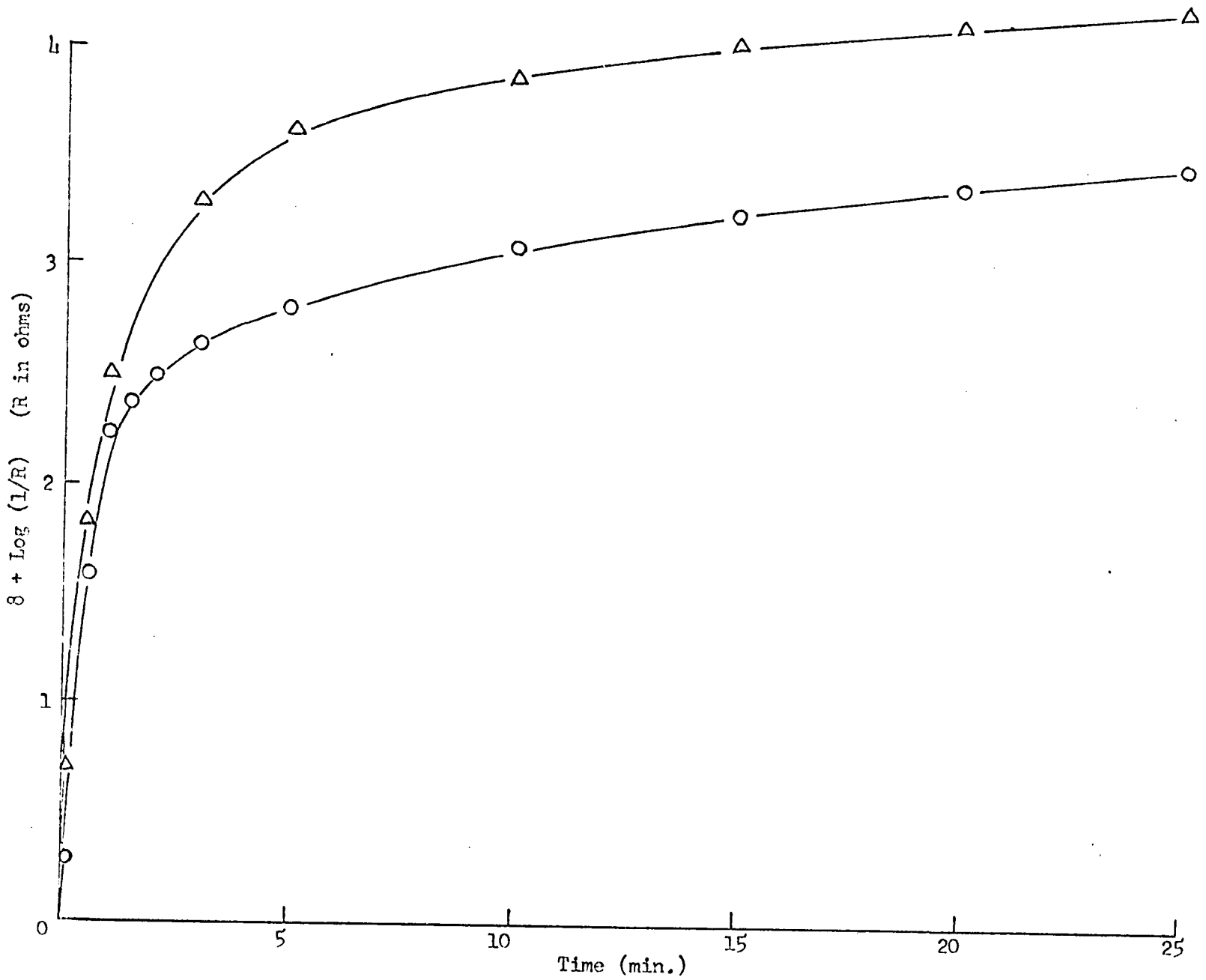

8 + Log (1/R) (R in ohms)
4
3
2
1
0
5
10
15
20
25
Time (min.)

Table 9 The effect of propene and cyclohexene on the cis-trans isomerization of cis-butene-2 on allyl bromide carbon*

Temperature(°C)	Pressure(mm)		$k_{ct} \times 10^6 (sec^{-1})$
	cis-butene-2	propene	
363.4	63	0	12.6
363.4	60	64	11.3
363.4	65	65	11.0
363.4	60	110	10.8
363.4	60	260	6.3
	cis-butene-2	cyclohexene	
369.5	60	0	13.7
369.5	60	59	13.2
369.5	61	65	12.1
369.5	61	305	10.8

* The carbon prepared from six successive standard pyrolyses

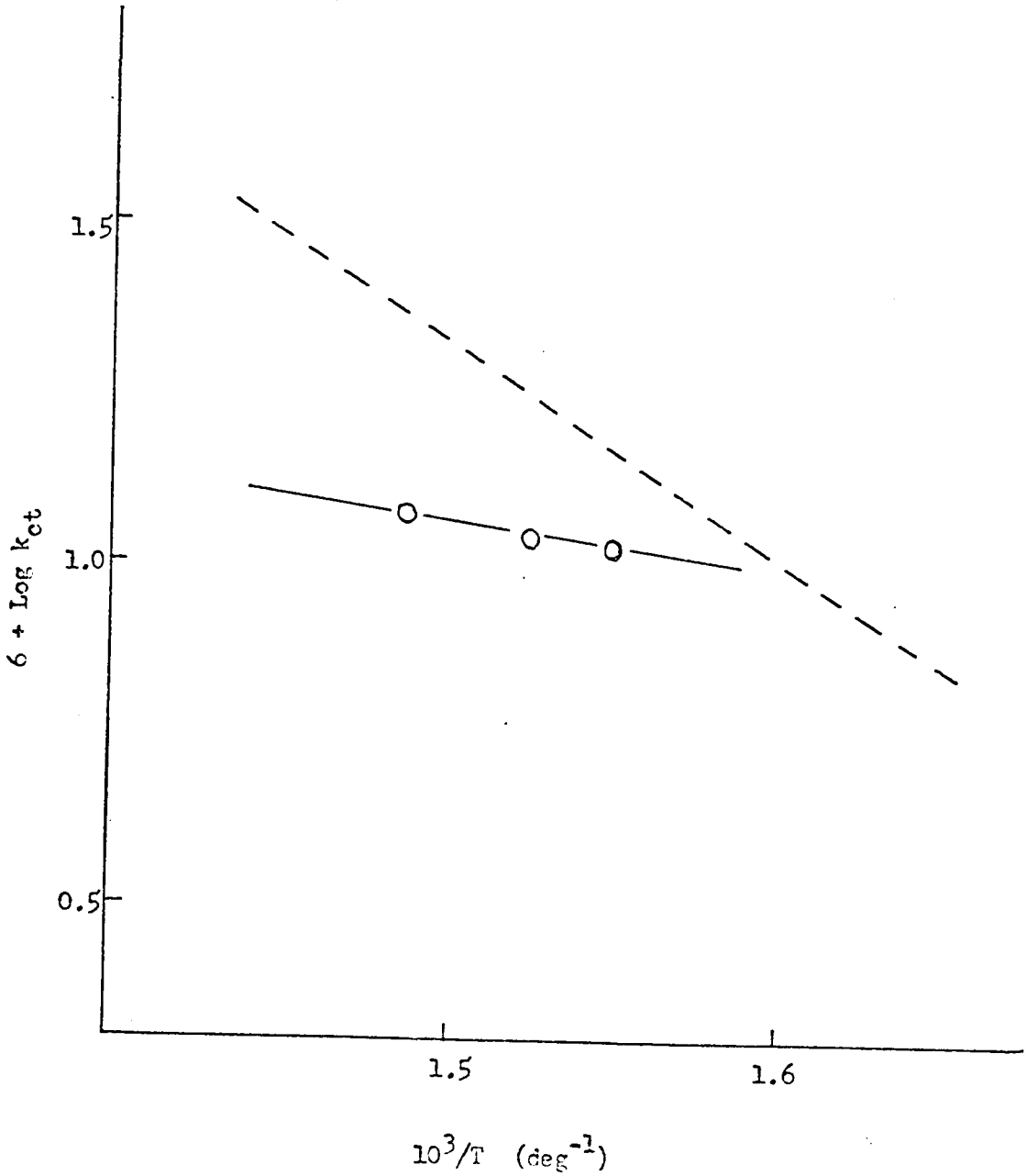
Table 10 The rate constants of the cis-butene-2 isomerization on allyl bromide carbon which had been deactivated by treating with propene and cyclohexene (as in Table 9).

Temperature(^{o}C)	$k_{ct} \times 10^{6}(sec^{-1})$	$k_{cl} \times 10^{6}(sec^{-1})$
372.3	10.5	1.57
383.2	10.8	1.62
400.2	11.7	2.33

Figure 14

Arrhenius plot for cis→trans isomerization of butene-2 on deactivated allyl bromide carbon

Dashed line from original Arrhenius plot before the carbon deactivation by propene(see text)


1.5
1.0
0.5
6 + Log k_{ct}
1.5
1.6
$10^3/T$ (deg^{-1})

the treatment, the isomerization rate constant was redetermined and had fallen to $k_{ct}=4.4x10^{-6}$ sec^{-1}. Other results for propene deactivated allyl bromide carbon are summarised in Table 11. The carbon could not be reactivated by prolonged evacuation.

The effect of oxygen on the activity of an allyl bromide carbon was also briefly studied. $A_{\lambda}^{Standard}$ carbon was deposited on the surface of the reaction vessel and the rate of the cis-trans isomerization was determined as $k_{ct}= 17.1 \times 10^{-6}$ sec^{-1} at 380°C. It was found, after a small quantity of oxygen(3 mm air) had been admitted to the reaction vessel for 30 minutes and then pumped away, that the rate constant had decreased to $k_{ct}= 10.2 \times 10^{-6}$ sec^{-1}. If the reaction vessel was exposed to atmospheric pressure for 30 minutes and reevacuated, the carbon became very active and no rate constants could be measured at 380°C owing to the large number of decomposition products found(see Figure 15). Those decomposition products were not all identified. This enhanced activity persisted for five trial isomerizations and is therefore unlikely to be due to inadequate evacuation. When this carbon was treated with one standard allyl bromide pyrolysis only the isomerization products were found in subsequent experiments with cis-butene-2, but rates were irreproducible; at 380°C k_{ct} from 3 runs varied from $5.6x10^{-6}$ to 11.6×10^{-6} sec^{-1}.

Table 11 The effect of propene on allyl bromide carbon

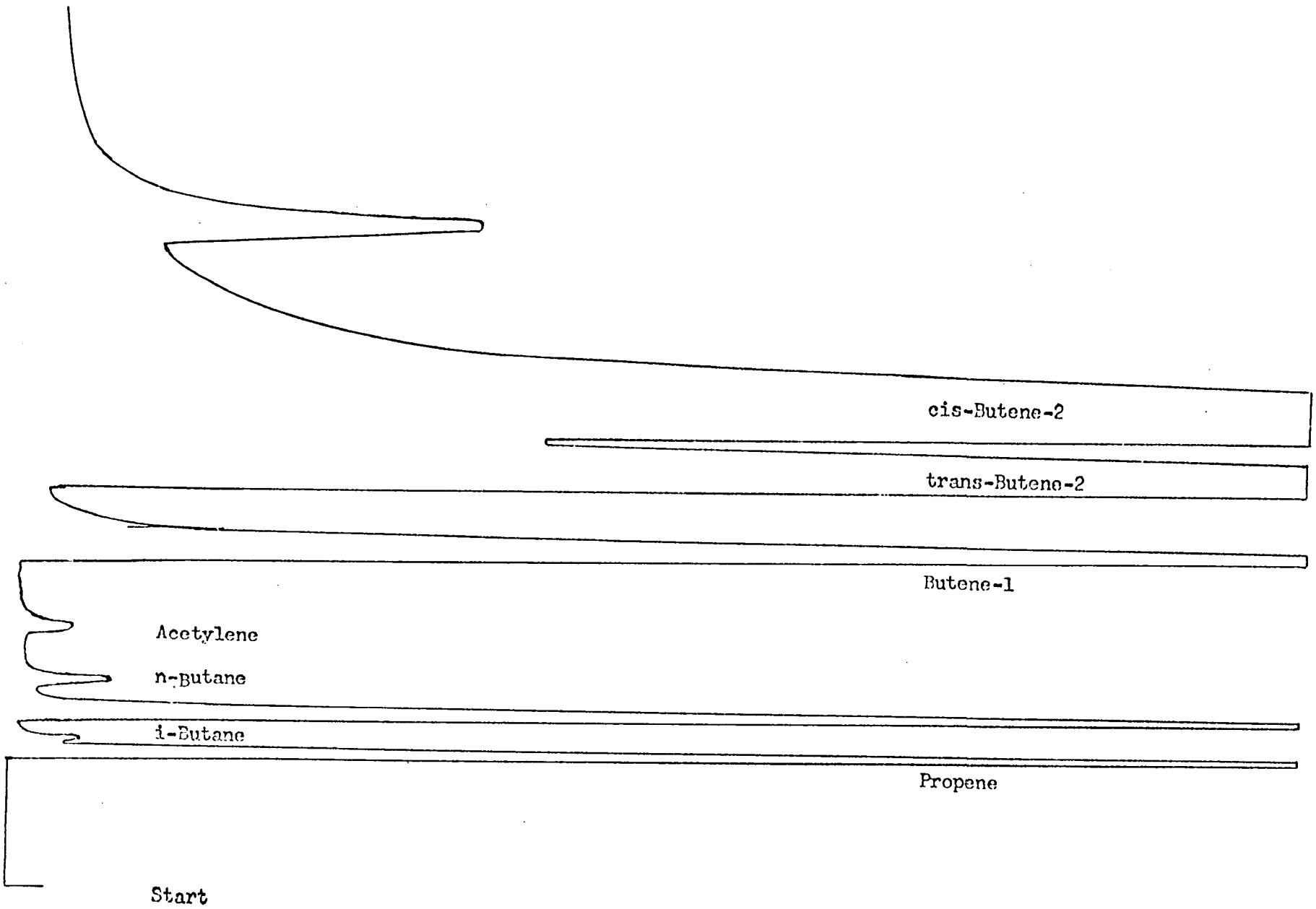
Carbon	Heat treatment	Propene treatment	Temperature(°C)	$k_{ct} \times 10^6 (sec^{-1})$	$k_{ct}' \times 10^6 (sec^{-1})$
1/2 pyrolysis	450°C, 18 hrs.	62.5mm, 16.5 hrs.	390	9.44	5.4
1/30 pyrolysis	450°C, 18 hrs.	602mm, 15.5 hrs.	390	2.85	1.0
6 pyrolyses	none	65mm, 17 hrs.	375	4.94	3.2

Note: k_{ct} is the rate constant of cis-trans isomerization before the treatment of propene where k_{ct}' is after the treatment.

Figure 15

Gas chromatographic trace for cis-butene-2 isomerization and decomposition at 380°C on atmospheric air exposed allyl bromide carbon (Initial pressure = 58 mm, Time = 30 min.)

Note: 25-ft. columns of 15% dimethylsulfolane on 60-80 mesh non-acid washed Chromosorb P were used for the separation.


cis-Butene-2
trans-Butene-2
Butene-1
Acetylene
n-Butane
i-Butane
Propene
Start

Un-packed vessel

The isomerization of cis-butene-2 in an un-packed vessel was also studied. Reaction vessels with surface : volume ratio of 1.1 and 1.4 cm^{-1} were used. The reaction vessels were coated with the carbon deposited from standard pyrolyses of allyl bromide and were heat treated. The cis-butene-2 isomerization was subsequently performed in the reaction vessels and the first order rate constants were determined. The results are summarised in Table 12.

Table 12 The rate constants of cis-butene-2 isomerization on allyl bromide carbon in un-packed vessel

S/V (cm^{-1})	Carbon	Heat treatment	Temperature(°C)	$k_{ct} \times 10^6 (sec^{-1})$	$k_{cl} \times 10^6 (sec^{-1})$
1.1	3 pyrolyses	450°C,18 hrs.	439	30.2	5.53
			389	15.14	3.19
1.4	6 pyrolyses	460°C,62 hrs.	428	43.93	8.03

II. Isomerization of cis-butene-2 on cis-butene-2 carbon

In their study of the homogeneous cis-butene-2 isomerization, Rabinovitch and Michel(5) found that the homogeneous rate constants increased with the number of experiments done and they attributed this increasing rate to a heterogeneous process caused by the slow build-up of an active surface contaminant. Furthermore, in our e.s.r. measurements we have shown that cis-butene-2 carbon has an absorption spectrum and an odd electron content similar to that obtained from allyl bromide carbon. It might therefore be supposed that its activity towards the butene isomerization would be similar to that of allyl bromide carbon and that the deposition of cis-butene-2 carbon was the cause of the increase of rate observed by Rabinovitch.

This series of experiments were brought about on a surface prepared by pyrolysing cis-butene-2 as described in chapter 2 and the resulting carbonaceous film on the reaction vessel surface was used to catalyse the isomerization of cis-butene-2. The isomerization was studied in the temperature range 390 — 452°C. No products could be detected other than the two isomers trans-butene-2 and butene-1. A typical percentage trans-butene-2 formation against time plot is given in Figure 16. The cis→trans isomerization showed first order kinetics but with a lower rate constant than that obtained from allyl bromide carbon. The results are summarised in Table 13. A series of kinetic experiments were performed on prepared carbon at sucessively increasing temperature from 390 — 430°C, then the reaction vessel was heated to 450°C for ~ 10 hours and a new set of rate constants at decreasing temperatures were obtained.

Figure 16

Percentage production against time plot for trans-butene-2 formation in cis-butene-2 isomerization on cis-butene-2 carbon

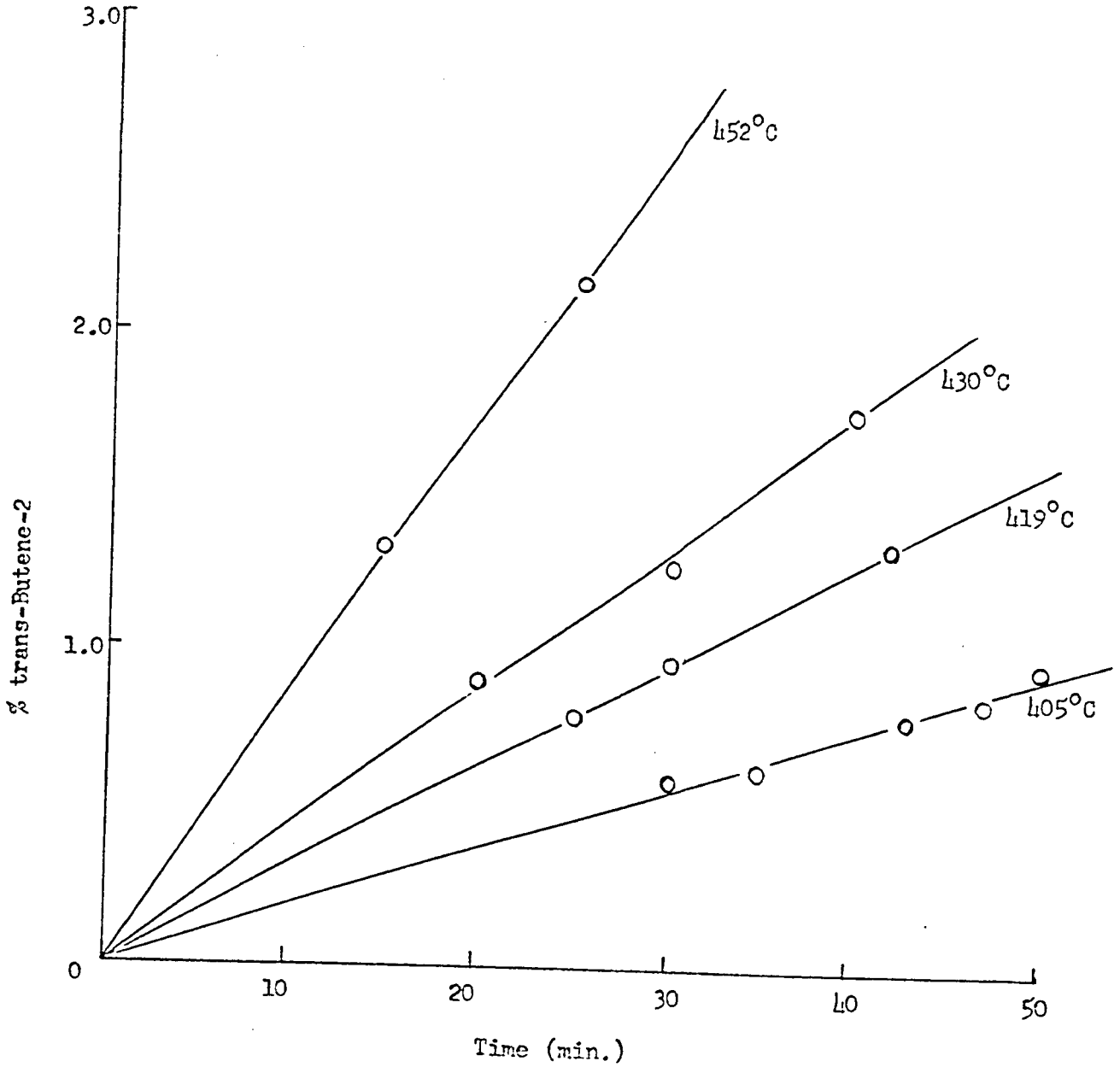

3.0
2.0
1.0
0
% trans-Butene-2
452°C
430°C
419°C
405°C
10
20
30
40
50
Time (min.)

Table 13 The rate constants of cis→trans isomerization of cis-butene-2 on cis-butene-2 carbon as a function of temperature (Initial pressure = 60 mm)

Temp.(°C)	Reaction time(min.)	%Conversion	$k_{ct} \times 10^6$(sec^{-1}) (Average)
390	40	0.24	
390	50	0.36	
390	60	0.40	1.09
390	45	0.26	
390	55	0.34	
410	30	0.56	
410	50	0.99	
410	40	0.65	
410	45	0.69	2.8
410	35	0.59	
410	25	0.36	
410	30	0.48	
430	30	1.02	
430	40	1.78	5.2
430	20	0.62	
430	32.5	1.01	
452	20	2.00	
452	15	1.32	14.7
452	25	2.16	

(continue)

430	20	0.90	
430	30	1.25	7.4
430	40	1.76	
419	30	1.60	
419	24	0.90	
419	30	0.99	5.4
419	42	1.34	
419	25	0.80	
419	35	0.99	
405	30	0.71	
405	50	0.97	
405	35	0.62	3.2
405	47	0.82	
405	43	0.79	

Figure 17

Arrhenius plots for cis→trans isomerisation of butene-2 on cis-butene-2 carbon

□ Result from another cis-butene-2 carbon

(see page 64)

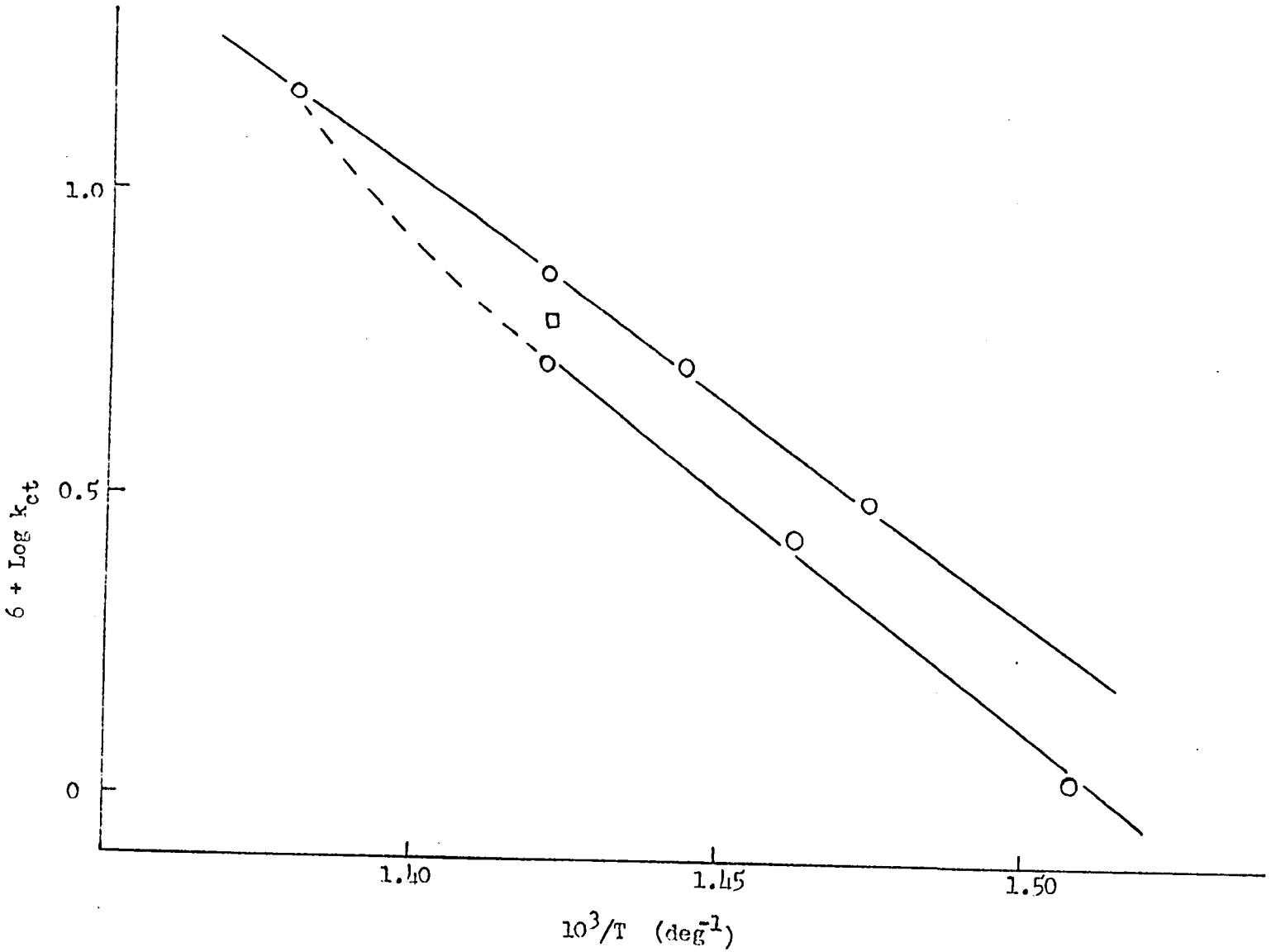

1.0
0.5
0
6 + Log k_{ct}
1.40
1.45
1.50
$10^3/T$ (deg^{-1})

Figure 17 illustrates that the activity of cis-butene-2 carbon was affected by heat treatment as was the case for allyl bromide carbon. The isomerization on the heat treated carbon gave a linear Arrhenius plot with

$$k_{ct} = 9.2 \times 10^{4} e^{-32,500/RT} \text{ sec}^{-1}.$$

The activation energy for this cis → trans isomerization of butene-2 is appreciably higher than that obtained using allyl bromide carbon as catalyst.

The kinetics of butene-1 formation on cis-butene-2 carbon were not measured since the quantities produced were very small. At 452°C only traces of butene-1 could be detected with the rate less than 1/10 of the trans-butene-2 formation.

The reproducibility of the activity of cis-butene-2 carbon is similar to that found with allyl bromide carbon. Figure 17 also shows the rate constant obtained for another cis-butene-2 carbon, prepared by decomposing 437 mm of cis-butene-2 at 480°C for 18 hours.

III. The relationship between the activities of allyl bromide carbon and cis-butene-2 carbon

The results described in the previous two sections showed that allyl bromide carbon was markedly more active than cis-butene-2 carbon towards the butene isomerizations, even though the carbons have similar odd electron contents as observed from the e.s.r. measurements. One possible interpretation of this difference was that allyl bromide carbon contained bromine which might be responsible for enhancing activity. Two samples of allyl bromide carbon were prepared and sent for microanalysis for bromine content; the results were 1.2 and 1.7% bromine.

The effect of the pyrolysis of various bromine containing compounds(in which bromine atoms act as chain carrier) on cis-butene-2 carbons was examined. 39 mm ethyl bromide were first pyrolysed at 405°C for 60 minutes and the reaction vessel was then thoroughly evacuated. On this ethyl bromide treated cis-butene-2 carbon, the rate constant of cis-trans isomerization of cis-butene-2 was larger but the results were irreproducible as seen in Table 15.

Next, the effect of the pyrolysis of n-propyl bromide was studied by pyrolysing 135 mm n-propyl bromide at 430°C for 30 minutes; subsequent pyrolyses were for 15 minutes. The results are summarised in Table 15. The effect of the bromine containing compound was generally to increase the rate constant of the cis-butene-2 isomerization but the results were irreproducible.

Finally, a fresh cis-butene-2 carbon was prepared and was

Table 15 Effect of the bromine containing compounds on the cis→trans isomerization of cis-butene-2 on cis-butene-2 carbon

Carbon*	Pyrolysed compound	Temp.(°C)	$k_{ct} \times 10^6 (sec^{-1})$
E	none	405	3.1
E	ethyl bromide	405	5.5
E	ethyl bromide	405	3.5
F	none	430	5.9
F	1st n-propyl bromide	430	8.0
F	1st n-propyl bromide	430	6.8
F	2nd n-propyl bromide	430	12.5
F	2nd n-propyl bromide	430	10.6
F	3rd n-propyl bromide	430	7.9
F	4th n-propyl bromide	430	20.9
F	5th n-propyl bromide	430	12.4
F	6th n-propyl bromide	430	5.9
F	7th n-propyl bromide	430	8.7
F	7th n-propyl bromide	430	8.7
F	7th n-propyl bromide	430	5.7

* Carbon E was prepared by pyrolysing 520 mm of cis-butene-2 for 15 hours while carbon F was from 440 mm for 18 hours at 480 °C.

treated with about 50 mm bromine for 5 minutes at 105°C. The reaction vessel was then evacuated for several hours at a pressure of less than 10^{-4} mm Hg to ensure that excess bromine was pumped away. Isomerization rates were then measured at 105°C and the results are summarised in Table 16 and shown in Figure 18 where it can be seen that the first isomerizations were very fast but k_{ct} fell continuously with sucessive runs and levelled off at a value close to that obtained previously with allyl bromide carbon(k_{ct}= 13.9 x 10^{-6} sec^{-1} at 103°C, see also Figure 10). The results of k_{cl} were scattered but showed behaviour similar to the cis-trans isomerization(see Table 16).

The bromine activated cis-butene-2 carbon was then treated with propene as a deactivator and the results of subsequent cis-trans isomerisations are shown in Table 17. After the propene treatment, the rate constant of cis→trans isomerization had fallen to a value not much greater than those homogeneous rate constants calculated from the results of Rabinovitch(5) and Liftshitz(7).

Table 16 Isomerization of cis-butene-2 on bromine activated cis-butene-2 carbon at 405°C

Order of run	Initial pressure	$k_{ct} \times 10^6 (sec^{-1})$	$k_{cl} \times 10^6 (sec^{-1})$
1	61	108	92
2	61	117	47
3	61	106	9.2
4	61	83.4	5.6
5	61	59.8	3.3
6*	420	34.9	2.9
7	61	17.7	1.7
8	59	15.6	1.4
9#	60	13.6	2.2
10	60	13.7	1.7

* The run was performed with 69 mm of cyclohexene.

The run was performed with 60 mm of cyclohexene.

Figure 18

cis→trans Butene-2 isomerization rates at 405°C

on bromine-treated cis-butene-2 carbon

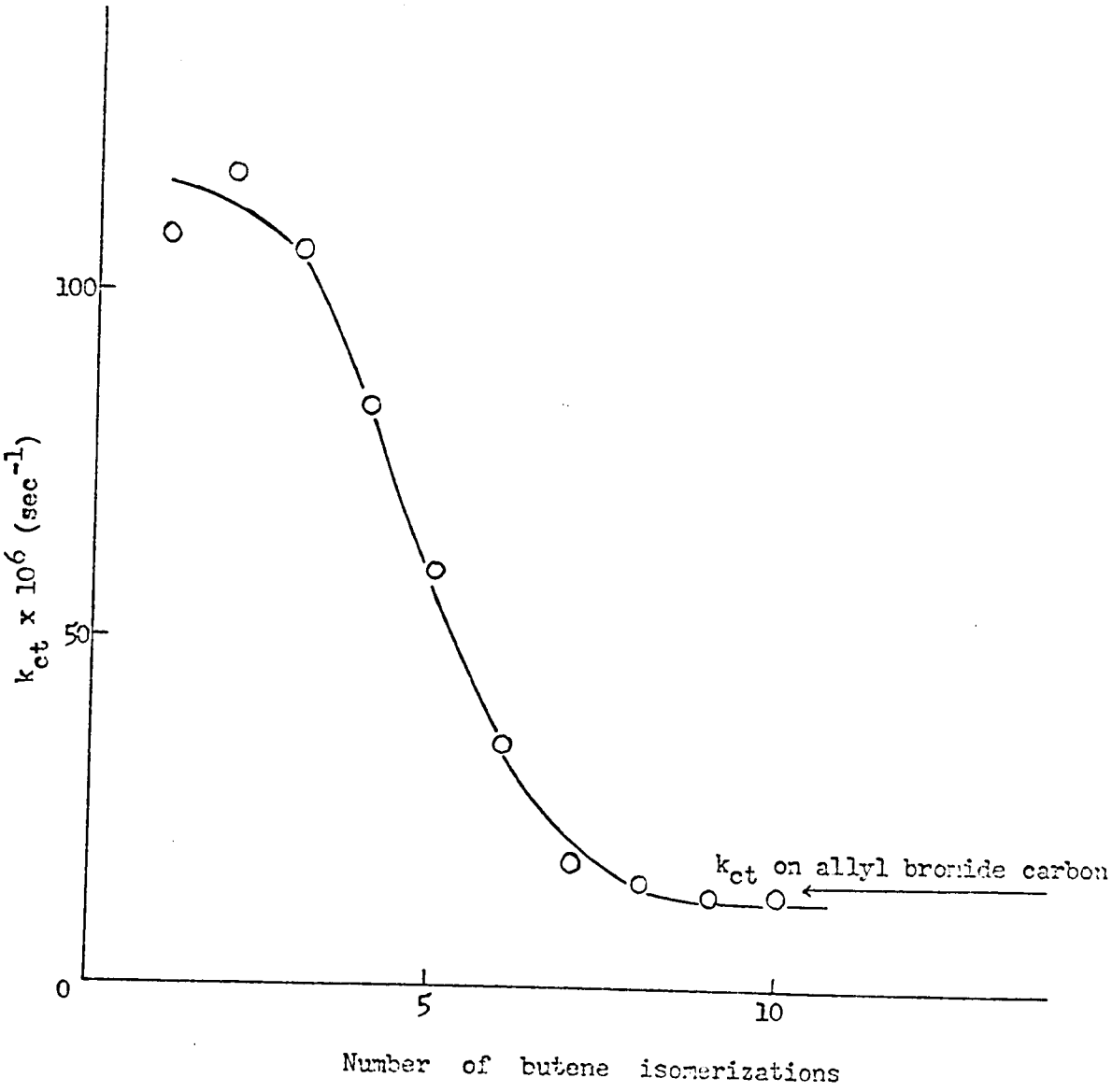

100
50
0
k_{ct} x 10^6 (sec^{-1})
5
10
k_{ct} on allyl bromide carbon
Number of butene isomerizations

Table 17 The effect of propene on cis→trans isomerization of cis-butene-2 on bromine activated cis-butene-2 carbon (Temp.= 405°C, Initial pressure = 60 mm)

Propene treatment*	$k_{ct} \times 10^6$ (sec^{-1})
None	13.7
725 mm, 16.5 hrs., 430°C	1.08
700 mm, 12 hrs., 430°C	0.51
Homogeneous isomerization	0.36 (ref. 5)
Homogeneous isomerization	0.40 (ref. 7)

* The second propene treatment was performed after the rate constant was measured on the first propene treated carbon.

IV. The isomerization of cis-butene-2 on ethyl bromide carbon and 3-chloro-2-methyl propene carbon

E.s.r. measurements showed that ethyl bromide carbon also has a single absorption line and has a smaller odd electron content than allyl bromide and cis-butene-2 carbons(see Table 1). It might also be supposed to catalyse the n-butene isomerizations but less rapidly than the other carbons.

A series of experiments were performed on the carbon prepared by pyrolysing ethyl bromide as described in chapter 2. This produced a thin carbonaceous film on the reaction vessel surface and was used to catalyse the isomerization of cis-butene-2. No side products could be detected in addition to the two isomers, trans-butene-2 and butene-1. No kinetic measurement was made for the butene-1 formation since the quantities produced were very small. The results for the cis-trans isomerization showed that rate constants on ethyl bromide carbon were somewhat irreproducible. The results are summarised in Table 18.

3-Chloro-2-methyl propene carbon has a single e.s.r. absorption line and a similar odd electron content to that of allyl bromide carbon. Therefore again, it might also be supposed to have an activity similar to allyl bromide carbon towards the butene isomerizations.

This series of experiments were performed on a surface coated with three successive standard pyrolyses of 3-chloro-2-methyl propene at 400°C as described in chapter 2. In order to avoid the thermal effect(see Figure 10) during the course

Table 18 The cis→trans isomerization rate constants on ethyl bromide carbon
(Temp.= 430°C, Initial pressure = 60 mm)

Carbon*	Run no.	$k_{ct} \times 10^6 (sec^{-1})$
G	1	16.9
G	2	13.3
G	3	8.8
H	4	34.7
H	5	14.7
H	6	5.6

* Carbon G deposited from the pyrolysis of 500 mm ethyl bromide for 19 hours at 490°C and carbon H was another pyrolysis for 22 hours on carbon G.

of experiments the carbon was heated to 450°C for 18 hours before use. It should give a unchanged carbon activity when the isomerisations are performed at lower temperatures. Rates of cis-butene-2 isomerizations were measured on the carbon in the temperature range of 421 - 436°C. The cis-trans isomerization rates on this carbon were much lower than those obtained on allyl bromide carbon but close to the rates on cis-butene-2 carbon. Reproducible results were obtained and are summarised in Table 19. No side products were observed in the temperature range studied. In Figure 19 the Arrhenius plot was a straight line; indicating the carbon activity was probably independent of temperature. One more pyrolysis of 3-chloro-2-methyl propene at 490°C on top of the carbon prepared at 400°C did not change the activity. The reproducibility of rate constants with this carbon was similar to that of the allyl bromide carbon.

The Arrhenius activation energy of cis→trans isomerization, 38 Kcal $mole^{-1}$, is appreciably higher than that found with allyl bromide carbon, although the odd electron content of 3-chloro-2-methyl propene carbon is close to that of allyl bromide carbon. The kinetics of the butene-1 formation were not studied since again only very small quantities were produced.

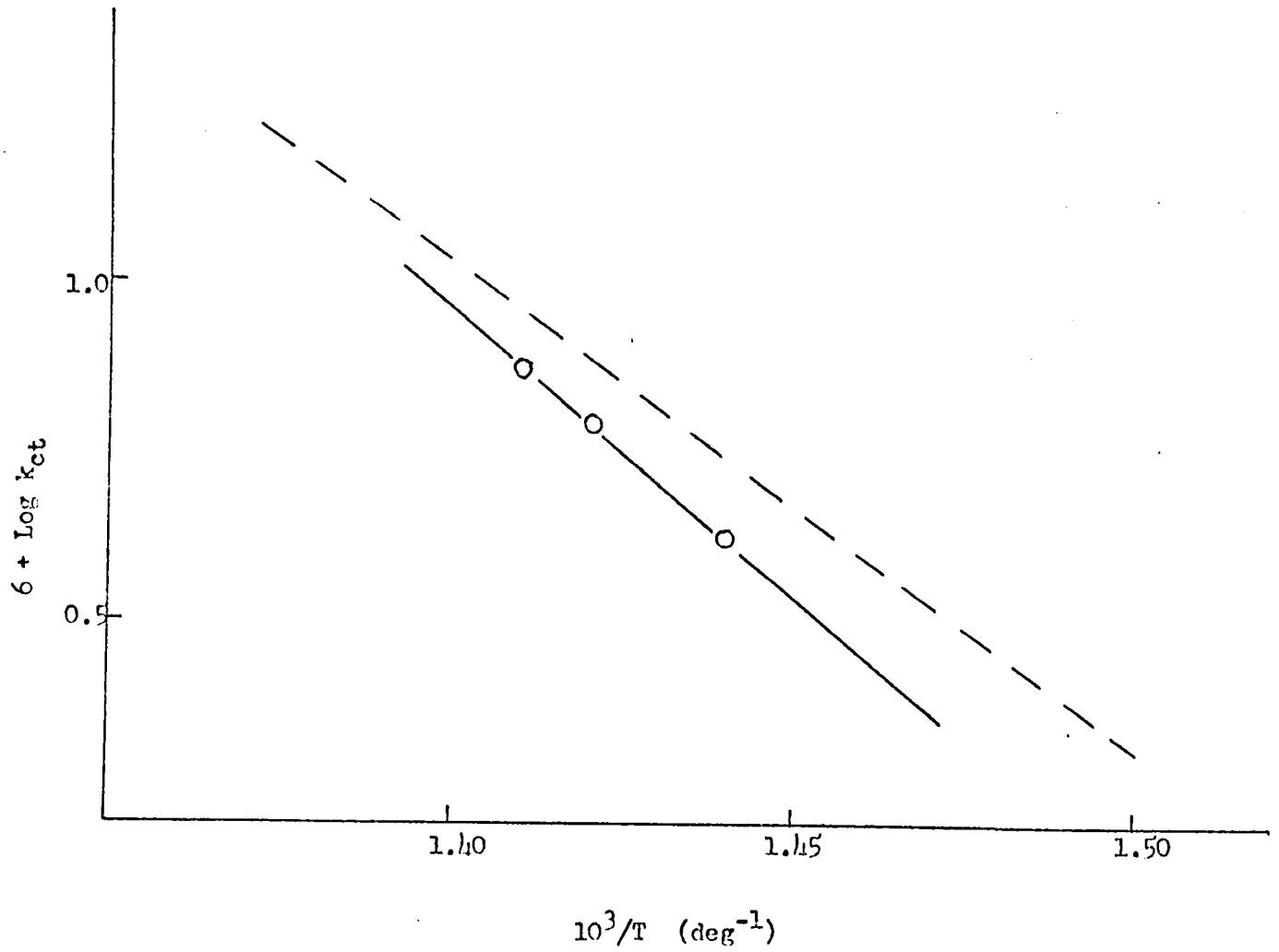
Table 19 The rate constants for the cis→trans isomerization of cis-butene-2 on 3-chloro-2-methyl propene carbon

Carbon*	Temperature(°C)	$k_{ct} \times 10^6$ (sec^{-1})
I	421.6	4.22
I	430.5	6.14
I	436.1	7.42
J	430.2	5.9

* Carbon I was prepared from three successive standard pyrolyses of 3-chloro-2-methyl propene at 400°C and was heated to 450°C for 18 hours where carbon J was from one more pyrolysis at 490°C on top of the carbon I.

Figure 19

Arrhenius plot for cis→trans isomerization of butene-2 on 3-chloro-2-methyl propene carbon Dashed line on cis-butene-2 carbon.


1.0
0.5
6 + Log k_{ct}
1.40
1.45
1.50
$10^3/T$ (deg^{-1})

V. Isomerization of trans-butene-2 on allyl bromide carbon

A series of experiments on the trans-butene-2 isomerization were performed on the carbon deposited from three successive standard pyrolyses of allyl bromide at 400°C. The carbon was heat treated to 460°C for 40 hours in vacuo before use. The trans-butene-2 isomerizations were studied in the temperature range of 380 - 428°C. The cis-butene-2 isomerizations on this carbon were also checked at the corresponding temperatures at the end of a series of runs on trans-butene-2. At 428°C, traces of side products, methane, n-butane and isobutane were observed in addition to cis-butene-2 and butene-1 formations. However, the side products represented only 4% of the isomerization products at total conversion of 10%. At temperatures lower than 400°C, products other than the two isomers fell below the limit of detection of the apparatus and represented less than 0.1% of the products. The first order rate constants are summarised in Table 20. Straight Arrhenius lines were obtained when $\log k_{tc}$ and $\log k_{t1}$ were plotted against $1/T$ as shown in Figure 20 for the trans→cis (O-P line) and the corresponding cis→trans (R-S line) isomerizations, and in Figure 21 for the trans→1(O'-P' line) and the cis→1(R'-S' line) isomerizations.

The Arrhenius activation energies for the trans→cis isomerization on the carbon was 26.1 Kcal $mole^{-1}$ and the corresponding cis→trans was 25.4 Kcal $mole^{-1}$, while those for the trans→1 and cis→1 isomerizations were 26.2 and 25.2 Kcal $mole^{-1}$, respectively.

Table 20 The rate constants of trans-butene-2 isomerizations on allyl bromide carbon with the corresponding results for cis-butene-2 isomerizations (Initial pressure = 60 mm)

Temp.(°C)	$k_{tc} \times 10^6 (sec^{-1})$	$k_{tl} \times 10^6 (sec^{-1})$	$k^*_{ct} \times 10^6 (sec^{-1})$	$k^*_{cl} \times 10^6 (sec^{-1})$
428.5	13.0	5.37	19.1	3.78
414.5	8.36	3.61	12.6	2.69
400	5.65	2.45	8.67	1.69
385.5	3.74	1.56	-	-
380	3.22	1.32	5.1	1.11

* The rate constants were determined after the rates of trans-butene-2 isomerization were measured.

Figure 20

Arrhenius plots for trans→cis-butene-2 and corresponding cis→trans-butene-2 isomerizations on allyl bromide carbon

○ trans→cis-Butene-2 isomerization(line O—P);

△ cis→trans-butene-2 isomerization(line R—S)

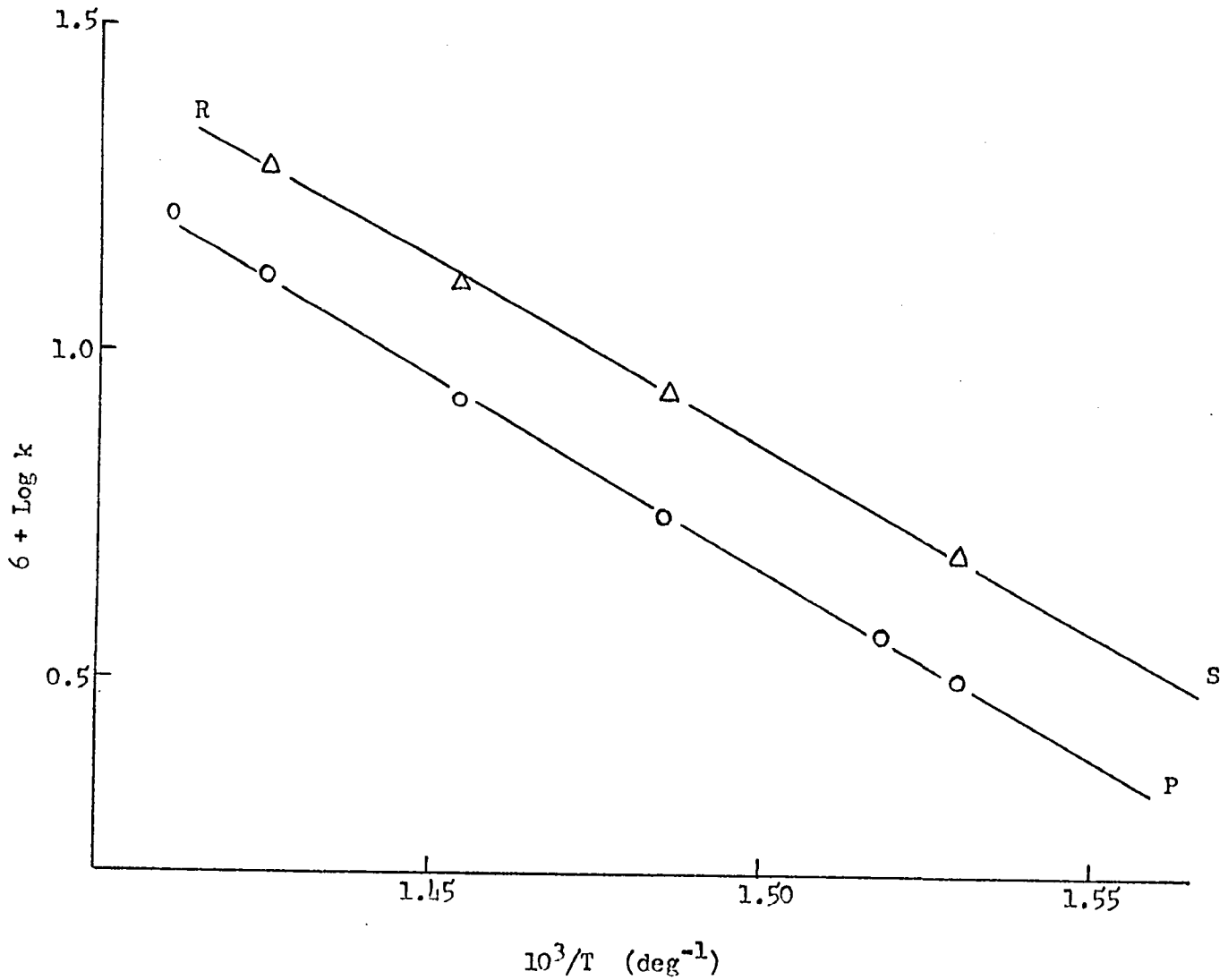
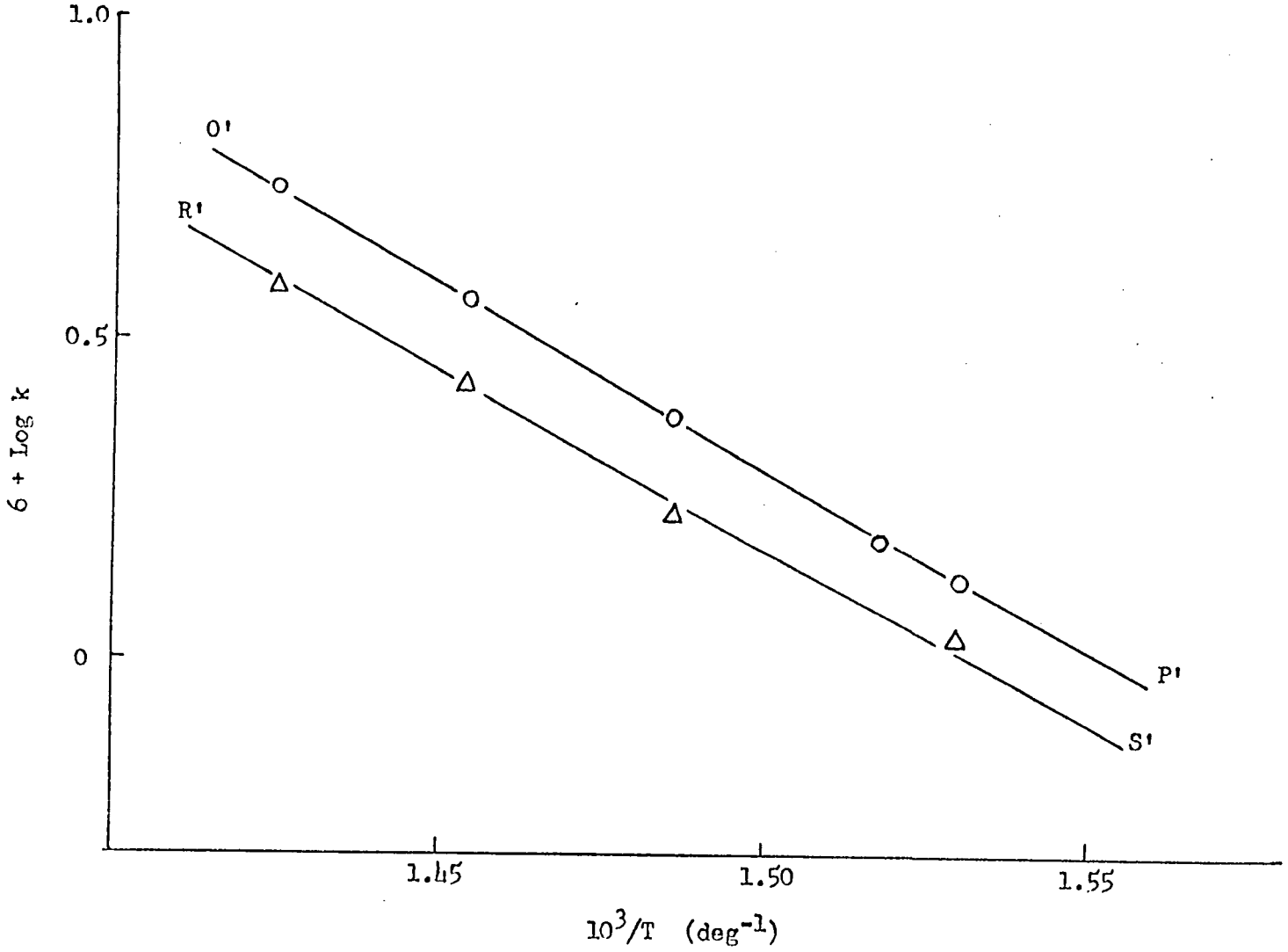

1.5
1.0
0.5
6 + Log k
R
S
P
1.45
1.50
1.55
10³/T (deg⁻¹)

Figure 21

Arrhenius plots for trans-butene-2 ——→ butene-1 and cis-butene-2 ——→ butene-1 isomerizations on allyl bromide carbon

○ trans-Butene-2 ⟶ butene-1 isomerization (line O'-P');

△ cis-butene-2⟶ butene-1 isomerization (line R'-S')


1.0
0.5
0
6 + Log k
O'
R'
P'
S'
1.45
1.50
1.55
10³/T (deg⁻¹)

The activation energy of the cis→trans isomerization in this series of experiments showed that the allyl bromide carbon activity was quite different from the previous(section I) carbon for cis→trans isomerization. Therefore, it might be supposed that the activity of carbon depended also on the substance with which it was first treated. A series of experiments were then designed to investigate this effect. A new carbon was deposited from six successive standard pyrolyses of allyl bromide and it was heated to 460°C for 60 hours. A series of cis-butene-2 isomerizations were first performed and then a series of trans-butene-2 isomerizations. Two series of cis-butene-2 isomerizations were carried out by lowering the temperature from 430 to 379°C and again from 432 to 350°C. They are in good agreement in that a straight Arrhenius plot was found as can be seen in Figure 22(X-Y line). The result showed that the carbon had a "constant activity" after the heat treatment at 460°C. A series of trans-butene-2 isomerizations were subsequently performed while progressively raising the temperature from 320 to 380°C. The results gave a slightly curved Arrhenius plot (see Figure 22) which was taken as indicating that the carbon was being gently deactivated by the trans-butene-2. The results are summarised in Table 21.

The activation energies on this carbon were 16.4 Kcal $mole^{-1}$ for the cis→trans isomerization and 17.1 Kcal $mole^{-1}$ for the reverse reaction before the carbon was slightly deactivated by trans-butene-2 itself.

Figure 22

Arrhenius plots for cis→trans-butene-2 and corresponding trans→cis-butene-2 isomerizations on allyl bromide carbon, showing effect of trans-butene-2 deactivation on a "constant activity" carbon

△ cis→trans isomerization (line X-Y);

○ trans→cis isomerization

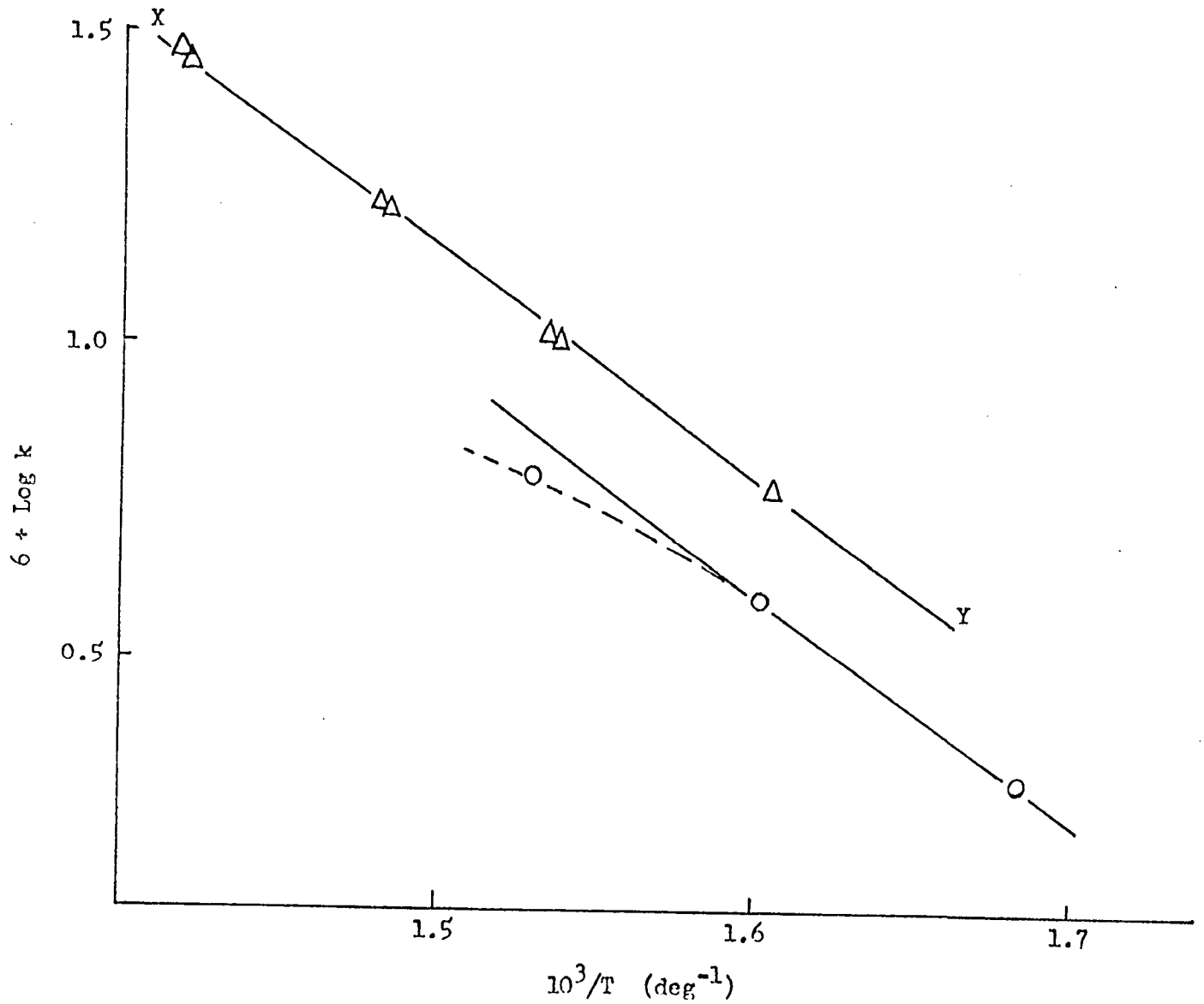

X
Y
1.5
1.0
0.5
6 + Log k
1.5
1.6
1.7
$10^3/T$ (deg^{-1})

Table 21 The rate constants of cis- and trans-butene-2 isomerizations on allyl bromide carbon*

Temperature(°C)	$k_{ct} \times 10^6 (sec^{-1})$	$k_{tc} \times 10^6 (sec^{-1})$
430	28.2	-
402	16.6	-
379	10.3	-
432	29.6	-
400	16.5	-
377.5	10.0	-
350	6.0	-
320.5	-	2.02
351	-	4.01
380	-	6.18

* The carbon was prepared from six successive standard pyrolyses of allyl bromide and was heated to 460°C for 60 hours.

VI. Isomerization of butene-1 on allyl bromide carbon

A series of experiments on the butene-1 isomerization were performed on the carbon deposited from three successive standard pyrolyses of allyl bromide at 400 °C. The carbon was heated to 450 °C for 18 hours in vacuo before use. The butene-1 isomerization were studied in the temperature range 340 - 420 °C. At 420 °C, the side products, methane, ethane, ethylene, n-butane and isobutane were observed in addition to the cis- and trans-butene-2 formations and these represented 15% of the isomerization products at a total conversion of 5%. At lower temperatures(< 390 °C) products other than the two isomers and traces of methane fell below the limit of detection. The first order rate constants are summarised in Table 22. Scattered Arrhenius plots were obtained(Figure 23) when log k_{1t} and log k_{1c} plotted against 1/T. From the order of the experiments done, it would appear that the carbon was being slowly and progressively deactivated by the butene-1. As shown in Figure 23 the deviation becomes greater in the later experiments. The rate of trans-butene-2 formation was roughly a constant factor greater than that of cis-butene-2 formation. Rough estimations of the activation energies for butene-1 to trans- and cis-butene-2 were approximately 19.2 and 20.3 Kcal $mole^{-1}$, respectively. These were the values before the carbon was deactivated.

To clarify the butene-1 deactivation effect, a higher pressure of butene-1 was then admitted to the reaction vessel and the rates of some cis-butene-2 isomerizations were measured

Table 22 The temperature dependence of the rate constants of butene-1 isomerization on allyl bromide carbon (Initial pressure ≃ 60 mm)

Order of expt.	Temp.(°C)	Time(min.)	% t-Bu-2	% c-Bu-2	$k_{1t} \times 10^6 (sec^{-1})$ (Average)	$k_{1c} \times 10^6 (sec^{-1})$ (Average)
1	390	30	0.78	0.30		
		45	1.15	0.46	4.2	1.75
		51	1.20	0.56		
2	420	18	0.74	0.28		
		31	1.21	0.54	6.44	2.83
		60	2.32	1.02		
		50	1.83	0.77		
3	375	70	1.18	0.42		
		80	1.21	0.46		
		90	1.30	0.51	2.48	0.98
		130	1.89	0.75		
		50	0.75	0.27		

(continue)

4	340	165	1.28	0.45		
		60	0.41	0.12	1.25	0.48
		245	1.81	0.71		
		100	0.63	0.25		
5	355	120	1.03	0.34		
		150	1.16	0.46	1.41	0.52
		250	2.05	0.75		
6	405.8	60	1.25	0.47		
		90	2.10	0.78	3.46	1.3
		150	2.62	1.08		

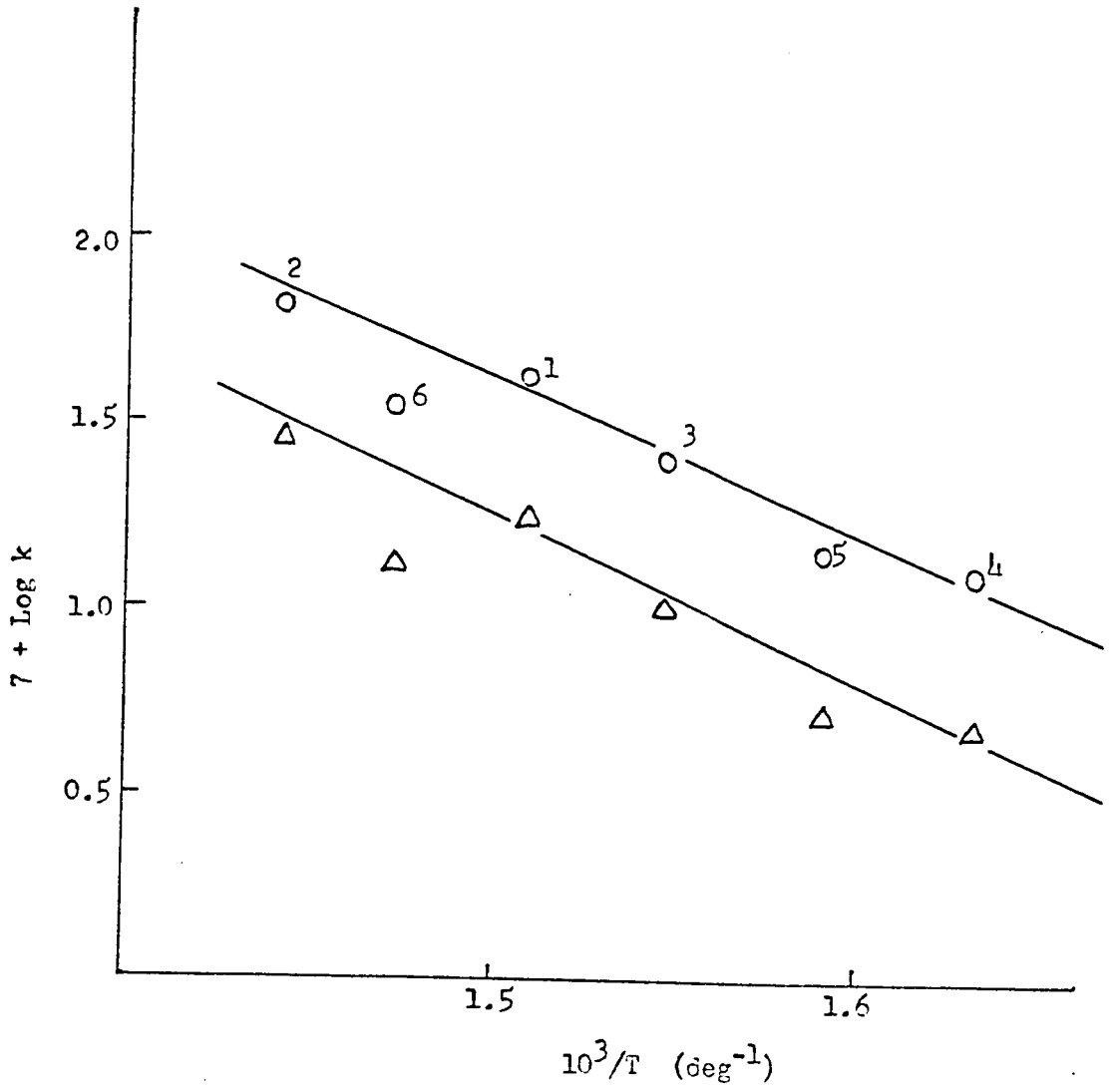
Figure 23

Arrhenius plots for butene-1 ⟶ cis- and trans-butene-2 isomerizations on allyl bromide carbon

○ Butene-1 ⟶ trans-butene-2 isomerization;

△ butene-1 ⟶ cis-butene-2 isomerization;

number shows the order of the experiments done


2.0
1.5
1.0
0.5
7 + Log k
1.5
1.6
$10^3/T$ (deg^{-1})

subsequently in order to compare with the results without the butene-1 treatment. The results are summarised in Table 23. The rate constants of cis→trans isomerization of cis-butene-2 on the butene-1 deactivated allyl bromide carbon were not much higher than the value of homogeneous rate constant at 406°C, 3.75×10^{-7} sec^{-1}, evaluated from the results of Rabinovitch and Michel(5). The deactivation effect could possibly be brought about by free radicals from the decomposition of the butene-1 because the decomposition of this compound is greater than that of cis-butene-2 and trans-butene-2.

Table 23 Effect of butene-1 seasoned allyl bromide carbon on the activity of the carbon towards the isomerization of cis-butene-2

Butene-1 treatment	Temp.(°C)	$k_{ct} \times 10^6 (sec^{-1})$
None	399	10.4 *
The experiment of butene-1 isom. and 470 mm, 15 hrs. at 406°C	406	2.12
Ditto + 470 mm, 17 hrs. at 406°C	406	0.64

* Obtained from the fresh prepared carbon which was deposited from three standard pyrolyses and heated to 450°C for 18 hours.

VII. The equilibrium between cis- and trans-butene-2 on allyl bromide carbon

Consider the reversible reaction

$$\text{cis-butene-2} \rightleftharpoons \text{trans-butene-2} ;$$

the equilibrium constant for the process is given by $K_{ct} = k_{ct}/k_{tc} = [\text{t-Bu-2}]_e/[\text{c-Bu-2}]_e$. The equilibrium among the two butene-2 isomers has been studied at a series of temperatures by several different techniques and the results obtained by different workers(18, 19, 20, 21, 22, 38) show a wide spread for the equilibrium constants(see Figure 24). In the present investigation, both the forward and reverse reaction rate constants were measured individually. The equilibrium constants were obtained from the ratios of the two rate constants, which were determined from initial rates at low conversion, instead of measuring the concentration of the two isomers at equilibrium(as was used in previous studies).

A series of experiments were carried out using the carbon deposited from six successive standard pyrolyses of allyl bromide as catalyst which had been heated to 460°C for 60 hours and then left at 430°C for ~ 3 days. A few isomerizations of cis-butene-2 were first performed to check that the carbon had an activity similar to that used in previous experiments(section I). The results were rather unsatisfactory at first when a series of isomerizations for cis-butene-2 was followed by a series of runs for trans-butene-2. It was decided to perform the isomerisations alternately i.e. a cis-butene-2 isomerization was followed by a trans-butene-2 isomerization and so vice-versa.

Figure 24

Arrhenius plots for the cis ⇄ trans equilibrium constant

○ Present work; dashed line A.P.I.values;

△ Benson, Egger, & Golden;

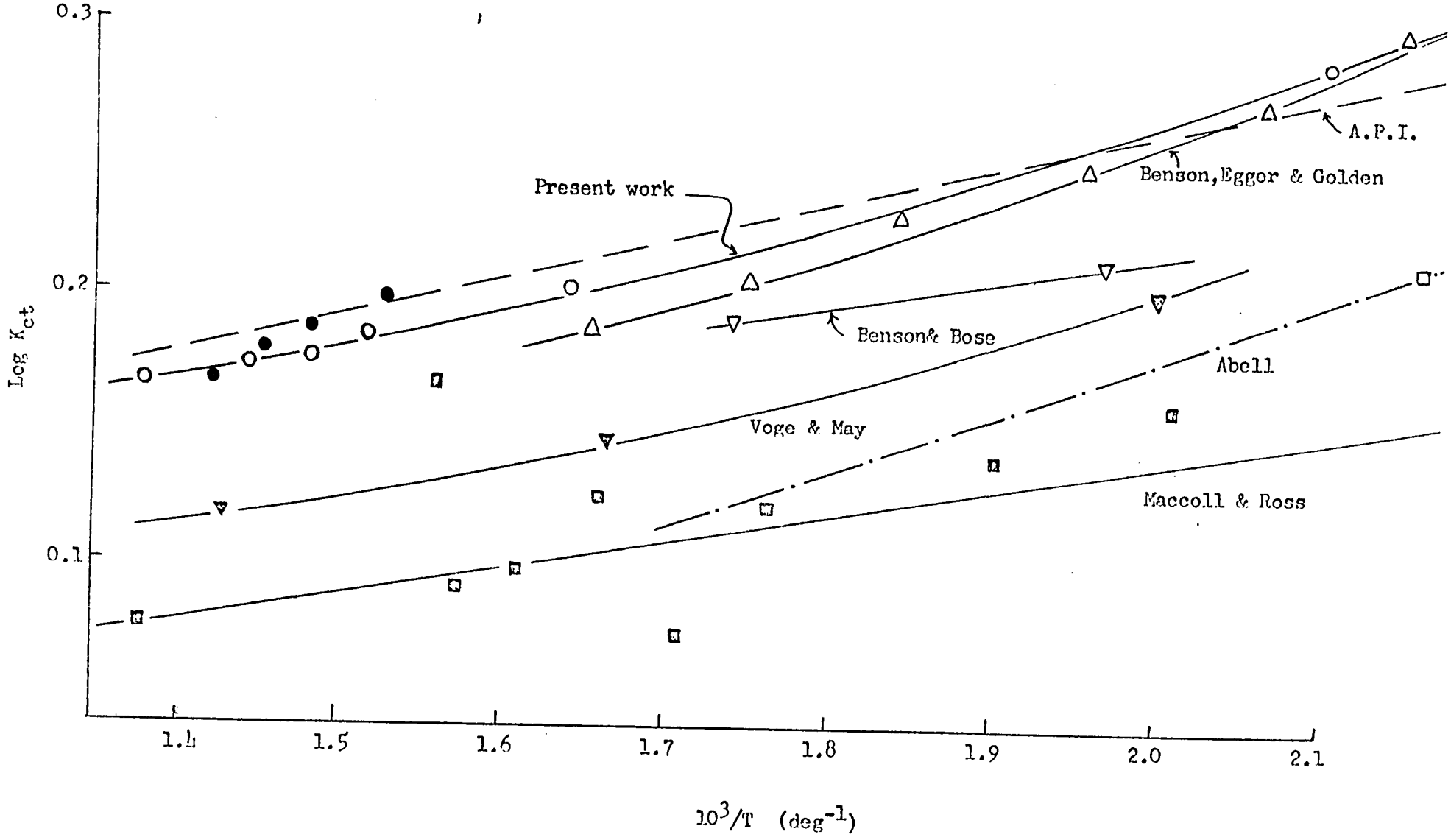
▽ Benson and Ross;

▼ Voge and May;

□ from Abell;

■ Maccoll and Ross;

● from non-alternating runs (see Table 26)


0.3
0.2
0.1
Log K_{ct}
Present work
A.P.I.
Benson, Eggor & Golden
Benson& Bose
Abell
Voge & May
Maccoll & Ross
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
$10^3/T$ (deg^{-1})

The main purposes of this technique were to compensate for the effect of trans-butene-2 on the surface, (the surface was slightly deactivated by trans-butene-2, see earlier Figure 22) and to compensate for any inadvertent change of surface activity by air etc. The results obtained from this technique gave good results for the equilibrium constant in the temperature range 200 - 450°C. The results are summarised in Table 24. When log K_{ct} was plotted against 1/T a slightly curved line was obtained as shown in Figure 24. The results are in good agreement with both the data from Golden, Egger and Benson (19) and A. P. I. value(20). The thermodynamic values of ΔH° and ΔS° were estimated and are shown in Table 25. The equilibrium constants(Table 26) evaluated from the previous series of trans-butene-2 isomerization experiments in the temperature range 380 - 430°C, were in good agreement with the equilibrium experiments (see Figure 24).

The present investigation seems simpler than previous studies on the cis-trans equilibrium because the system we used gave no appreciable side products; even at the highest temperature the side products were negligible. The system contained only a single substance with the odd electron containing carbon. The previous studies contained other reactive substances as catalysts which may increase the complexity of the gas phase reaction.

The equilibration between butene-1 and butene-2 was also briefly studied. Consider the equilibrium between three isomers of n-butene as following:

Table 24 The temperature dependence of rate constants and equilibrium constants for the cis- and trans-butene-2 isomerizations (Initial pressure = 56 mm)

Temp.(°C)	Reaction time(min.)	%t-Bu-2	%c-Bu-2	$k_{ct} \times 10^6$ (sec^{-1})	$k_{tc} \times 10^6$ (sec^{-1})	K_{ct}
202	570	0.87		0.26		
	910	1.17		0.22		
	400	0.44		0.19		
	905	1.13		0.21		
	880	0.75		0.14		
				(0.20)		
						1.93
	1630		1.39		0.14	
	1410		0.91		0.11	
	2470		1.60		0.11	
	1920		1.00		0.09	
	2370		1.26		0.09	
	1660		0.93		0.10	
	2550		1.44		0.10	
					(0.11)	
337	40	1.25		5.26		
	50	1.82		6.07		
	70	2.60		6.28		
	60	2.28		6.40		
	46	1.68		6.09		
	45	1.50		5.63		
	50	1.62		5.40		
	60	2.06		5.78		

(continue)

337	40	1.40	5.85		
	80	2.97	6.28		
			(5.90)		
					1.59
	60		1.27	3.58	
	65		1.43	3.72	
	70		1.40	3.35	
	60		1.37	3.81	
	65		1.58	4.10	
	60		1.34	3.71	
	90		1.97	3.71	
				(3.71)	
386	30	2.27	12.8		
	68	4.64	11.7		
	35	2.60	12.5		
	80	5.61	12.0		
	50	3.54	12.0		
	40	3.02	12.8		
	25	1.92	13.0		
	60	4.03	11.5		
			(12.3)		
					1.53
	46		2.31	8.49	
	55		2.54	7.75	
	60		3.00	8.44	
	70		3.22	7.79	
	40		1.78	7.49	

(continue)

386	35		1.63	7.79	
	50		2.45	8.28	
				(8.00)	
420	30	4.48		25.5	
	39	5.06		22.1	
	20	3.01		25.5	
	25	3.47		23.6	
	50	6.70		23.0	
	42.5	5.69		23.0	
	35	5.03		24.5	
	20	2.59		21.9	
				(23.6)	
					1.49
	55		5.07	15.7	
	40		3.66	15.5	
	35		3.43	16.6	
	45		4.06	15.4	
	62		5.94	16.4	
	50		4.62	15.8	
	30		2.81	15.8	
	27.5		2.57	15.7	
	37.5		3.56	16.1	
				(15.9)	
451	20	4.11		34.9	
	26	5.20		34.2	
	12	2.25		31.7	
	16	3.28		34.8	

(continue)

451	10	2.22	37.3		
	18	3.61	34.1		
	26	5.10	33.5		
			(34.4)		1.47
	35		4.88	23.8	
	28		3.88	23.6	
	22		3.05	23.6	
	18		2.53	23.6	
	25		3.66	24.9	
	32		4.20	22.2	
	20		2.65	22.5	
				(23.5)	
400	21	1.35	10.8		
	23	1.45	10.6		
	30	1.88	10.5		
	40	2.49	10.5		
	43	2.54	9.9		
	45	2.94	11.0		
			(10.5)		1.50
	43		1.70	6.61	
	30		1.10	6.14	
	40		1.74	7.29	
	34		1.68	7.34	
	48		1.98	6.96	
	45		2.06	7.85	
				(7.03)	

* Average values shown in parentheses

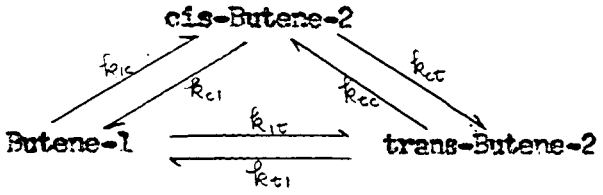
Table 25 Values of the thermodynamic functions for cis⇌trans butene-2 isomerization

	500°K	600°K	700°K
ΔG° (Kcal mole^{-1})	-0.60±0.005	-0.56±0.005	-0.56±0.005
ΔH° (Kcal mole^{-1})	-0.87±0.02	-0.69±0.02	-0.60±0.02
ΔS° (e. u.)	-0.54±0.04	-0.21±0.04	-0.07±0.04

Table 26 Equilibrium constants estimated from non-alternating runs

Temp.(°C)	$k_{tc} \times 10^6$ (sec^{-1})	$k_{ct}^* \times 10^6$ (sec^{-1})	K_{ct}
428.5	13.0	19.1	1.47
414.5	8.36	12.6	1.51
400.0	5.65	8.67	1.54
380	3.22	5.1	1.58

* Single runs performed at the end of each trans- series



At two temperatures all six rate constants were measured and are shown in Table 27. At the equilibrium of the three isomers, the condition of $K_{ct} \times K_{1c} \times K_{t1} = 1$ must be obtained. From the results of an independent determination the equilibrium constants can be obtained and these constants showed satisfactorily self-consistent behaviour at each temperature as shown in Table 26.

Table 27 The six rate constants for the equilibria between three n-butene isomers

(All rate constants are in sec^{-1})

Temp.(^{o}C)	$k_{ct} \times 10^6$	$k_{cl} \times 10^6$	$k_{tc} \times 10^6$	$k_{tl} \times 10^6$	$k_{lt} \times 10^6$	$k_{lc} \times 10^6$
451	34.9	6.14	23.8	9.43	10.3	5.02
	34.2	5.37	23.6	9.60	9.82	4.30
	31.7	6.03	23.6	8.38	10.2	4.61
	34.8	5.95	23.6	8.53	9.60	4.25
	37.4	6.77	24.9	9.89	9.21	4.99
	34.1	6.23	22.2	8.99	9.61	4.21
	33.5	6.13	22.5	8.25	9.54	4.04
					9.87	4.20
					9.44	4.41
Average	(34.4)	(6.09)	(23.5)	(9.01)	(9.73)	(4.45)

(continue)

400	10.8	1.83	6.61	2.59	3.97	1.54
	10.6	1.60	6.14	2.74	3.35	1.47
	10.5	1.73	7.29	2.64	3.57	1.54
	10.5	1.82	7.34	2.74	3.45	1.43
	9.9	1.79	6.96	2.72	3.38	1.41
	11.0	1.57	7.85	2.99	3.56	1.52
					3.57	1.45
Average	(10.6)	(1.72)	(7.03)	(2.74)	(3.55)	(1.48)

Table 28 The equilibrium constants between three isomers of n-butene isomerizations

Temp.(°C)	K_{ct}	K_{lc}	K_{tl}	$K_{ct} \times K_{lc} \times K_{tl}$
451	1.47	0.73	0.93	0.99
400	1.50	0.86	0.77	0.99

VIII. The halogen acid catalysed isomerization of cis-butene-2

Equilibrium values in the n-butenes system have been measured in the presence of hydrogen bromide by Maccoll and Ross(21); as can be seen in Table 29 their ΔS° values differ considerably from the other literature values(18, 19, 20, 48). In their study(21) of the kinetics of the hydrogen bromide catalysed isomerization of n-butenes they declared that cyclohexene had no effect on the rate of isomerization and thus the reaction must be molecular; a six-centered transition state favouring formation of the trans isomer for the butene-1 isomerization was postulated (see page 8). In 1967, Bridge and Holmes(49) found that the hydrogen bromide catalysed butene-1 isomerization can be inhibited by both propene and cyclohexene and therefore at least partially involves free-radical reactions. We have investigated both the hydrogen chloride and hydrogen bromide catalysed isomerizations.

(A). Hydrogen chloride catalysed isomerization

A series of experiments on the hydrogen chloride catalysed isomerization of cis-butene-2 were performed in a clean glass reaction vessel. The isomerization rates were measured at 350°C. The second order specific rate of disappearance of cis-butene-2 is given as follows:

$$\text{cis-Butene-2} + HCl \longrightarrow \text{trans-Butene-2} + HCl$$

$$\text{rate} = k_2[\text{cis-Butene-2}][HCl]$$

$$= k_{ct}[\text{cis-Butene-2}]$$

Table 29 Values of the thermodynamic functions for cis—trans isomerization of butene-2

	ΔH°(Kcal mole^{-1})	ΔS°(e.u.)	Temp. range($^{\circ}$C)
Voge and May (16)	-0.53	0.14	200-630
Benson and Bose(18)	-0.50±0.20	0.00±0.4	235-300
A.P.I. (20)	-0.60	0.00	-
Kaccoll and Ross(21 a)	-0.44	-0.25	90-451

Table 29A Values of the thermodynamic functions for cis—trans isomerization of butene-2 by Golden, Egger, and Benson(19)

	400°K	500°K	600°K
ΔF°(Kcal mole^{-1})	-0.694±0.03	-0.582±0.03	-0.489±0.02
ΔH°(Kcal mole^{-1})	-1.2±0.1	-1.15±0.1	-0.85±0.1
ΔS°(e.u.)	-1.2±0.2	-1.1±0.2	-0.6 ±0.2

At 350°C, butene-1 production was not observed and the above expression was used to determine the rate constant for the cis-trans isomerization. The reaction proceeded without any pressure change and the results(Table 30 and Figure 25) showed that the isomerization in the first experiment was very fast but thereafter k_2 fell continuously with successive runs and levelled off at a value of ~ 0.5 mole^{-1} cm^3 sec^{-1}. This effect can be explained as due to catalysis by metallic oxides or acid sites on the surface of the reaction vessel and in the subsequent runs these active catalyst sites were covered possibly by cis-butene-2 carbon even at this low temperature; the reaction was predominantly homogeneous as in the case of the "conditioned" Pyrex reaction vessel used by Maccoll and Ross(21 b). A possible explanation could be that the active sites on the glass surface are first covered by the deposition of polymeric carbon even at low temperature and that the thin layer of carbon between the active sites which ultimately leads to complete surface coverage is only formed at higher temperatures.

At 400°C, acetylene was observed in addition to the two isomers, butene-1 and trans-butene-2 and the results are summarised in Table 31(see also Figure 26). The order plots of butene-1, trans-butene-2 and acetylene formations with respect to hydrogen chloride are given in Figure 27. The rate constants of the cis-trans isomerization and decomposition to acetylene were shown to be proportional to hydrogen chloride concentration over the range of 42 - 286.5 mm, and those of

Table 30 The rate constants of hydrogen chloride catalysed isomerization of cis-butene-2 at 350°C

P_{Bu}(mm)	P_{HCl}(mm)	Time(min.)	$k_{ct} \times 10^6$(sec^{-1})	k_2(mole^{-1}cm^{3}sec^{-1})
67	88.5	35	-	-
60	23	11	5.23	8.84
61	26	30	3.84	5.74
60	13	30	1.02	3.06
56	46	30	1.54	1.30
55.5	30.5	30	0.77	0.98
57.5	61.5	30	0.90	0.57

Figure 25

Effect of several successive runs on hydrogen chloride catalysed cis → trans-butene-2 isomerization in clean reaction vessel

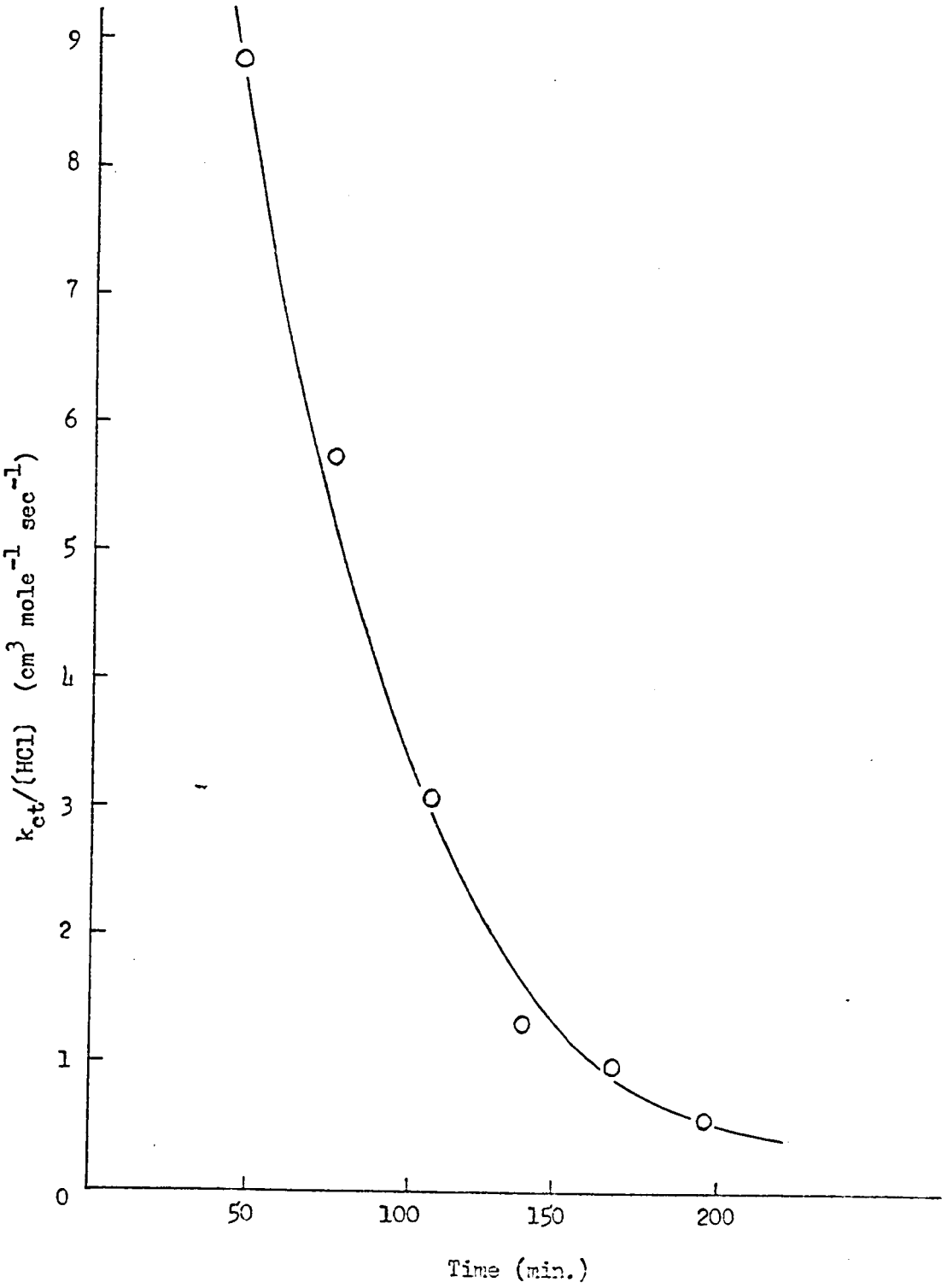

9
8
7
6
5
4
3
2
1
0
50
100
150
200
$k_{et}/[HCl]$ (cm^3 $mole^{-1}$ sec^{-1})
Time (min.)

Table 31 The results of the hydrogen chloride catalysed cis-butene-2 isomerization at 400°C (Reaction time = 40 min.)

P_{Bu}(mm)	P_{HCl}(mm)	Sample(μM) R.l.c.	%C_2H_2	%Bu-1	%Bu-2(trans)	$k_d \times 10^6$(sec^{-1})	$k_{cl} \times 10^6$(sec^{-1})	$k_{ct} \times 10^6$(sec^{-1})
56.5	42	230.4	0.12	0.11	0.47	0.53	0.65	2.02
56.5	92.5	227.4	0.22	0.57	1.00	0.96	2.40	4.22
56	112	226.4	0.26	0.76	1.42	1.06	3.17	5.97
55.5	142	225.6	0.39	1.18	1.83	1.63	4.89	7.68
56.5	194	224.9	0.66	2.13	2.86	2.78	8.98	12.1
57	234	237	0.71	2.33	3.08	2.98	9.88	13.0
56.5	286.5	230.6	0.93	4.19	4.60	3.93	17.8	19.7

Figure 26

Hydrogen chloride catalysed isomerisation of cis-butene-2 at 400°C, showing the relations between rate constants of trans-butene-2, butene-1, and acetylene formations and HCl concentration

○ trans-Butene-2 formation,

△ butene-1 formation, and

□ acetylene formation

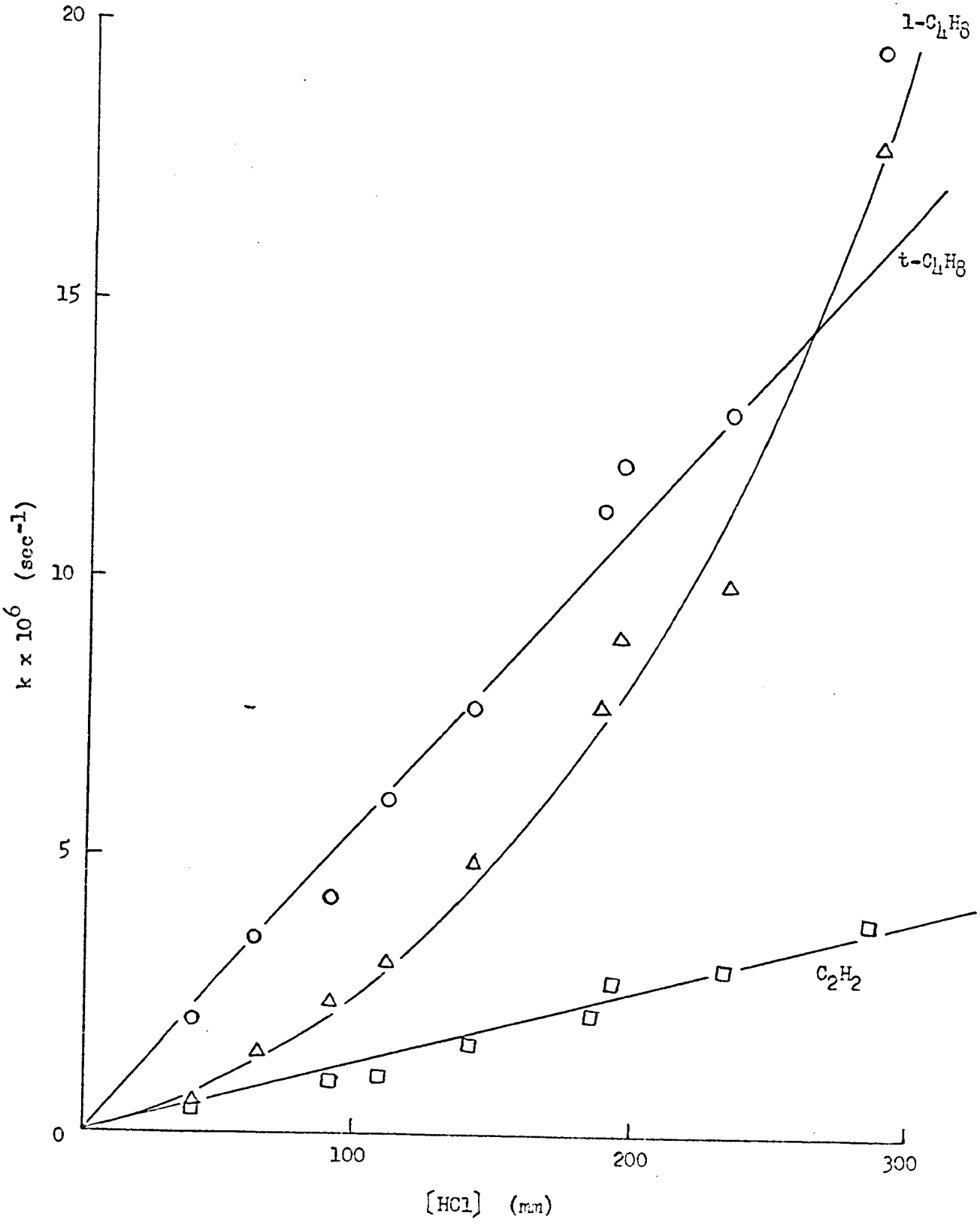
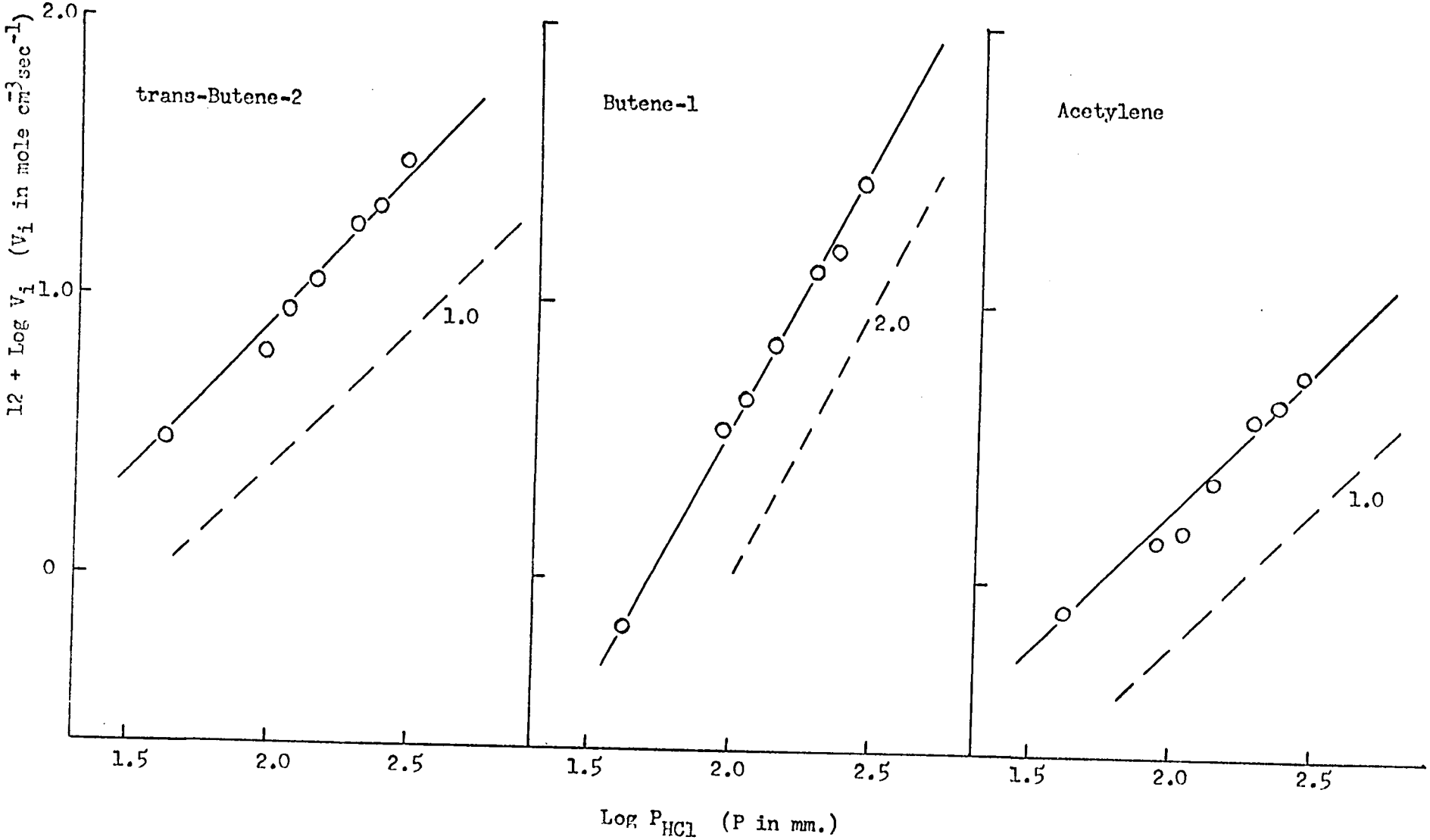

20
15
10
5
0
k x 10^6 (sec^-1)
100
200
300
[HCl] (mm)
1-C4H8
t-C4H8
C2H2

Figure 27

Order plots for hydrogen chloride catalysed isomerization of cis-butene-2 at 400°C


trans-Butene-2
Butene-1
Acetylene
12 + Log V_i (V_i in mole $cm^{-3} sec^{-1}$)
2.0
1.0
0
1.0
2.0
1.0
1.5
2.0
2.5
Log P_{HCl} (P in mm.)

butene-1 were more complicated having a second-order dependence on hydrogen chloride concentration.

Some catalysed isomerizations were performed in the presence of cyclohexene as a possible homogeneous free radical reaction inhibitor. The results are summarised in Table 32. Figure 28 shows the effect of the inhibitor on the rate constant of the cis→trans isomerization. The production of acetylene apparently was not affected by cyclohexene. These results show that the hydrogen chloride catalysed isomerization of cis-butene-2 can be inhibited and therefore possibly involves, at least in part, free-radical reactions.

Some isomerizations of butene-1 and trans-butene-2 were performed at 400°C in the presence of hydrogen chloride. The results are summarised in Tables 33 and 34. The order plots are given in Figures 29 and 30. It is shown that the rate constant of trans→1 isomerization is second-order in hydrogen chloride as in the case of cis→1 isomerization but the reverse 1→cis and 1→trans isomerization rate constants were close to first-order in hydrogen chloride concentration.

Table 32 The results of the hydrogen chloride catalysed cis-butene-2 isomerisation inhibited by cyclohexene at 100.5°C (Reaction time = 10 min.)

P_{Bu}(mm)	P_{HCl}(mm)	$P_{C_6H_{10}}$(mm)	Sample* (μM) g.l.c.	%C_2H_2	%t-Bu-2	%Bu-1	$k_d \times 10^6$(sec^{-1})	$k_{cl} \times 10^6$(sec^{-1})	$k_{ct} \times 10^6$(sec^{-1})
64	103	68	251.8	0.27	0.79	0.64	1.15	2.69	3.28
57	209	114	231.6	0.74	1.34	1.48	3.07	6.24	5.56
57	129	124	240.6	0.39	1.03	0.85	1.63	3.55	4.32

* Mixture of butene and acetylene

Figure 28

Effect of cyclohexene in hydrogen chloride catalysed isomerization of cis-butene-2 at 100°C

HCl CATALYSED ISOMERISATION OF cis-BUT-2-ENE 400°

EFFECT OF CYCLOHEXENE AS INHIBITOR

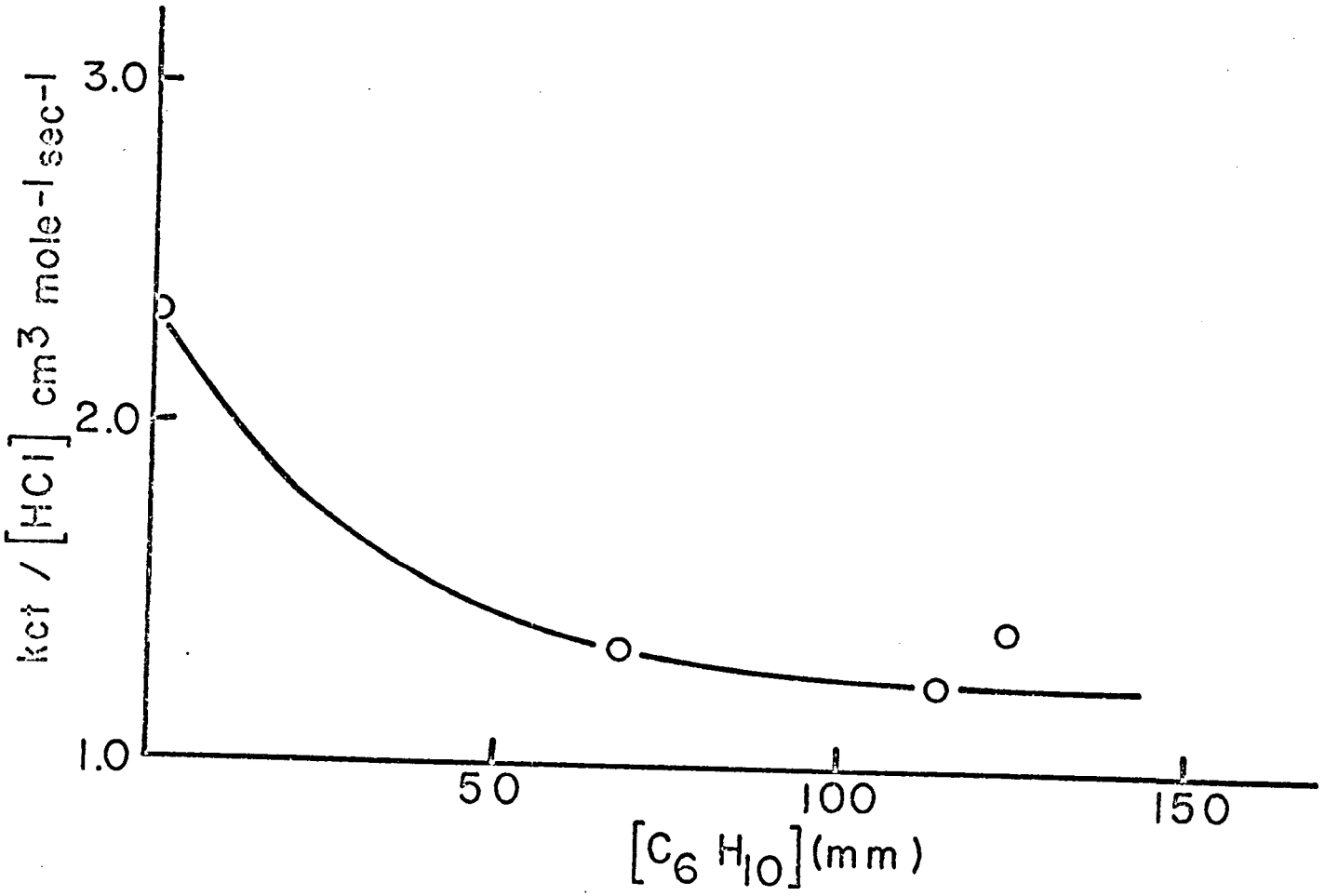


Table 33 The results of the hydrogen chloride catalysed butene-1 isomerisations at 400°C (Reaction time = 50 min.)

P_{Bu}(mm)	P_{HCl}(mm)	Sample(μl) f.l.c.	$\%C_2H_2$	%t-Bu-2	%c-Bu-2	$k_d x10^6(sec^{-1})$	$k_{1t} x10^6(sec^{-1})$	$k_{1c} x10^6(sec^{-1})$
56.5	46.5	219.5	0.11	0.81	0.57	0.36	2.69	1.89
57	63.5	228.0	0.12	0.85	0.61	0.43	2.84	2.06
56	114.5	234.1	0.29	1.70	1.24	1.00	5.68	4.15
56.5	120	231.5	0.29	1.67	1.20	1.00	5.60	3.99
55	161.5	227.4	0.52	2.58	2.01	1.75	8.67	6.76
55	175	232.6	0.57	2.92	2.23	1.92	9.83	7.49
59	202	210.6	0.59	3.04	2.40	1.98	10.3	8.14

Table 34 The results of the hydrogen chloride catalysed trans-butene-2 isomerisations at 400°C (Reaction time = 90 min.)

P_{Bu}(mm)	P_{HCl}(mm)	Sample(μM) g.l.c.	%C_2H_2	%Bu-1	%c-Bu-2	$k_t \times 10^6$(sec^{-1})	$k_{t1} \times 10^6$(sec^{-1})	$k_{tc} \times 10^6$(sec^{-1})
56	124	213.4	0.33	0.98	1.01	1.08	3.33	3.38
56.5	189	224.5	0.49	1.93	2.84	1.66	6.53	9.63
57	241	219.6	0.64	3.08	2.85	2.18	10.5	9.67

Figure 29

Order plots for hydrogen chloride catalysed isomerization of butene-1 at 400°C

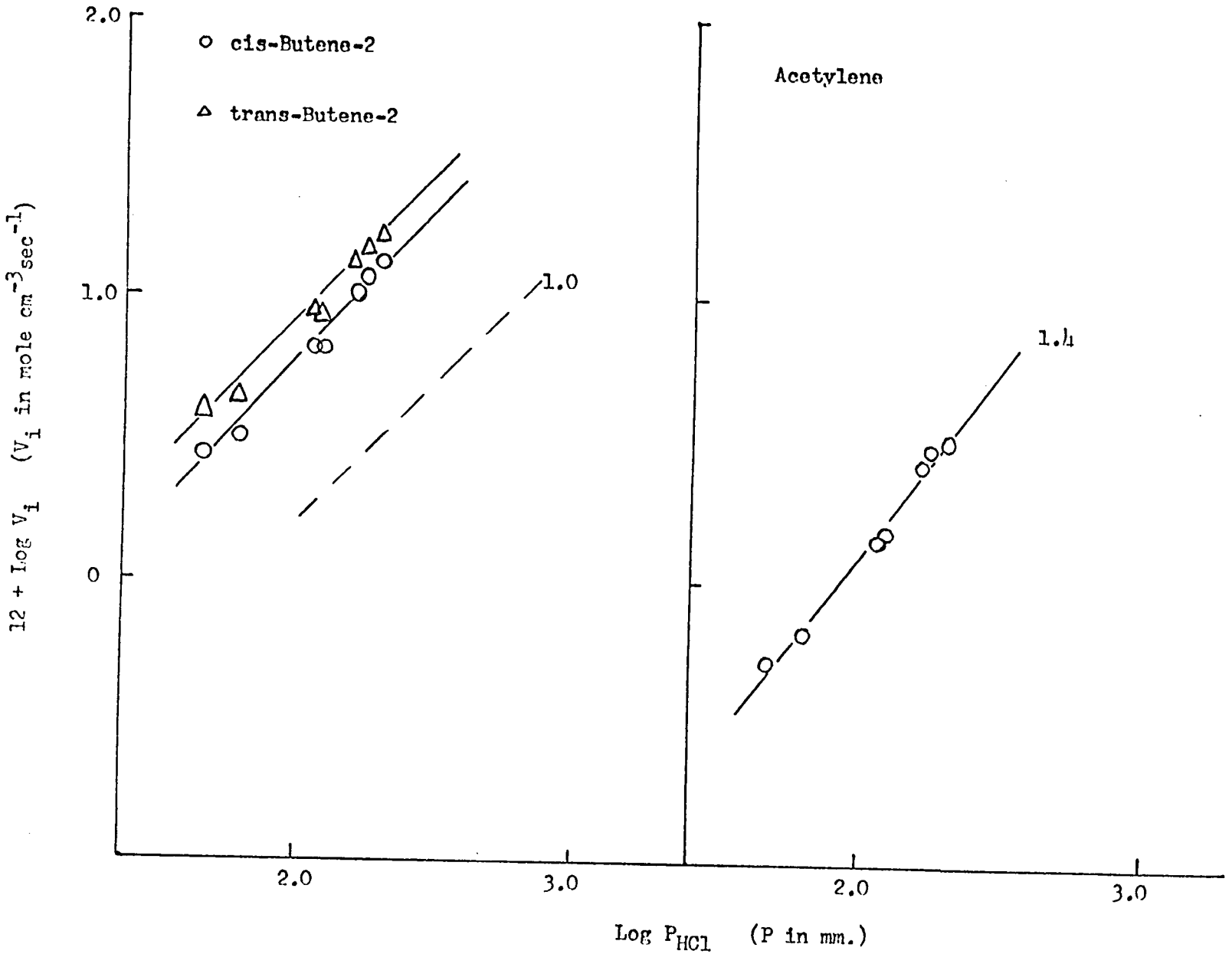
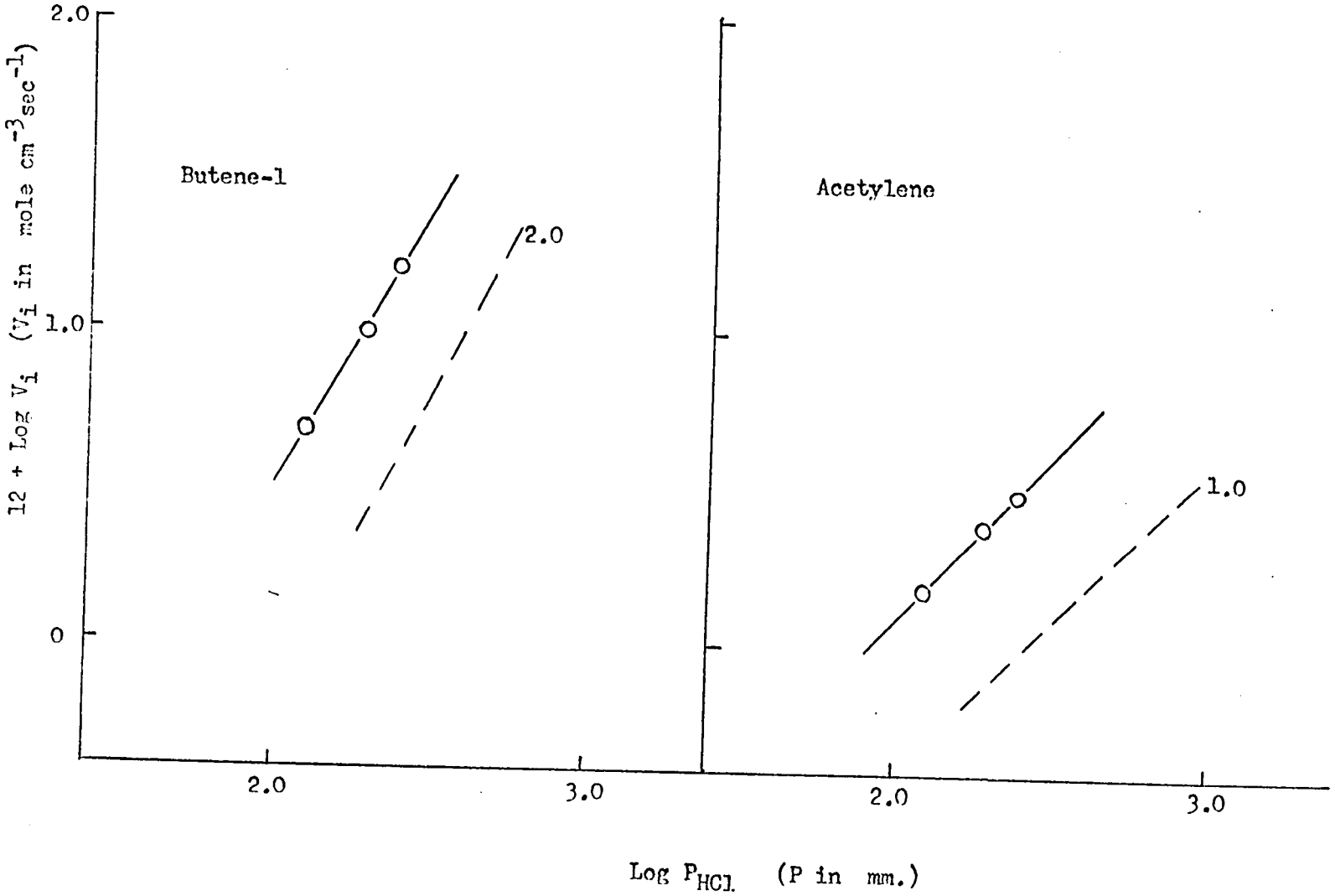

2.0
1.0
0
cis-Butene-2
trans-Butene-2
1.0
Acetylene
1.4
12 + Log V_i (V_i in mole $cm^{-3} sec^{-1}$)
2.0
3.0
2.0
3.0
Log P_{HCl} (P in mm.)

Figure 30

Order plots for hydrogen chloride catalysed isomerization of trans-butene-2 at 400°C


2.0
1.0
0
12 + Log V_i (V_i in mole $cm^{-3}sec^{-1}$)
Butene-1
2.0
Acetylene
1.0
2.0
3.0
2.0
3.0
Log P_{HCl} (P in mm.)

(B). Hydrogen bromide catalysed isomerization

Since the hydrogen chloride catalysed isomerization of cis-butene-2 was found to be kinetically complex, hydrogen bromide was then tried as a homogeneous catalyst. The results showed that the hydrogen bromide catalysed cis-butene-2 isomerization was kinetically simpler than that of the hydrogen chloride catalysis. Only two isomers, butene-1 and trans-butene-2, were observed and some of the results are summarised in Table 35. The kinetics of butene-1 formation were not measured because only very small quantities were produced at 236°C. The rate of trans-butene-2 formation is given as

$$\text{cis-Butene-2} + \text{HBr} \longrightarrow \text{trans-Butene-2} + \text{HBr}$$

$$\text{rate} = k_2[\text{cis-Butene-2}][\text{HBr}]$$

$$= k_{ct}[\text{cis-Butene-2}] .$$

Inhibition experiments were also studied in the hydrogen bromide catalysed cis-butene-2 isomerizations. Cyclohexene caused a marked reduction of the rate constants for the cis-butene-2 isomerizations (see Figures 31, 32, 33). The results are summarised in Table 36.

Table 35 The dependence of k_{ct} for cis-butene-2 isomerization on the concentration of hydrogen bromide at 236°C (Initial pressure = 28 mm)

P_{HBr}(mm)	Time(min.)	Sample g.l.c. (μM)	t-Bu-2	$k_{ct} \times 10^5$ (sec^{-1})	$k_{ct}/[HBr]$ (mole^{-1}cm^{3}sec^{-1})
17	5	152.2	2.21	7.45	139
24	6	141.8	2.53	7.10	94.1
31.5	5	158.1	2.22	7.45	75.2
35.5	5	132.3	3.66	12.4	111
41	5	148.6	4.22	14.4	111
41	5	150.4	3.64	12.4	95.9
52	5	156.2	3.83	13.0	79.8
62	5	154.6	4.70	16.0	82.3
81.5	5	147	6.78	23.4	91.5

Mean value of $k_{ct}/[HBr] = k_2 = 97.9$ mole^{-1}cm^{3}sec^{-1}.

Figure 31

Effect of cyclohexene as inhibitor in hydrogen bromide catalysed isomerization of cis-butene-2 ⟶ trans-butene-2 at 236°C

HBr CATALYSED ISOMERISATION OF cis-BUT-2-ENE

236°C EFFECT OF CYCLOHEXENE AS INHIBITOR

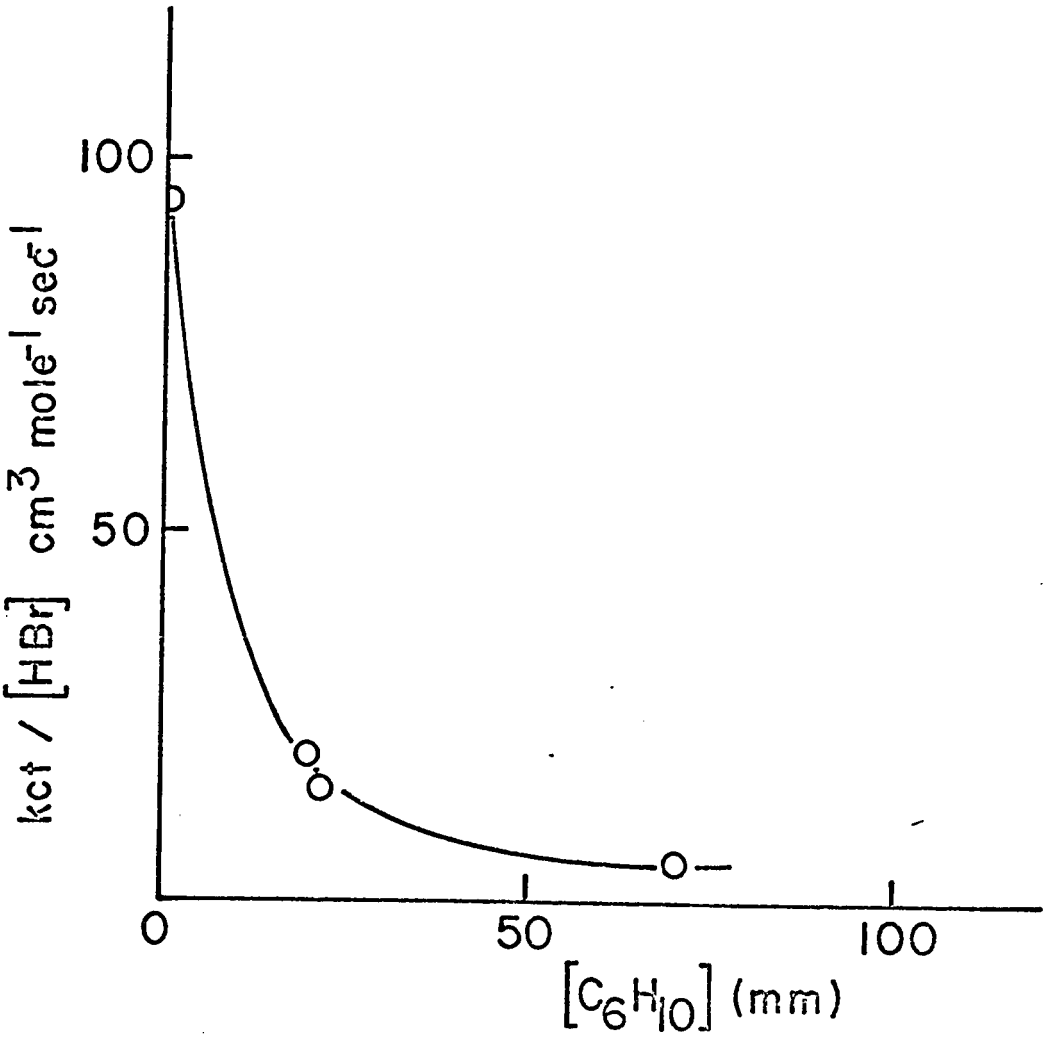


Figure 32

Effect of cyclohexene as inhibitor in hydrogen bromide catalysed isomerization of cis-butene-2 ⟶ trans-butene-2 at 291.0°C

HBr CATALYSED ISOMERISATION OF cis-BUT-2-ENE

294°C EFFECT OF CYCLOHEXENE AS INHIBITOR

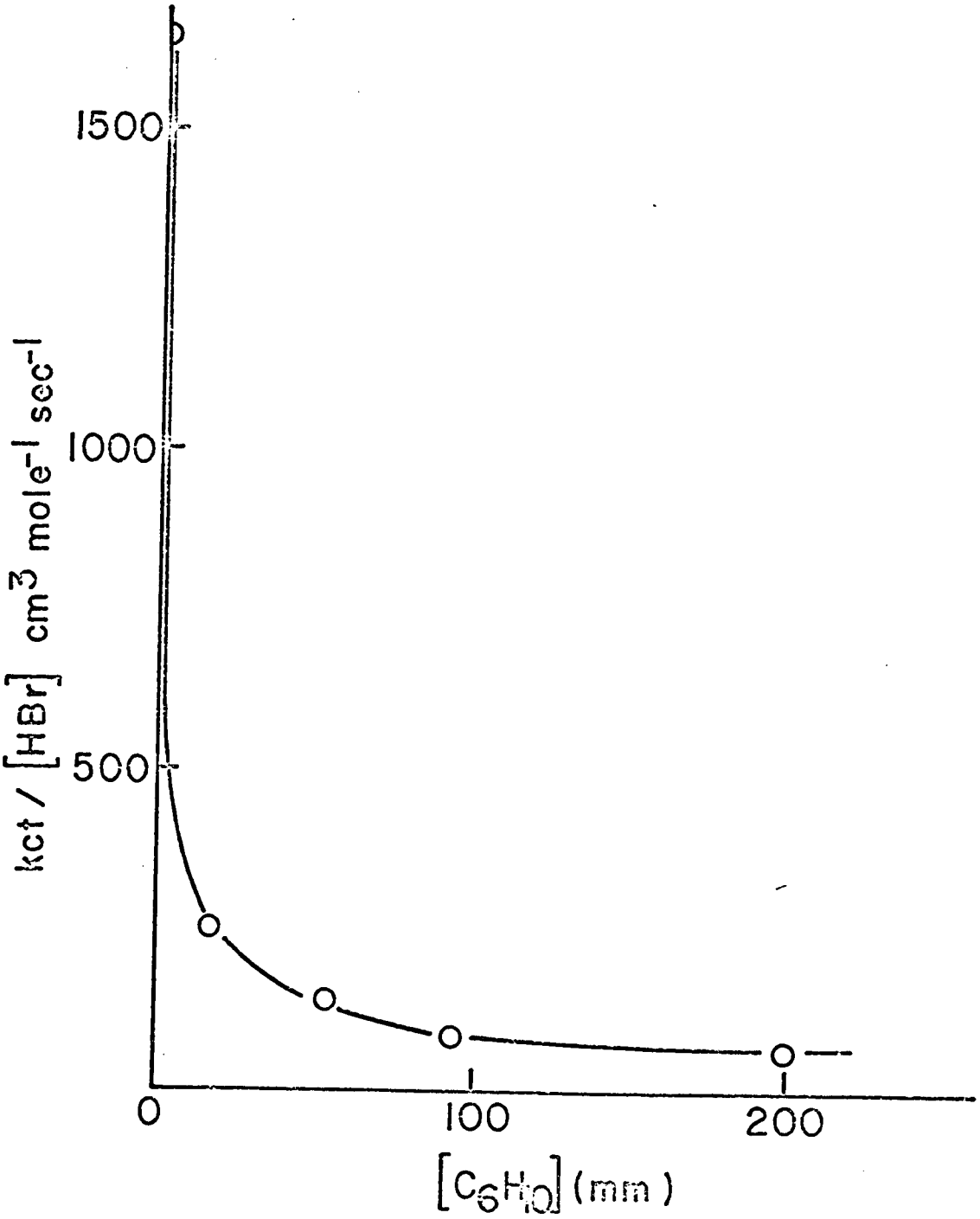


Figure 33

Effect of cyclohexene as inhibitor in hydrogen bromide catalysed isomerization of cis-butene-2 ⟶ butene-1 at 29½°C

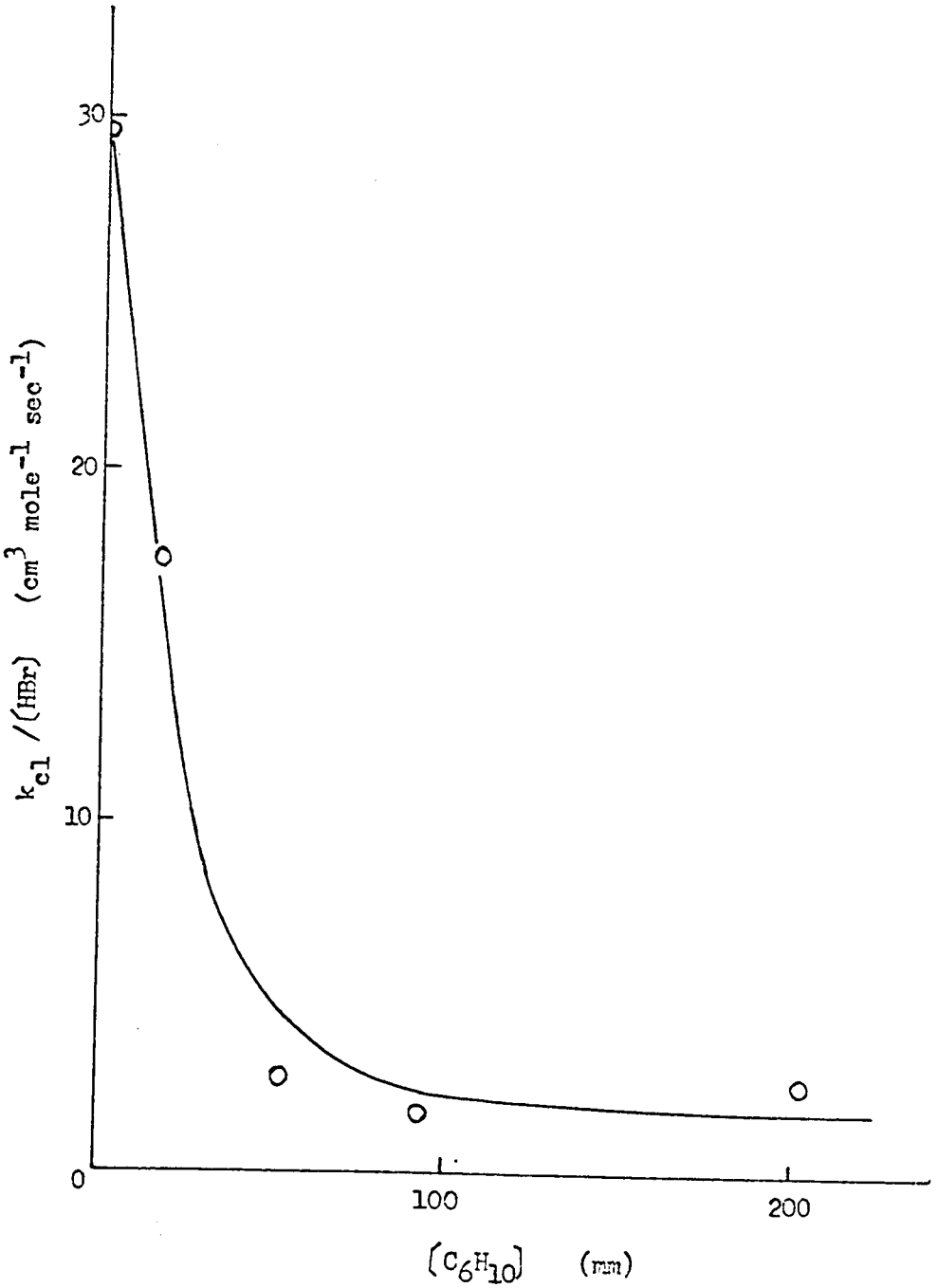

30
20
10
0
100
200
k_{cl} /(HBr) (cm^3 mole^{-1} sec^{-1})
$[C_6H_{10}]$ (mm)

Table 36 The results of the hydrogen bromide catalysed cis-butene-2 isomerization inhibited by cyclohexene

P_{Bu} (mm)	P_{HBr} (mm)	$P_{C_6H_{10}}$ (mm)	Temp. (°C)	Time (min.)	Sample glc(μM)	%Bu-1	%t-Bu-2	$k_{cl} \times 10^5$ (sec^{-1})	$k_{ct} \times 10^5$ (sec^{-1})	$k_{ct}/[HBr]$ ($mole^{-1} cm^3 sec^{-1}$)
28	43.5	22	236.5	5	147.9	0	0.63	-	2.2	15.7
28	90	70	236.4	5	143.2	-	0.46	-	1.5	5.4
28.5	101.5	20	237.2	5	155.2	0.20	1.89	0.69	6.4	20.0
27.5	26.5	0	294.0	4	128.4	0.54	25.7	2.21	123	1649
27.5	52.5	17.5	293.5	4	117.5	0.61	8.61	2.59	37.5	252
27	47	54	294.1	10	135.1	0.26	10.9	0.35	19.2	144
27	60	93	294.1	10	135.8	0.16	8.37	0.28	14.6	86.0
27	55	202	294.2	30	137.4	0.70	18.4	0.40	11.3	72.5

CHAPTER 4

DISCUSSION

I. The chemical reactivity of pyrolytic carbon and its physical properties

It is concluded from the results shown in Figure 12 that only active areas at or near the surface of allyl bromide carbon are responsible for the reaction, the limiting "thick layer" rate constant for the heterogeneous cis-trans isomerization of butene-2 is almost reached before the completion of one standard coating process. It would appear then, that the nature and concentration of odd electrons at or near the surface are therefore more important than the total number of odd electrons in the system. The electrical conductivity of allyl bromide carbon shows similar behaviour; e. g. Fig. 13, where log(1/R) (R is the resistance of the carbon in ohm) is plotted against time of the coating process. The curves in both kinetic experiments and measurements of the conductivity show that they begin to level off quite sharply after some five minutes of carbon deposition. This "leveling-off" point can be interpreted as indicating the completion of surface coverage. If the density of allyl bromide carbon is similar to that of graphite(50), i.e. $\sim 2 gm.cm^{-3}$, then the average thickness of the layer produced after five minutes of a standard coating is $\sim 25 Å$ (see Fig. 5 relating mass of carbon deposited to time of pyrolysis) and the specific conductance of the carbon is therefore ~ 0.025 ohm cm(45). The carbon deposited in five minutes is not visible to the eye. Knispel and Swinbourne(51) indicated that carbon from the ethyl chloride

pyrolysis had a specific resistance of 0.7 ohm cm at 449°C. They estimated the thickness of their sample by the optical density method of Agar(52), who had demonstrated that a nearly linear relationship exists between the optical density and the thickness of evaporated carbon films. In the measurements of electrical conductance Knispel and Swinbourne observed that on fresh glass surfaces there was an initial induction period of approximately 30 minutes after which the conductance rose steadily. They believed that the time of induction could be was attributed largely to the removal of some substance such as water or oxygen from the glass surface. They also found that the measured resistance depended markedly on the pressure of gaseous reactant and products in the system. This phenomenon was not found in the resistance measurements on allyl bromide carbon. Apart from the proposed correlation between conductivity and kinetics with respect to surface coverage it seems that further significance cannot at present be given to measurements of electrical resistance.

If the chemical reaction is confined to surface regions then it follows that e.s.r. measurements on thick carbon layers cannot be expected to give much information about activity changes taking place in the surface region only. The heat treatment of allyl bromide carbon yields an increase of both spin concentration and the rate of butene isomerisation; this shows that spin concentration and the carbon activity are connected phenomena.

The effect of cis-butene-2 on the e.s.r. signal from the four-pyrolysis allyl bromide carbon is small, as shown in Table 3. This small reduction of spin content is probably outside the experimental error since care was taken always to replace the

sample tube in the same position in the spectrometer cavity. The result suggests that some reversible interaction between the butene and the carbon does take place but the smallness of the reduction in the height of the first derivative absorption curve does not allow further conclusions to be drawn. However, if the reaction is confined to surface regions of the carbon, then a study of changes in odd electron concentration during a chemical reaction would require a spectrometer of greater sensitivity than those available for the present investigation. Further evidence of the insensitivity of e.s.r. measurements can be drawn from the propene deactivation experiments(Table 11 and Fig. 14) where no significant change in odd electron concentration was observed even when a great reduction in chemical activity had been achieved.

II. The kinetics of butene isomerisation on pyrolytic carbon

The first-order kinetics of the cis-butene-2 isomerizations can be explained by the simplest treatment of surface reactions involving one molecule of a reactant in terms of the Langmuir adsorption isotherm with a low surface coverage condition(53). Isomerization rate constants were very reproducible on a given carbon; the points on Arrhenius plot K-L in Figure 10 were obtained from two series of experiments, the first going from the highest to the lowest temperature and the second in the same direction; the same effect is shown in Figure 22. Rate constants measured at the same temperature in each series agreed within 10%.

The kinetic experiments on the cis→trans butene-2 isomerization on allyl bromide carbon show that the heterogeneous activation energy is about 50 Kcal $mole^{-1}$ lower than that of the homogeneous

reaction(5,6,7). Comparing the rates at 369 °C, the rate of the heterogeneous isomerization is 240 times faster than the homogeneous rate(Table 37).

It was suggested that the surface provided a heterogeneous initiation process in the acetaldehyde decomposition on allyl bromide carbon(54). This experimental result does not allow us completely to rule out the possibility that the cis-butene-2 isomerization is brought about homogeneously by free radicals produced heterogeneously at the carbon surface. The chief evidence against such a homogeneous isomerization is the small by-product formation and the failure of even large partial pressures of propene and cyclohexene to change significantly the isomerization rate. They would decrease the rate if they acted as radical traps; conversely, if they acted as new radical sources then they would be expected to increase the rate of isomerization.

Heat treatment of the pyrolytic carbons caused an increase in the rate of isomerization, as can be seen in Figures 10 and 17. The effect is related to the increase of spin content of the carbon. For this reason, most of the experiments were carried out after the carbons had been heated to a temperature higher than the experimental temperature.

cis-Butene-2 carbon displays catalytic activitytowards the cis-butene-2 isomerizations but is less reactive than allyl bromide carbon. Comparison of the rates of cis→trans isomerization is given in Table 38. Rabinovitch and Michel(5) observed that runs at pressures above 100 mm revealed an acceleration of rate with time which increased with pressure, for example, at 190 mm from an initial value of 2.8×10^{-5} sec^{-1}, k increased to 3.2×10^{-5} sec^{-1}

Table 37 Rate constants for the homogeneous and heterogeneous* reactions of cis→trans isomerization of butene-2 and CH_3CHO, HI decomposition

Reactant	Temp.(°C)	Homogeneous k	Homogeneous E_a(Kcal mole^{-1})	Heterogeneous k	Heterogeneous E_a(Kcal mole^{-1})	V_{hot}/V_{hom}	Ref.
cis-C_4H_8	369	5×10^{-8} sec^{-1}	63	1.2×10^{-5} sec^{-1}	15	240	-
CH_3CHO	480	0.16 cm$^{3/2}$ mole$^{-\frac{1}{2}}$ sec^{-1}	49.1	0.30 cm$^{3/2}$ mole^{-1} sec^{-1}	-	1.9	(54)
HI	454	4.6×10^{-3} l.mole^{-1} sec^{-1}	42.5	2.4×10^{-5} sec^{-1}	9.5	10	(55)

* The heterogeneous agent was allyl bromide carbon.

Table 38 Rates of cis→trans isomerisation of cis-butene-2

	Homogeneous	cis-Butene-2 carbon	Allyl bromide carbon
Relative rate (at 390°C)	1	16	240
Activation energy (Kcal mole^{-1})	63	32.5	15

for total reaction time of 55 minutes at 470 °C. They concluded that the reaction was sensitised by processes attendant on polymerization and was presumably a result of a free radical catalysed isomerization consequent on side reactions such as decomposition. In the present investigation, we observed that the cis-butene-2 isomerization in the presence of cis-butene-2 carbon was indeed heterogeneous. It becomes clear that the rate acceleration results obtained by Rabinovitch and Michel(5) in the homogeneous cis-butene-2 isomerization are due to the heterogeneous catalysis by the carbonaceous deposit. This could also account for those reactions with strikingly low frequency factors observed in the early studies (56,57,58). It can be concluded that those reactions did not occur via the triplet state mechanism proposed by Magee, Shand, and Eyring(2). The experiments of Holbrook and Rooney(38) showed that 1 % of cis-butene-2 isomerised to trans-butene-2 at 333 °C in 30 minutes on their cis-butene-2 carbon. In the present study the rate is slower than that obtained by Holbrook and Rooney, only 0.7 % isomerization taking place at 405 °C in the same reaction time; Since they showed only two runs of the cis-butene-2 isomerization on their cis-butene-2 carbon (prepared at 480 °C by decomposing 28 mm cis-butene-2 in 30 minutes). The activation energy evaluated from their experimental result at two temperatures gave a surprising value of ~ 125 Kcal mole^{-1}. Therefore, it can be concluded that results obtained in their experiment on cis-butene-2 isomerization involved a great uncertainty.

The effect of changing the surface: volume ratio of the reaction vessel coated with allyl bromide carbon, shows that the rate constant is to some extent proportional to the value of

surface : volume ratio. As can be seen in Figure 34 the rate constant of cis-butene-2 isomerization on allyl bromide carbon in an unpacked vessel will reach as high a value as that obtained in a packed vessel when the heat treatment is prolonged for an appreciable period. At 429°C, $k_{ct} = 4.44 \times 10^{-5}$ sec^{-1} in the packed vessel with surface : volume ratio 5.2 cm^{-1}, in which the allyl bromide carbon was heated to 460°C for ~16 hours and $k_{ct} = 4.39 \times 10^{-5}$ sec^{-1} in the unpacked vessel with surface : volume ratio 1.4 cm^{-1} in which carbon was heated to 460°C for ~62 hours. This correlation also shows that the increase of the isomerization rate can be achieved by heating the carbon instead of increasing the surface area of the reaction vessel.

Unlike the preferential formation of cis-butene-2 in most heterogeneous catalysed isomerizations of butene-1(59,60,61), the butene-1 isomerization reaction on allyl bromide carbon yields product ratios of trans : cis-butene-2 greater than unity. The difference of activation energies in 1→cis and 1→trans isomerizations is 1.2± 0.3 Kcal mole^{-1}(see Fig. 23), which is reasonably close to the difference in the enthalpy changes for the two reactions(20) $\Delta H_{1c} - \Delta H_{1t} = 0.56$ Kcal mole^{-1} and the values of H_{tc} from Benson and present work at 400°C (~1 Kcal mole^{-1}).

It is proposed that the mechanism of the carbon catalysed n-butene isomerizations involves the attachment of the double bond carbon to active sites on the surface thus allowing free rotation of the σ bond. The double bond shift requires a higher activation energy since the hydrogen migration is more difficult than the simple attachment of active site to double bond carbon without hydrogen shift.

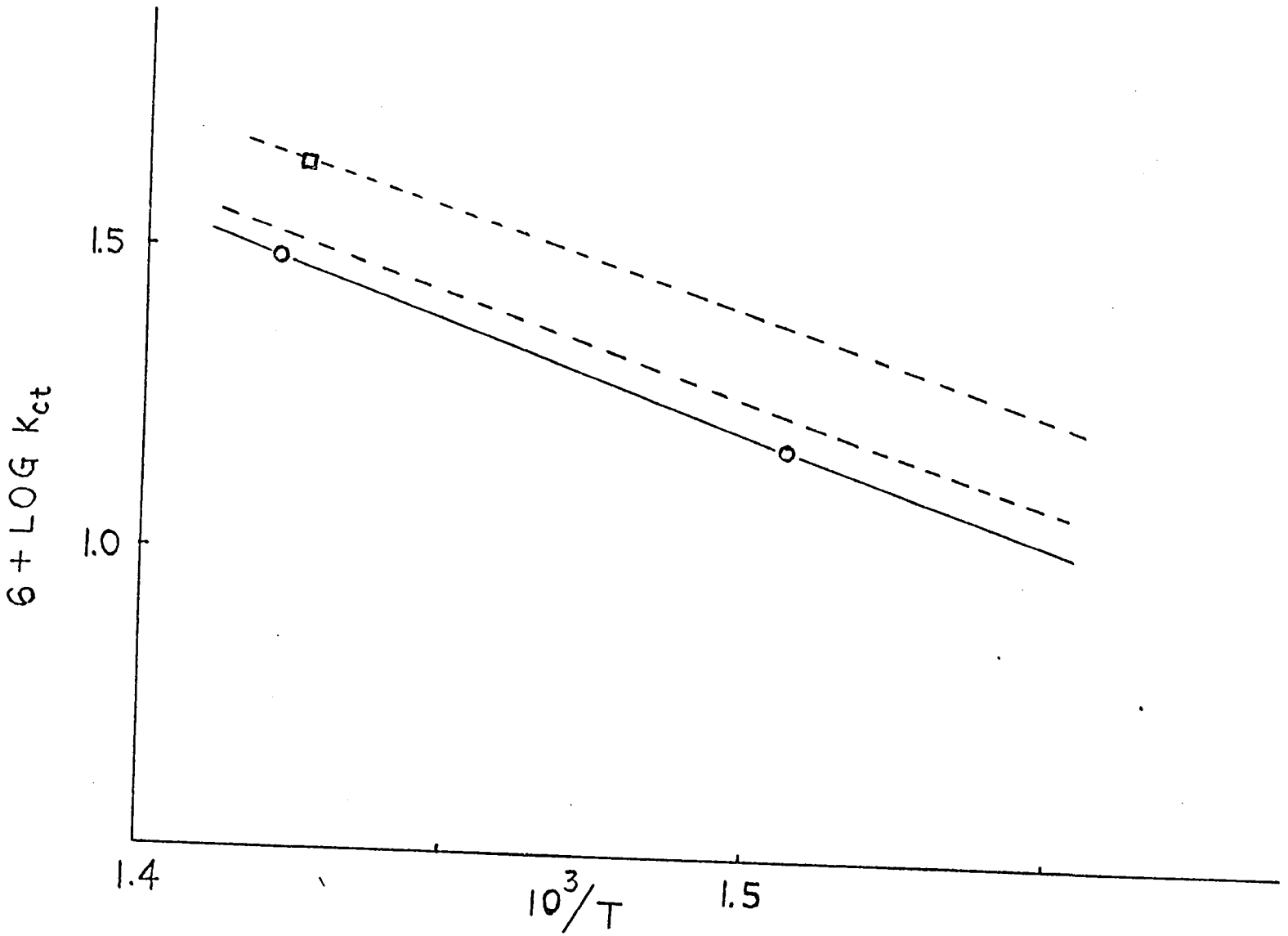
Figure 38

Arrhenius plots for the cis-butene-2 isomerization on allyl bromide carbon in an unpacked and packed reaction vessel (see also Table 12)

○ 18 hours heat treated carbon;

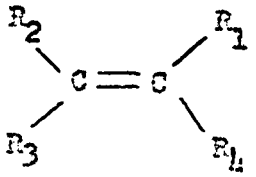
□ 62 hours heat treated carbon;

dashed lines from packed vessel(line K-L & M-N in Figure 10)


6 + LOG k_{ct}
1.5
1.0
1.4
$10^3/T$
1.5

III. Deactivation and activation phenomena on pyrolytic carbon

The experiments on the cis-butene-2 isomerization in the presence of propene and cyclohexene on the allyl bromide carbon showed that propene and cyclohexene did not directly take part in the cis-butene-2 isomerization but instead effected a deactivation of the carbon. Butene-1 and trans-butene-2 also effected the deactivation of allyl bromide carbon when its homologue cis-butene-2 did not. The results indicate that the carbon may well be sensitive to some extent to the geometrical structure of the molecule which is adsorbed on it. If the molecules are adsorbed on the carbon in a "lying-down" position as mentioned by Hoory and Prausnitz(62) (i.e. with both carbons of the double bond in the same plane as the surface) then the terminal olefins may act more efficiently than non-terminal double bonds to block the active sites on carbon by forming more stable adsorbed molecules, i.e. for the species



will interact more strongly with the surface if $R_1 = R_2 = R_3 = H$ and R_4 = alkyl than if $R_1 = R_2 = H$ and $R_3 = R_4$ = alkyl. The chemical reactivity of allyl bromide carbon does depend on the substrate treatment as can be seen in the experiments in those series of trans-butene-2 isomerizations. The activation energy for the butene-2 isomerisations were about 10 Kcal mole^{-1} greater in the case of allyl bromide carbon which had first been treated with trans-butene-2 than those initially treated with cis-butene-2. ~~carbon.~~ In general, the apparent activation energy E_a is given by $E - \lambda$,

where λ is the heat evolved per mole of reactant gas in the adsorption process; it is the "true" activation energy E reduced by the heat of adsorption of the reactant. If the "true" activation energy E is the same for the cis-butene-2 molecules adsorbed on carbons which pretreated with cis-butene-2 or trans-butene-2 then the difference in the apparent activation energy of the cis-butene-2 isomerization must due to the difference in the heat of adsorption on the two differently treated carbons. Therefore the freshly prepared carbon must always be handled with caution.

The effect of a small pressure(3 mm air) of oxygen on allyl bromide carbon is to reduce the rate of the cis-butene-2 isomerisation. It can be estimated that in the experiment described on page 55 the ratio of number of oxygen molecules admitted : total number spins is ~ 0.2. The cis $\rightarrow$ trans isomerisation rate constant was reduced by 40%. This result does not correlate with that obtained in the e.s.r. experiment illustrated(45) from which it can be calculated that at room temperature a concentration of about 10 oxygen molecules per spin were required to reduce the spin content by 40%. There may however be a temperature effect which accounts for the discrepancy since the kinetic experiments were performed at much higher temperature($\sim 400^{\circ}C$) than the e.s.r. measurement temperature($\sim 25^{\circ}C$). Carbon which had been exposed to air at atmospheric pressure was much more reactive than unexposed carbon and many unidentified products of both greater and shorter retention times than the butenes were observed. The sensitivity of allyl bromide "seasoned" reaction vessels to oxygen has been recorded in pyrolytic studies(63).

The difference in activity between cis-butene-2 carbon and allyl bromide carbon seems to lie in the bromine content of the

latter. This is supported by the observation that cis-butene-2 carbon can be activated by exposure to the n-propyl bromide pyrolysis, in which bromine atoms are the chain carriers(33c), and that treatment with molecular bromine raises its activity close to that of allyl bromide carbon. How the presence of bromine in the carbon enhances activity is unkown; possibly the electronegative halogen atom lessens delocalization of the odd electrons giving rise to regions of higher spin density. The carbon deposited from 3-chloro-2-methyl propene displays lower catalytic activity than allyl bromide carbon which indicates that the possibility of enhancing the carbon activity could also be due to the geometrical structure of the carbon itself. The 3-chloro-2-methyl propene carbon could possibly contain chlorine atoms which, with more electronegative character than bromine atoms would be expected to produce a carbon of greater activity. Contrarily, the 3-chloro-2-methyl propene carbon was found to be less active than the allyl bromide carbon in the kinetic experiments. Unfortunately, the chlorine content of 3-chloro-2-methyl propene carbon was not measured. It might be concluded that the 3-chloro-2-methyl propene carbon contains little or no chlorine.

The bromine-activated cis-butene-2 carbon, whose activity is close to that of allyl bromide carbon, can be readily deactivated by propene. This deactivated carbon acts as an surface inert to the isomerization and gives a rate of reaction similar to the homogeneous rate. However, propene did not deactivate allyl bromide carbon so easily or so completely. This effect could be due to a difference in location of the bromine

atoms in the two carbons; the bromine atoms in activated cis-butene-2 carbon may be more easily removed by propene owing to their occupying a position on or near the surface.

IV. The equilibrium of cis⇌trans butene-2 on allyl bromide carbon

The results from the investigation of the equilibrium between cis⇌trans butene-2 in the temperature range 200–450°C (see Table 24) agree excellently with those of Golden, Egger, and Benson (19) and the A. P. I. value(20) as can be seen in Figure 24. Also shown in Figure 24 are the results of Voge and May(48), Abell(22) and Maccoll and Ross(21). Voge and May's experiments involved isomerisation using various silica-alumina-magnesia catalysts and their infrared analytical technique was not very sensitive. The poor agreement of the results of Abell(22) and Maccoll(21) with our values and those of Golden, Egger, and Benson(19) and the A. P. I. value(20) may be due to complications in their reaction systems involving participation of free radicals. It is however difficult to assess why the equilibrium constants of Abell(22), Voge and May(48), and Maccoll and Ross(21) are in such bad agreement. Benson and Bose's results(18) were obtained from few experiments and this may account for their poor agreement with the later results from their laboratory. Voge and May(48) reported increasing formation of by-products with increase in temperature and this may account for the discrepancies at high temperature.

The agreement between our values for K_{tl} and those of other workers(18,19,20,21,22,48) is less good. We believe(82) that this poor agreement may be due to the larger participation of thermal decomposition reactions in the butene-1 isomerisations.

The results of the independent measurements of the rate constants in cis-butene-2 $\rightleftharpoons$ butene-1 and trans-butene-2 $\rightleftharpoons$ butene-1 gave good agreement with the direct measurements of cis $\rightleftharpoons$ trans butene-2 as mentioned previously in chapter 3 (see Tables 27, 28). This investigation of the equilibria among the three n-butene isomers on the allyl bromide carbon confirms that the equilibrium constants obtained by the direct rate constant measurements between cis $\rightleftharpoons$ trans butene-2 isomerisation are reliable values.

V. Halogen acid catalysed isomerization

(A). Hydrogen chloride catalysis

Acetylene is found as a minor by-product in the hydrogen chloride catalysed isomerisations of the n-butene isomers. This indicates that the reaction system is quite complicated. Acetylene was not found in the thermal decomposition of sec-butyl chloride (40,64), but our reaction conditions correspond to completion of the pyrolysis and product analyses were performed (40) after ~50 % decomposition. The only reported observation of acetylene in alkyl chloride pyrolyses is in the methyl chloride pyrolysis(65) which gave as the main products hydrogen chloride, methane and acetylene in the approximate ratio 3 : 1 : 0.5. The activation energy(85 Kcal $mole^{-1}$) obtained for this reaction suggests that carbon—chlorine bond breaking is rate controlling and the authors suggest the following scheme :

$$CH_3Cl \longrightarrow CH_3\cdot + Cl\cdot$$

$$Cl\cdot + CH_3Cl \longrightarrow HCl + CH_2Cl\cdot$$

$$CH_3\cdot + CH_3Cl \longrightarrow CH_4 + CH_2Cl\cdot$$

$$CH_2Cl\cdot + CH_2Cl\cdot \longrightarrow C_2H_4Cl_2$$

$$C_2H_4Cl_2 \longrightarrow C_2H_2 + 2\ HCl$$

as the probable mechanism. The present system containing hydrogen chloride and cis-butene-2 could possibly form radicals that would lead to acetylene formation, e.g.

$$HCl + CH_3CH=CHCH_3 \longrightarrow CH_3CHClCH_2CH_3$$

$$CH_3CHCl-CH_2CH_3 \longrightarrow CH_3\dot{C}HCl + \dot{C}H_2CH_3$$

$$CH_3\dot{C}HCl \longrightarrow CH_2CHCl + H^{\cdot}$$

$$CH_2CHCl \longrightarrow CH\equiv CH + HCl \quad .$$

This particular scheme would probably lead to formation of some hydrogen, ethylene, ethane, ethyl chloride etc. which were not found as products. Further speculation as to the origin of the acetylene does not appear profitable. The acetylene production was not inhibited by cyclohexene which leads one to suspect that its origin may not involve free radicals.

The orders of the hydrogen chloride catalysed n-butene isomerizations are shown in Table 39. If the isomerization passes through state "X" in both forward and reverse reactions, then the back reaction must also be second-order in hydrogen chloride concentration. The experimental result showed a surprising first-order kinetics in hydrogen chloride concentration for butene-1 $\longrightarrow$ cis- and trans-butene-2 isomerizations. It seems therefore that the forward and reverse reactions between butene-2 and butene-1 do not pass through a common transition state.

The ratio of the rate constants for the production of trans-butene-2 and butene-1 is different from that ratio observed in the pyrolysis products of sec-butyl chloride(40,64), as can be

Table 39 The order with respect to hydrogen chloride concentration in n-butene isomerizations (also see Figures 27, 29, 30)

Reaction	Order in [HCl]
cis-Butene-2 → trans-butene-2	1
cis-Butene-2 → butene-1	2
trans-Butene-2 → cis-butene-2	1
trans-Butene-2 → butene-1	2
Butene-1 → cis-butene-2	1
Butene-1 → trans-butene-2	1

seen in Table 10. We suggest that the isomerization of cis-butene-2 in the presence of hydrogen chloride is therefore not solely via sec-butyl chloride which in any case was not detectable in the reaction products. Butene-2 was not found in the n-butyl chloride pyrolysis (40) this indicates that the isomerization is not via n-butyl chloride.

The hydrogen chloride catalysed isomerization of cis-butene-2 → trans-butene-2 was inhibited by cyclohexene. The reaction cis-butene-2 → butene-1 was also slightly affected by the inhibitor. Since the maximum reduction of the cis → trans isomerization rate in the inhibition experiments is only about one half (see Fig. 28) at pressure ~ 130 mms cyclohexene, we suggest that the cis → trans catalysed isomerization occurs at least partially via a free radical reaction. At maximum inhibition in the cis-butene-2 isomerization the ratio of the rate constants for trans-butene-2 and butene-1 production is 0.91, which is comparable to that found in the sec-butyl chloride pyrolysis (in which the ratio 0.87 was obtained (40). Therefore, one may conclude that the residual catalysed cis → trans isomerization is

$$HCl + cis\text{-}C_4H_8 \xrightarrow{(a)} sec\text{-}C_4H_9Cl \xrightarrow{(b)} \text{"normal" pyrolysis products}$$

The reaction (a) is exothermic, i.e. $\Delta H_a = -15.7$ Kcal mole^{-1} (67), and has an activation energy $E_a = 33.2$ Kcal mole^{-1} (68). The inhibitable isomerization could be due to the presence of chlorine atoms in the system. A comparison of the present investigation with the results of Holbrook and Rooney (38) is made in Table 41, it is seen that the rate constants of butene-1 isomerization obtained by Holbrook are much faster than those obtained in the present work

Table 40 Ratio of k_{ct}/k_{cl} in the various reactions

Reaction	Temp.(°C)	k_{ct}/k_{cl}	Ref.
s-C_4H_9Cl pyrolysis	390	0.87	40
"	350	0.92	79*
"	360 - 410	0.86	64
n-C_4H_9Cl pyrolysis	390 - 450	0	66
HCl catalysed cis-butene-2 isomerization	400	3.15	Present work

* The experiment was carried out on cis-butene-2 coating and at low conversion where catalytic olefin conversion is negligible.

Table 4.1 The results of hydrogen chloride catalysed isomerization of cis-butene-2 and butene-1 (no inhibitor present)

Compound	(Bu)/(HCl)	Temp.(°C)	$k_{ct} \times 10^6$ (sec^{-1})	$k_{cl} \times 10^6$ (sec^{-1})	k_{ct}/k_{cl}	Ref.
cis-Butene-2	0.94	332	13.05	1.43	9	(38)
	0.94	400	3.3	1.1	3	Present work

Compound	(Bu)/(HCl)	Temp.(°C)	$k_{1t} \times 10^6$ (sec^{-1})	$k_{1c} \times 10^6$ (sec^{-1})	k_{1t}/k_{1c}	Ref.
Butene-1	1.03	316	259.5	150.6	1.7	(38)
	1.03	400	3.25	2.3	1.4	Present work

but the k_{1t}/k_{1c} ratios are similar. They believed that their cis-butene-2 seasoned surface (at 480 °C, 28 mms for 30 minutes) was inactive toward cis → trans isomerization in the presence of hydrogen chloride but was active in promoting butene-1 isomerization at the same condition. The present investigation indicates that the cis-butene-2 seasoned surface (the seasoning effect of surface at 400 °C can be seen in Fig. 25) does not display any especially important role for the butene-1 isomerization in the presence of hydrogen chloride.

(B). Hydrogen bromide catalysis

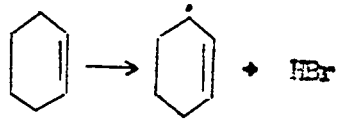
The hydrogen bromide catalysed cis-butene-2 isomerization is strongly inhibited by cyclohexene (Figures 31,32,33). It is evident that the isomerization involves free radical reactions, which are probably due to bromine atoms. Since there was no acetylene observed in the hydrogen bromide catalysed cis-butene-2 isomerization, the reaction is certainly simpler than in the hydrogen chloride catalysis! The residual isomerization rates at 294 °C at maximum inhibition are

$$k_{ct}/(HBr) \doteq 70 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1}, \text{ and}$$

$$k_{cl}/(HBr) \doteq 1.8 \text{ cm}^3\text{mole}^{-1}\text{sec}^{-1},$$

giving the ratio $k_{ct}/k_{cl} \doteq 39$. The uninhibited ratio is ~56. If one supposes that bromine atoms are responsible for the isomerization, then at maximum inhibition the concentration of bromine atoms may be reduced to a new, lower stationary state concentration or reduced to zero. This would yield no change in k_{ct}/k_{cl} for the former case and for the latter, the residual reaction could be

either molecular, or be brought about by new radicals such as $C_6H_9^{\cdot}$ resulting from hydrogen abstraction by bromine atom from the inhibitor,



or a combination of a molecular plus a residual free radical reaction.

Since the ratio of trans-butene-2 to butene-1 formation in the maximally inhibited cis-butene-2 isomerization shows a value much greater than that found in the sec-butyl bromide pyrolysis (40), where the ratio is ~1.8,* then therefore the reaction mechanism

$$cis\text{-}C_4H_8 + HBr \longrightarrow sec\text{-}C_4H_9Br \longrightarrow C_4H_8 + HBr$$

can be ruled out. The mechanism proposed by Maccoll and Ross(21), is that the reaction is purely molecular and passes through a six-centered transition state; this may not be easy to achieve owing to steric hindrance by the two methyl groups at the same side of the double bond in the reactant; in any case theirs is an oversimplification since we find that the reaction can be inhibited.

It has been found that the sec-butyl bromide pyrolysis(69, 70) contains a small chain component, since the decomposition is weakly inhibited by the addition of cyclohexene. Kalo(69) proposed that the bromine atoms abstract hydrogen from the reactant, but that this reaction does not make a great contribution to the overall rate in the sec-butyl bromide pyrolysis; a weak C—H bond is necessary from which the abstraction of hydrogen would

* Note: The ratio obtained by Capoor(79) is 1.2

lead to a propagating radical. Bromine atom abstraction of hydrogen from sec-butyl bromide can lead to a propagating radical $CH_3\dot{C}HCHBrCH_3$ or a stopping radical $CH_3CH_2\dot{C}BrCH_3$; the chain mode of decomposition only contributes 15% to the overall rate at 300 °C as mentioned by Hale, Maccoll, and Thomas(69).

$$s\text{-}C_4H_9Br \longrightarrow C_4H_9^{\bullet} + Br^{\bullet}$$

$$Br^{\bullet} + s\text{-}C_4H_9Br \longrightarrow C_4H_8Br^{\bullet} + HBr$$

$$C_4H_8Br^{\bullet} \longrightarrow C_4H_8 + Br^{\bullet}$$

Thus, it is possible to suggest that the hydrogen bromide catalysed cis-butene-2 isomerization proceeds via the partial formation of sec-butyl bromide (by addition) which then decomposes to the bromine atom and s-butyl radical in low concentration.

In the iodine atom catalysed n-butene isomerization, Benson and Bose(18) consider that the iodine atom abstracts hydrogen from butene, leading to a radical stabilised by allylic resonance; this could also be the case in the present study.

$$cis\text{-}C_4H_8 + HBr \longrightarrow s\text{-}C_4H_9Br \qquad (i)$$

$$s\text{-}C_4H_9Br \longrightarrow C_4H_9^{\bullet} + Br^{\bullet} \qquad (ii)$$

$$Br^{\bullet} + cis\text{-}C_4H_8 \longrightarrow C_4H_8Br^{\bullet} \qquad (iii)$$

$$C_4H_8Br^{\bullet} \longrightarrow trans\text{-}C_4H_8 + Br^{\bullet} \qquad (iv)$$

$$\longrightarrow cis\text{-}C_4H_8 + Br^{\bullet} \qquad (iv\ a)$$

$$Br^{\bullet} + cis\text{-}C_4H_8 \longrightarrow CH_2 \overset{\cdots}{\underset{CH=CH}{\diagdown}} \overset{\cdots}{\diagup} CH_2 + HBr \qquad (v)$$

$$HBr + CH_3\!-\!\underset{CH=CH}{\overset{\cdot\cdot}{\cdot\cdot}}\!-\!CH_2 \longrightarrow 1\text{-}C_4H_8 + Br\cdot \qquad \text{(vi)}$$

$$\longrightarrow 2\text{-}C_4H_8 + Br\cdot \qquad \text{(vi a)}$$

Benson(18) has also shown that for the unsaturated hydrocarbons with α-H atoms, allylic resonance interaction reduces the α(C-H) bond energy by about 15 Kcal. so that the equivalent of α-H abstraction by an iodine atom will be $\sim 10^7$ times faster for an alkene than for an alkane in the same temperature range. In the bromine atom reaction with hydrocarbons, Van Artsdalen and his co-workers(71) determined the activation energies of hydrogen abstraction by bromine atoms for ethane and iso-butane and obtained the respective values of 13.3 and 11.4 Kcal mole^{-1}. Kerr(72) has given the values 98, 94.5, and 91 Kcal mole^{-1} for the bond dissociation energies of primary, secondary, and tertiary C-H bonds in ethane, propene, and isobutane. It is to be expected that this variation in bond dissociation energy would be reflected in the activation energies of hydrogen abstraction reactions by bromine atoms but would not lead to such a large alkene/alkane abstraction ratio as in the case of iodine atom reactions. It is clear that the hydrogen abstraction by bromine atoms in cis-butene-2 will be faster than in the sec-butyl bromide or butane systems. Hydrogen abstraction from cis-butene-2(v) would yield butene-1 in the products. The direct addition of a bromine atom to the double bond carbon(iii) leads to a freely rotating σ complex. The latter reaction will occur at a much faster rate than that of hydrogen abstraction(18).

The activation energy of the hydrogen bromide catalysed cis→ trans butene-2 isomerization is estimated ~ 28.1 Kcal mole^{-1} (see Fig. 35). This value is close to the activation energy of the addition reaction of hydrogen bromide to butene-2, i.e. 27.9 Kcal mole^{-1}(68). The molecular elimination(pyrolysis) reaction has an activation energy E_a= 44 Kcal mole^{-1},

$$s\text{-}C_4H_9Br \longrightarrow C_4H_8 + HBr$$

and the carbon — bromine bond dissociation energy is 68 Kcal mole^{-1}. Since the activation energies for these two processes are higher than that of the addition reaction(i), then the reaction(i) cannot be the rate determining step in the overall reaction. Maccoll(21) found that the hydrogen bromide catalysed isomerisation of butene-1 —→ butene-2 had an activation energy(for the homogeneous bimolecular reaction) of 26.3 Kcal mole^{-1}. Further work is clearly necessary to elucidate the detailed mechanism.

If bromine atoms are responsible for the uninhibited hydrogen bromide catalysed cis-butene-2 isomerisation, then the ratio k_{ct}/k_{cl} would be that for the rates of the bromine addition reaction(iii) and the hydrogen abstraction reaction(v) (provided that the reactions(iv) and (vi) are fast). If trans-butene-2 production in reaction(vi a) is negligible compared to its' production from reaction(iv), then

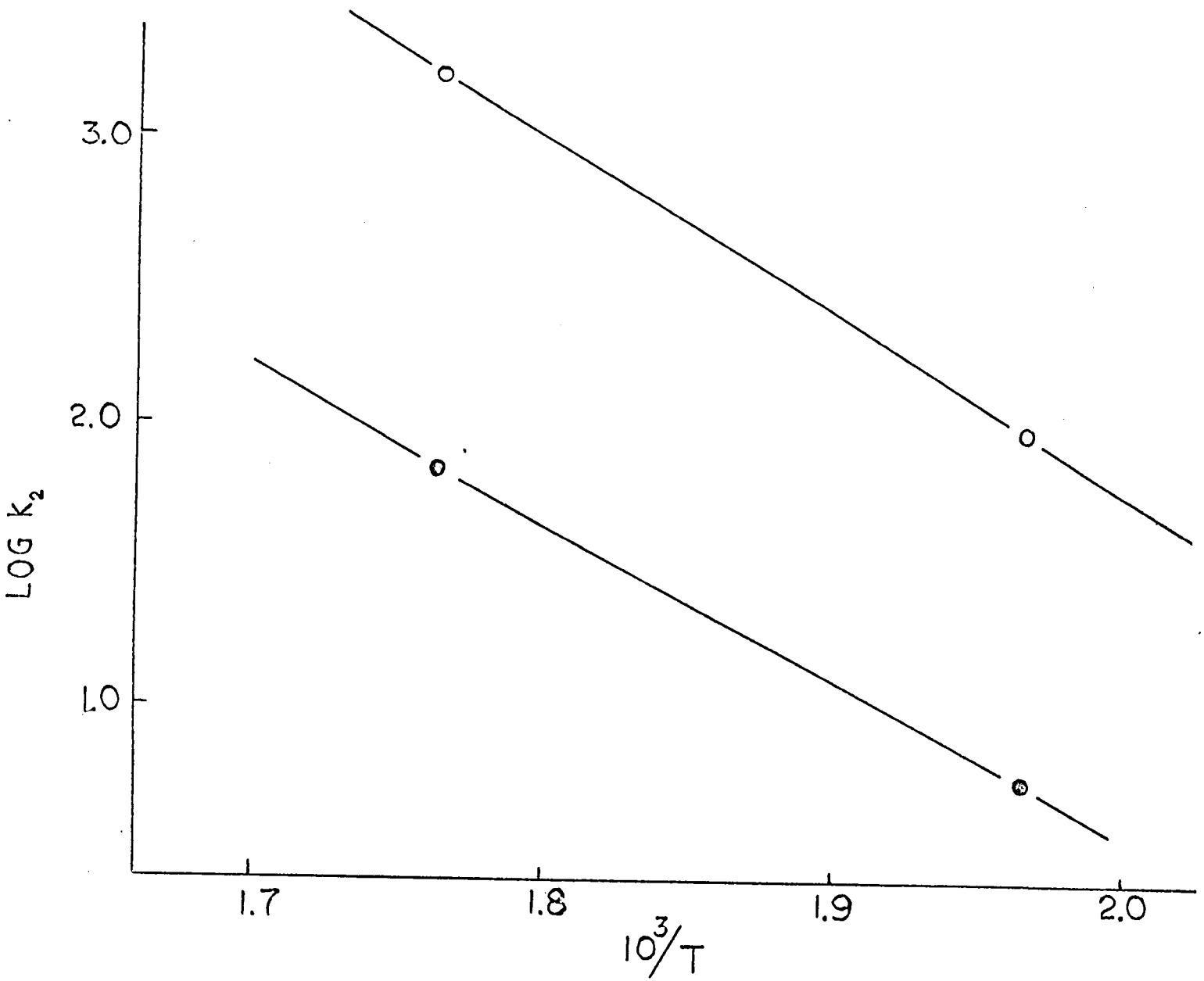
$$k_{ct}/k_{cl} \approx k_{add.}/k_{abs.} = 56$$

for the uninhibited isomerisation. If the frequency

Figure 35 Arrhenius plot of the hydrogen bromide catalysed cis→trans butene-2 isomerizations.

○ Uninhibited result

● Inhibited result


3.0
2.0
1.0
LOG K_2
1.7
1.8
1.9
2.0
$10^3/T$

factors for the two reactions are the same (or closely similar), then

$$\log (k_{add.}/k_{abs.}) \simeq (E_{abs.} - E_{add.})/2.303RT ,$$

and $$E_{abs.} - E_{add.} \simeq 4.5 \text{ Kcal mole}^{-1}.$$

If a weighting factor of 3 is included (i.e. ratio of no. extractable hydrogen to no. carbons in double bonds), then

$$E_{abs.} - E_{add.} \simeq 2.303 RT \log 3k_{add.}/k_{abs.}$$

$$\simeq 5.8 \text{ Kcal mole}^{-1}.$$

Unfortunately, the activation energies of these two reactions have not been determined. If one compares this presumed value of the activation energy difference between abstraction and addition with the literature values for the similar reactions in olefins, e. g.

(1) $CH_3^{\cdot} + CH_3{-}CH{=}CH_2 \xrightarrow{1} C_4H_9^{\cdot}$ $E_1 = 6.0$ Kcal mole^{-1},

(2) $CH_3^{\cdot} + CH_3{-}CH{=}CH_2 \xrightarrow{2} CH_4 + \dot{C}H_2{-}CH{=}CH_2$ $E_2 = 8.2$ Kcal mole^{-1},

(3) $CH_3^{\cdot} + CH_3{-}CH_2{-}CH_3 \xrightarrow{3} CH_4 + CH_3\dot{C}HCH_3$ $E_3 = 10.3$ Kcal mole^{-1},

the difference $(E_{abs.} - E_{add.}) \simeq (E_2 - E_1) \simeq 2.2$ Kcal mole^{-1} is obtained for the methyl radical(73,74). The corresponding rate ratio $(k_{add.}/k_{abs.})$ for $CH_3^{\cdot}$ radicals and propene at 295°C is $\simeq 5$. The difference in activation energies of the hydrogen abstraction by methyl radicals in unsaturated and saturated hydrocarbons is only $(E_3 - E_2) \simeq 2.1$ Kcal mole^{-1}(75) and would certainly be similar for butene and butane.

For a bromine atom, the reaction

(4) $Br^{\cdot} + C_4H_{10} \xrightarrow{4} HBr + CH_3\dot{C}HCH_2CH_3$

has an activation energy E_4 = 10.2 Kcal mole^{-1}(76); the activation energy of

$$Br^{\cdot} + CH_3CH=CHCH_3 \longrightarrow HBr + \dot{C}H_2CH=CHCH_3 \qquad (v)$$

has not been determined, but by analogy with the methyl radical reactions (2) and (3) we may estimate E_v = 8.1 Kcal mole^{-1}. This activation energy can also be estimated by considering the following data.

(5) $Br^{\cdot} + C_6H_5CH_3 \underset{-5}{\overset{5}{\rightleftharpoons}} HBr + C_6H_5CH_2^{\cdot}$

The activation energies for the forward and reverse reactions of (5) have been determined(77) as E_5 = 7.2 Kcal mole^{-1} and E_{-5} = 5.0 Kcal mole^{-1}, whence

$$D(C_6H_5CH_2-H) - D(H-Br) = \Delta H_5 = -2.2 \text{ Kcal mole}^{-1}.$$

The bond dissociation energies $D(CH_3CH=CHCH_2-H)$ and $D(C_6H_5CH_2-H)$ are both 85 Kcal mole^{-1}(72), therefore ΔH_v must also be -2.2 Kcal mole^{-1}. ΔH_f for $\dot{C}H_2CH=CHCH_3$ can also be found:-

$$\Delta H_f(R) = \Delta H_f(R-H) - \Delta H_f(H) + D(R-H)$$

$$= -1.7 - 52.1 + 85$$

$$= 31.2 \text{ Kcal mole}^{-1},$$

where $\Delta H_f(R-H)$, $\Delta H_f(H)$ and $D(R-H)$ are obtained from references (76,72). ΔH_v can then be estimated by combining this heat of

formation with the appropriate thermodynamic data(78)

$$\Delta H_f(Br) = 26.7 \text{ Kcal mole}^{-1},$$

$$\Delta H_f(cis\text{-}C_4H_8) = -1.7 \text{ Kcal mole}^{-1},$$

$$\Delta H_f(HBr) = -8.7 \text{ Kcal mole}^{-1},$$

$$\Delta H_f(\dot{C}H_2CH=CHCH_3) = 31.2 \text{ Kcal mole}^{-1},$$

this yields $\Delta H_v = -2.5$ Kcal mole^{-1}. This is the same as that which can be obtained similarly from thermodynamic data for reaction (5) $\Delta H_5 = -2.4$ Kcal mole^{-1}, where

$$\Delta H_f(Br) = 26.7 \text{ Kcal mole}^{-1} \qquad \text{(ref. 78)},$$

$$\Delta H_f(C_6H_5CH_3) = 12 \text{ Kcal mole}^{-1} \qquad \text{(ref. 78)},$$

$$\Delta H_f(HBr) = -8.7 \text{ Kcal mole}^{-1} \qquad \text{(ref. 78)},$$

$$\Delta H_f(C_6H_5CH_2^{\cdot}) = 45 \text{ Kcal mole}^{-1} \qquad \text{(ref. 72)}.$$

This result supports the former conclusion that ΔH is same in both (v) and (5). Therefore it is reasonable to conclude that the activation energies of reactions (v) and (5) are similar. The estimated result of $E_v = 8.1$ Kcal mole^{-1} is close to the E_5 obtained by Anderson, et al.(77). If the assumption (that bromine atoms are responsible for the cis-butene-2 isomerization) is true then for reaction(iii)

$$Br^{\cdot} + CH_3CH=CHCH_3 \longrightarrow CH_3\dot{C}HCHBrCH_3 \qquad \text{(iii)}$$

$E_{iii} = E_v - 5.8 \pm 2.3$ Kcal mole^{-1}. This value is reasonably low

which has been suggested by Steinmetz, et al.(80) and Muller, et al.(81) for bromine atom addition to a double bond.

At maximum inhibition the ratio of the rates k_{ct}/k_{cl} is smaller than that of the uninhibited reaction. It is possible that in this case a radical such as $C_6H_9^{\cdot}$ (with allylic resonance stabilisation) may have largely replaced the bromine atoms in the system. If $C_6H_9^{\cdot}$ radicals were responsible for the maximally inhibited rate of the HBr catalysed isomerization of cis-butene-2, then the ratio k_{ct}/k_{cl} would probably be reduced from the uninhibited reaction value (which we have supposed to be due to $Br^{\cdot}$ atoms) since the reaction(iii') could be subject to some steric hindrance due to the bulky $C_6H_9^{\cdot}$ radical.

$$C_6H_9^{\cdot} + CH_3CH=CHCH_3 \longrightarrow C_6H_9CH(\dot{C}H)CH_3 \qquad \text{(iii')}$$

$$C_6H_9^{\cdot} + CH_3CH=CHCH_3 \longrightarrow C_6H_{10} + \dot{C}H_2CH=CHCH_3 \qquad \text{(v')}$$

Reaction(v') is similar to that for a bromine atom (reaction(v)) insofaras the bond energy for α(C—H) in cyclohexene is close to the bond energy of H—Br. Thus one could predict that the rate of k_{ct} will be less in the inhibited reaction and that k_{cl} would be little affected, The activation energy for the cis trans isomerization at maximum inhibition was ~25.2 Kcal $mole^{-1}$, only ~3 Kcal $mole^{-1}$ different from the uninhibited isomerisation.

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CLAIMS TO ORIGINAL RESEARCH

1. The odd electron content of some pyrolytic carbons have been examined. The spin content increases linearly with the weight of carbon deposited. The spin concentration of 'standard' allyl bromide carbon was estimated to be 5×10^{20} spins gm^{-1}, approximately. The chemical activity of the carbon could be enhanced by heat treatment which agrees well with the increase of spin content by heating the carbon.

2. Isomerizations of cis-butene-2 on allyl bromide carbon showed that at the studied temperatures, products other than trans-butene-2 and butene-1 are negligible. The activation energies of the cis→trans and cis→butene-1 isomerizations are ~ 15 and ~ 17.7 Kcal $mole^{-1}$, respectively.

3. The effect of carbon deposit thickness on the rate of the geometric isomerization indicated that only active areas at or near the surface of allyl bromide carbon are responsible for reaction.

4. Small amounts of oxygen decrease either the chemical activity of allyl bromide carbon or the spin content of the carbon.

5. The effects of propene and cyclohexene were examined. They could act as possible homogeneous free radical reaction inhibitors or as competitors for active sites in the cis-butene-2 isomerization on allyl bromide carbon. The results indicated that these additives were somehow deactivating the carbon. The carbon could not be reactivated by prolonged evacuation.

6. Isomerization of cis-butene-2 on cis-butene-2 carbon gave a higher activation energy(32.5 Kcal $mole^{-1}$) for the cis→trans isomerization than that obtained on the allyl bromide carbon. The cis-butene-2 carbon can be activated by treatment with bromine. After activation, the rate of the cis→trans butene-2 isomerization was observed to be close to that obtained with allyl bromide carbon.

7. Isomerization of cis-butene-2 was also studied on ethyl bromide carbon and 3-chloro-2-methylpropene carbon. The latter gave rate constants that were close to those obtained with cis-butene-2 carbon.

8. The results of trans-butene-2 isomerization on allyl bromide carbon showed that the trans→cis isomerization needed ~ 1 Kcal $mole^{-1}$ activation energy more than the corresponding cis→trans isomerization on the same carbon. The activation energies for butene-1 to trans- and cis-butene-2 were estimated as 19.2 and 20.3 Kcal $mole^{-1}$, respectively.

9. Initial rate constants for the six n-butene isomerizations were determined by using allyl bromide carbon as catalyst. The equilibrium constants, free energies, and entropies for the n-butenes were calculated and the cis⇌trans results agree well with thermodynamic data and with recent data from equilibrium studies of the homogeneous iodine-catalysed isomerizations.

10. The homogeneous hydrogen chloride and bromide catalysed isomerisation of cis-butene-2 can be inhibited by cyclohexene. A kinetic complexity in the hydrogen chloride catalysed isomerisation of the n-butenes was due to the formation of acetylene.