

PREFACE.

The problem of inhibition and catalysis by nitric oxide of various organic thermal decompositions has attracted the attention of kineticists during the last three decades. At one time it was thought that nitric oxide, which is the simplest stable molecule with a definite radical character, acted in a straightforward manner as a scavenger of pyrolytic radicals, thus simplifying rather than complicating thermal decompositions. However, as product analyses have increasingly made clear, the opposite is the case. It is now recognized that pyrolyses in the presence of nitric oxide show all the complications of multi-reactant decompositions, into which group they must be classed. The present study was undertaken as an attempt to further elucidate the character of the acetaldehyde-nitric oxide copyrolysis, emphasis being placed on the kinetics of product formation, in the hope of clarifying the nature of the action of the nitric oxide on simple organic molecules in the gas phase at elevated temperatures.

ACKNOWLEDGEMENTS.

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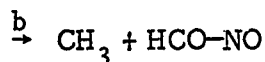
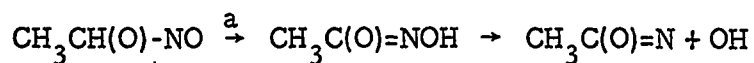
ABSTRACT.

The pyrolysis of acetaldehyde in the presence of nitric oxide has been investigated gas-chromatographically between 450°C and 525°C, the nitric oxide pressure ranging from 0 to 40 torr, with the acetaldehyde pressure at 176 torr. The following products have been identified and their concentrations measured at various times: CH₄, CO, N₂, H₂, CO₂, N₂O, C₂H₄, C₂H₆, H₂O, C₃H₆, HCN, CH₃NCO, C₂H₅CHO, CH₃COCH₃, C₂H₅NCO, and vinyl acetate. It was found that acetaldehyde vapour can react with nitric oxide slowly in the dark at room temperature, giving rise to H₂O, N₂, CH₃COOCH₃, NO₂, CO₂, HCN, N₂O, CH₃NO₂, CH₃NO₃, and CO. The rates of formation of the pyrolysis products, particularly those of N₂ and C₂H₅NCO, depend on how long an acetaldehyde-nitric oxide mixture is kept at room temperature before pyrolysis.

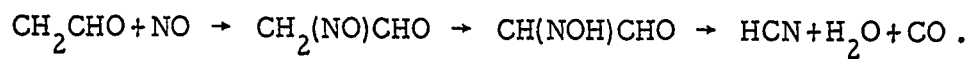
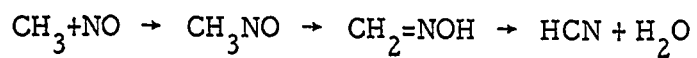
A mechanism is proposed which can explain the results.

Some features of this mechanism are:

1. There are two chain carriers, CH₃ and CH₂CHO, their concentrations being interdependent and influenced by NO in different ways.
2. An important mode of initiation by NO is its addition to the carbonyl group with the formation of the radical CH₃CH(O)-NO, which subsequently reacts in one of two ways:



3. Important modes of termination are:



Approximate values of various parameters, functions of elementary rate constants, have been obtained by fitting, to the experimental data, the rate expressions based on the mechanism, for several products.

INTRODUCTION.

I. Previous Pyrolytic Studies.

The first investigation into the effect of nitric oxide on the pyrolysis of acetaldehyde was undertaken in 1935 (1), and it was found that large amounts of NO (both acetaldehyde and nitric oxide pressures were of the order of 10^2 torr) accelerate the reaction.

Several studies of this pyrolysis have been carried out since then (2, 3, 4, 5, 6), based mainly on manometric measurements, although some products were analyzed in one investigation (5). As it may be argued that the acetaldehyde pyrolysis commands interest in the context of the general field of organic decompositions rather than by itself, it is proposed to consider the studies mentioned in the course of an outline showing the development of ideas on the pyrolysis of carbonyl compounds, paraffins, and ethers, with special emphasis on the role played therein by nitric oxide.

The theory that organic pyrolyses are chain reactions propagated by free radicals or H atoms was first formulated in 1934 by Rice and co-workers (7-10), after previous studies had shown the reality of such radicals. The first experimental proof of this was given in 1929 by Paneth and Hofeditz (11), who thermally decomposed $\text{Pb}(\text{CH}_3)_4$ carried through a tube in a stream of hydrogen, the lead being deposited in the hot zone and the fission products being able to remove a metal mirror (Sb, Zn, Pb) downstream, forming the metal alkyls which could be identified.

Retardation of a pyrolysis reaction by relatively small amounts of NO was first found with diethyl ether (12). This was

attributed to the suppression of the radical-chain reaction thought to operate side by side with a non-radical, molecular, decomposition unaffected by the NO. Various other organic substances were subsequently studied by Hinshelwood and co-workers, among them CH_3CHO (4), whose pyrolysis was found to be retarded by addition of small amounts of NO, while acceleration was observed when the pressure of NO was high.

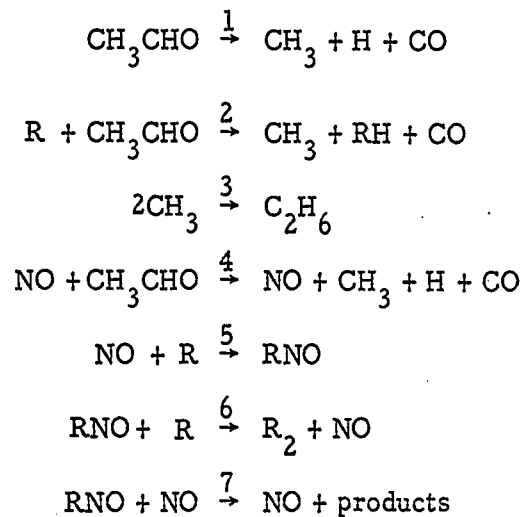
The main aim of these experiments with NO and other inhibitors, carried out by the Hinshelwood group, was to break down a pyrolysis into its molecular and free-radical components, and to study their mechanisms separately. The opinion that in an organic pyrolysis both a molecular and a free-radical reaction mode were important seemed justified since different inhibitors, though in different amounts, led to the same limiting rate in many cases. The study of the molecular processes thus sharply defined would then be important in the development of the theory of unimolecular reactions (cf. 13,14,15). A controversy developed between two different points of view, the dualistic one supported by the Hinshelwood school, and the opinion that pyrolyses even in their fully inhibited region were largely free-radical reactions with only a negligible molecular component (3).

A. Inhibition. The Hinshelwood Hypothesis.

In 1958, the pyrolysis of CH_3CHO together with NO was re-investigated (5). Products were analyzed by mass spectrometry and gas chromatography, and besides the major products CH_4 and CO HCN, CH_3CN , CO_2 , H_2 , C_2H_6 , and C_2H_4 were found. The production of the latter three which occur also in the pure acetaldehyde

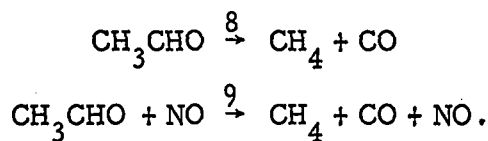
pyrolysis was enhanced by the addition of NO. It was found that $v_{\text{HCN}} = k[\text{CH}_3\text{CHO}][\text{NO}]^{3/2}$. The conclusions as to the mechanism of the pyrolysis were again based on pressure measurements, and were formulated as before within the dualistic concept:

a) the chain reaction



(R represents H or CH₃) ;

b) the molecular mode



Small amounts of NO would thus inhibit the reaction by virtue of steps 5 and 6, while much NO would accelerate it because of steps 4, 7, and 9. Step 9 was thought to be quite probable since the nitric-oxide-induced reaction itself was only suppressed to about one quarter of its initial amount by the addition of a second inhibitor, propylene.

B. All-radical Theories of Inhibition.

In the meantime, the view that the pyrolysis of acetaldehyde as well as other aldehydes, hydrocarbons, ethers, and ketones was of a radical nature throughout had begun to prevail. It had been pointed out in 1953 by Poltorak and Voevodsky (16), that it was quite improbable that a variety of substances (paraffins, aldehydes, ethers, etc.) should all decompose, over a wide temperature and pressure range, with comparable (within about one order of magnitude) velocities following two different mechanisms, which furthermore result in practically the same products. When C_3H_8 and D_2 were copolyzed in the presence and absence of NO, the extent of isotopic mixing was found to be virtually the same (16). Copolylysis of CH_3CHO and C_2D_6 in the presence and absence of NO was undertaken at $500^\circ C$ by Rice and Varnerin (17). The methane produced was analyzed in a mass spectrometer. If methyl radicals participate at all, then some CH_3D must be formed by $CH_3 + C_2D_6 \rightarrow CH_3D + C_2D_5$. Should CH_4 be formed also via an intramolecular split, $CH_3CHO \rightarrow CH_4 + CO$, then $v_{CH_3D}/v_{CH_4} = f([NO]) = \text{const. } [CH_3]/(\text{const}' \cdot [CH_3] + \text{const}'')$. At maximum inhibition, if this is due to an almost complete suppression of radicals, this ratio should be much smaller than for the pyrolysis without NO, at least if the rate of methane formation by the molecular route is not much smaller than the corresponding rate by the radical chain route. The results suggested that there is no significant contribution to the decomposition of acetaldehyde by direct intramolecular split into CH_4 and CO. The absence of such a split was confirmed for the pyrolysis of butane (18). Co-pyrolysis of $n-C_4H_{10}$ and $n-C_4D_{10}$ in the presence and absence of NO yielded CD_3H and CD_4 in virtually the same ratio. The conclusion was that practically no methane (less than 2%) is formed by a direct split under these conditions.

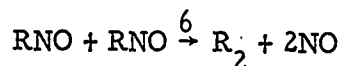
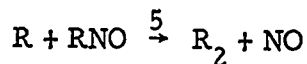
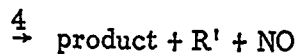
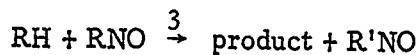
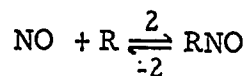
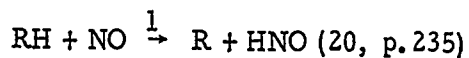
The hypothesis of the molecular residual reaction having been abandoned, attention became focused on the question of how NO and other inhibitors act, in order to create a unified theory. The following hypotheses have been put forward.

1. Initiation is unaffected by the additive, but additional reaction paths are opened up due to the formation of "stabilized radicals" which may undergo the same kind of reactions as the free radicals, but are somewhat less reactive than these (19). However, this mechanistic hypothesis was later (20) modified and an additional initiation $\text{RH} + \text{NO} \rightarrow \text{R} + \text{HNO}$ admitted.
2. Heterogeneous initiation and inhibition. The additive may block one kind of active site, while another kind of active site is not affected, on which reversible dissociation and recombination continues to take place (21).
3. Homogeneous initiation and termination by NO in addition to the intrinsic reactions.

1. Szabó's Theory. The concept of stabilized radicals (22, 23) was developed on the basis of the observation that in experiments showing an induction period it is sometimes possible to interrupt the reaction by cooling, and continue it after subsequent warming up to the previous level, without any further induction. As examples may be mentioned the thermal decompositions of O_3 , catalyzed by Cl_2 (24), and of Cl_2O (25). In both cases ClO is assumed to be the reactive intermediate (26). The appearance of Cl_2O_6 in the chlorine-sensitized decomposition of ozone is explained by the reactions $\text{ClO} + \text{O}_2 \rightarrow \text{ClO}_3$; $2\text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_6$ (23). Thus ClO_3 is considered a stabilized form of the

ClO radical and similarly HO₂, NO₂, ClO₂, O₃, alkyl-O₂ are considered oxygen-stabilized forms of H, N, Cl, O, and alkyl. In the limit, when the energy liberated at stabilization is great, the stabilized radical will exist as a fairly stable compound, e.g. NO₂ (23). The rule is enunciated: "Paramagnetic radicals can be stabilized by combining with paramagnetic additives, the degree of stabilization being governed by the bond energy of the resulting complex", and its scope then further extended to include the possibility of stabilization by weak interaction with other classes of compounds - those having π-electrons, lone electron pairs, and in fact any compound which can take part in a nucleophilic reaction (20, 27).

The mechanism of thermal organic decompositions in the gas phase, if NO is the stabilizer, has thus the following reactions woven into the Rice-Herzfeld scheme:



It is not clear what happens to the HNO formed in reaction 1; presumably it is thought to behave like RNO. With reaction 1 disregarded, the pyrolysis can be described by the "Influencing Factor" F, equal to the ratio of the rates in the presence and absence of inhibitor,

$$F = \frac{1 + a[\text{NO}]}{(1 + b[\text{NO}] + c[\text{NO}]^2)^{1/2}}$$

In this way the pyrolysis of $\text{C}_2\text{H}_5\text{CHO}$ has been explained quantitatively (28). (If reaction 1 is taken into account, the factor assumes a slightly different form (20),

$$F = \frac{(1 + a[\text{NO}]) (1 + h[\text{NO}])^{1/2}}{(1 + b[\text{NO}] + c[\text{NO}]^2)^{1/2}}$$

a, b, c, h constants). Despite this success, however, there is doubt whether the concept of the stabilized radical, which may be valid in inorganic systems, is relevant to the NO-influenced organic systems. It has been stated (29) that $\text{ClO} + \text{O}_2 \rightleftharpoons \text{ClO}_3$ and $2\text{ClO}_3 \rightarrow \text{Cl}_2\text{O}_6$ are almost thermoneutral, the dissociation energy of Cl_2O_6 being about 1.5 kcal/mole. But it seems difficult to consider nitrosoalkanes to be sufficiently unstable for the concept to be still useful. Very different values are given for the heat of reaction of $\text{R} + \text{NO} \rightarrow \text{RNO}$: on the one hand 39 kcal/mole (30) and 48 ± 4 kcal (31), when $\text{R} = \text{C}_2\text{H}_5$; ≤ 51 kcal/mole (32) and 30 ± 5 kcal/mole (33), when $\text{R} = \text{CH}_3$. On the other hand a value of 15 kcal/mole, called stabilization energy, is claimed when R is C_2H_5 (20). Documentation to support the latter value seems to be lacking.

A modification of this mechanistic proposal (34) takes the possibility of NO consumption into account: $\text{RNO} \rightarrow \text{products}$. There (34) the lessening of the RNO reactivity as compared to that of R is named the "saloon effect", to contrast it with the situation in the recombination of atoms, where (for instance in $\text{I} + \text{INO} \rightarrow \text{I}_2 + \text{NO}$, (35))

the reaction is facilitated by the "chaperon" NO, with which the iodine atom can form a feeble bond.

2. Voevodsky's Hypothesis. The idea that heterogeneous processes play a part in radical reactions must have suggested itself easily in view of the fact that atomic radicals recombine easily on surfaces, and that their rate of recombination depends on the surface material. Heterogeneous chain rupture is deemed possible in the first of Rice's papers (7); chain initiation might occur through abstraction of an H atom from the organic substrate by the silica surface (8), but in the last paper (10), where the Rice-Herzfeld mechanism is formulated, heterogeneous processes are no longer considered. In 1935, Semyonov, analyzing a study on the oxidation of C_2H_6 (36), was led to the conclusion that not only rupture, but also the branching of chains occurred at the surface. The reaction $3CO + SO_2 \rightarrow 2CO_2 + COS$, which is catalyzed by Al_2O_3 , was shown to occur by a homogeneous chain mechanism, since the heat of the reaction was liberated in the gas space, not on the catalyst, which during the experiment did not warm up, but cooled slightly (37), indicating an endothermic initiation step.

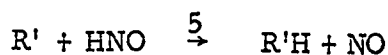
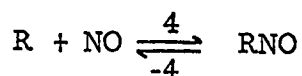
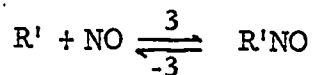
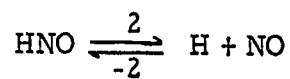
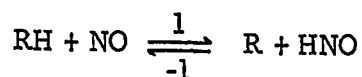
In 1953, Voevodsky showed (38) that heterogeneous initiation and termination might not be two completely independent processes, as had been hitherto assumed, but could be envisaged in the following way (39): There may occur at the walls of the reaction vessel irreversible decomposition reactions, stimulated by active sites. In the initial phases of the pyrolysis the radical concentration would thus be enhanced above its equilibrium value. Inhibitor action would result from the inhibitor blocking the active sites, thus reducing, at full inhibition, the radical concentration to its equilibrium value.

While different amounts of different inhibitors might be needed to achieve full inhibition, the limiting rate would always be the same, a fact which had been noted in various hydrocarbon pyrolyses (40). Different surface materials would be expected to display active sites at different surface concentrations, and one and the same surface, according to its history, could catalyze the pyrolysis to a greater or lesser degree, as has indeed been found in the pyrolysis of propane (21, 41). However, in these latter studies it was also found that the initial rate of the C_3H_8 pyrolysis decreased by a factor of 3 when the surface/volume ratio was increased by a factor of 10. According to the hypothesis outlined earlier, one must expect the opposite trend, and the authors considered that perhaps in order "to explain the surface effect on the thermal decomposition of hydrocarbons completely different concepts have to be applied" (41). From a later paper dealing with the question of inhibition in paraffin pyrolyses (42) such a new concept is not apparent. A suggestion which could help to explain why a reaction may slow down with increasing S/V has been made by Wojciechowski and Laidler (43); free valencies at the surface may bind radicals, removing them from the chain, but nevertheless keeping them available for termination reactions with free radicals.

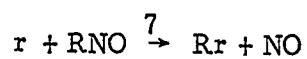
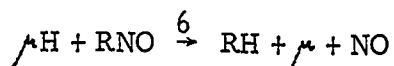
Finally, it is to be noted that Voevodsky's hypothesis does not explain the accelerating effect of NO on many pyrolyses at sufficiently high [NO].

3. a) Laidler's Mechanisms. The suggestion that NO may start as well as stop chains in pyrolyses was made by Rice and Polly in 1938 in a study of the acetaldehyde decomposition in the presence of CH_3ONO , NO, and propylene (3), when it was found that

small amounts of NO can accelerate the reaction under certain conditions. In 1960 Wojciechowski and Laidler (44) pointed out a way to explain all the features of organic NO-influenced pyrolyses as were then known. This was achieved through grafting onto the Rice-Herzfeld schemes some or all of the reactions:

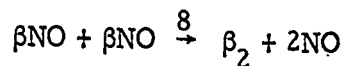


(R → R' + product). Reactions 1 and 2 would always have to be added. In the case of acetaldehyde, for instance, reactions 1, 2, and 3 are needed, C₂H₆ demands reactions 1, -1, 2, and -2. The choice as to which reactions were to be added (besides reactions 1 and 2) was determined by the requirements of the manometrically established kinetics, without the additional constraint which would have been imposed by an analysis of the minor products. Subsequently (43), reactions of the type



(r, R can be both β or μ)

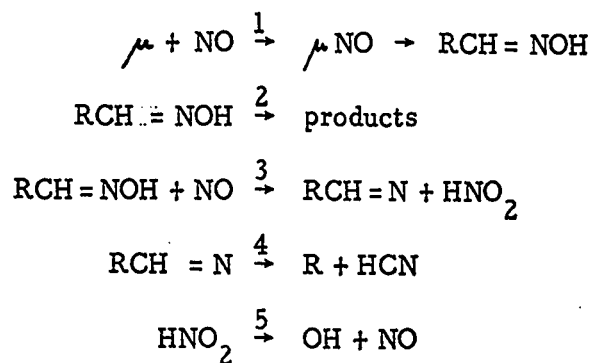
were also considered possible, and the concept of the "Stabilized Radical" (19) was in fact entirely adopted, when the additional reaction



was postulated in a study on acetaldehyde (6) and propionaldehyde (45). Thus quite a large number of possible elementary steps involving NO could be invoked to explain the kinetics of a pyrolysis whose course had been manometrically followed. Since then, however, the requirements to formulate a mechanism have become more stringent, the measurement of rates of product formation having widely become the rule.

3. b) The Norrish-Pratt Proposal. In a different attempt to give a unified scheme (46) explaining the influence of NO on paraffin pyrolyses the possibility was emphasized that oximes, formed according to $\text{RCH}_2 + \text{NO} \rightarrow \text{RCH}_2\text{NO} \rightarrow \text{RCH}=\text{NOH}$, play a decisive role. Already in 1937, formaldoxime had been assumed as an intermediate (47) in NO-influenced organic pyrolyses. The reaction of NO and CH_3OCH_3 was studied by absorption spectroscopy. As the NO-bands weakened, the bands of a product which was thought to be ammonia appeared (48). Formaldoxime was proven to be a product of the decomposition of di-t-butyl peroxide in the presence of NO (49). The dimer of CH_3NO formed at room temperature by photolysis of a mixture of NO and azomethane was found to isomerize to the oxime under certain conditions (50). Decomposition at 480°C of $\text{Hg}(\text{CH}_3)_3$ in the presence of NO followed mass spectrometrically showed a mass of 45 (CH_3NO or $\text{CH}_2=\text{NOH}$); other products were H_2O , HCN, CO, NH_3 , CO_2 and N_2 (51). It had further been demonstrated that the

thermal decompositions of oximes is markedly accelerated by NO ($\text{CH}_2 = \text{NOH}$, (52); $\text{C}_2\text{H}_4 = \text{NOH}$, (53, 54)). Thus the following elementary steps reflecting the action of the NO in hydrocarbon pyrolyses were proposed:



The essence of this scheme consists of providing an alternative quicker route for μ to decompose and generate a new chain barrier β , and therefore will lose its applicability when μ splits with greater ease, as is true for CH_3CO .

II. Aim of this Study.

Since the previous investigations of the thermal decomposition of acetaldehyde in the presence of NO had been carried out mainly manometrically, it was decided to study it again, from a more chemical point of view, emphasis being placed on the analysis of minor products. In the special case of the variable $[\text{NO}]$ being zero, this work would to some extent repeat a previous study (55) which at the same time would provide a check and base whence to consider the influence of NO.

EXPERIMENTAL.

Vacuum Apparatus and Procedure.

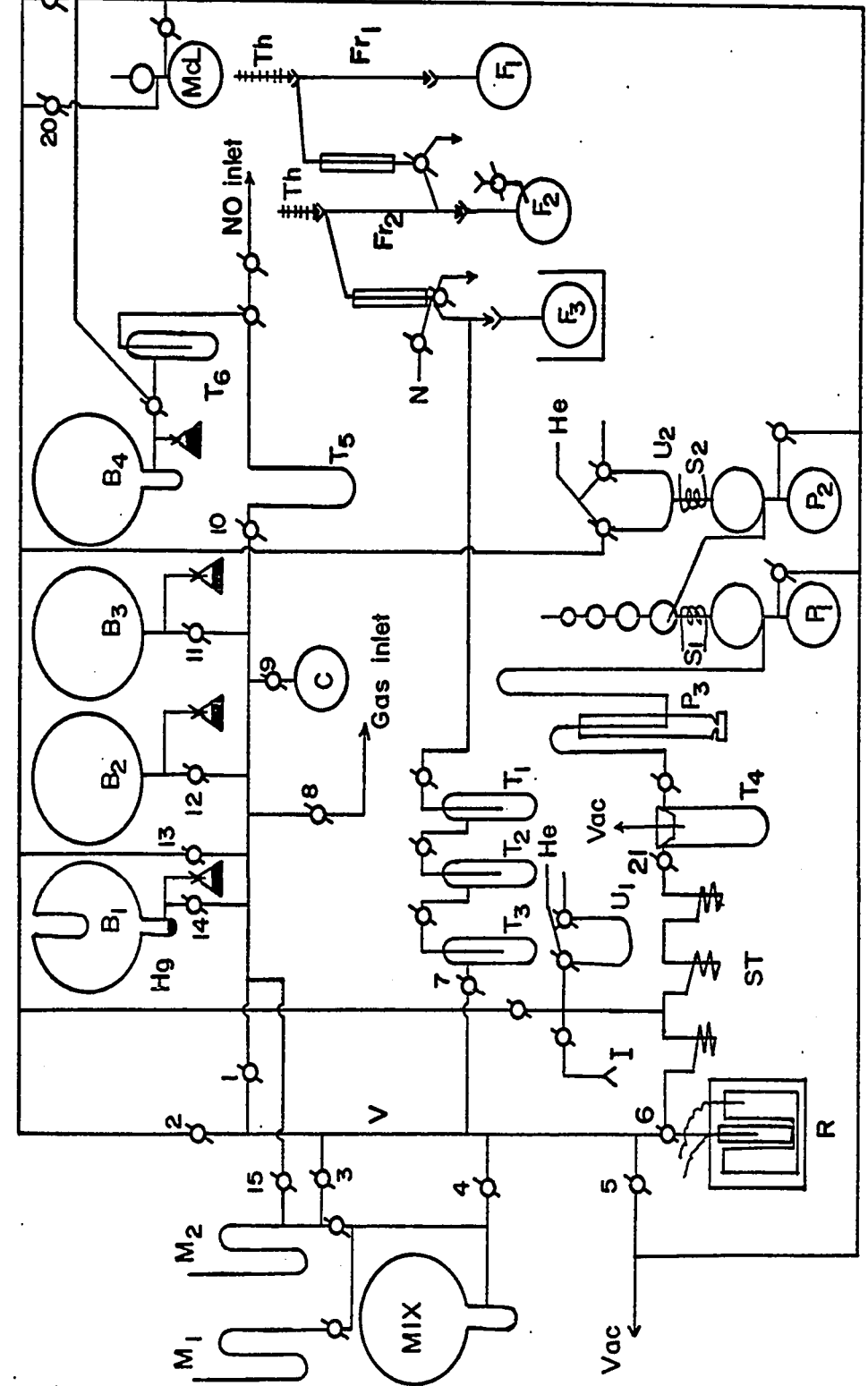
The static system used is shown in Figure 1; it could be evacuated to less than 10^{-5} torr. The stopcocks were lubricated with silicon grease; the stopcocks No. 6, 14, and 20 leading to the reaction vessel, the NO storage vessel, and the McLeod manometer, were also mercury sealed. Bulb C, its volume having been determined by weighing with water, was used to calibrate the volume of the mixing vessel (MIX) and of the section of the line enclosed between stopcocks No. 1, 2, 3, 4, 5, 6, and 7; this section is called V. The pyrex reaction vessel, of cylindrical shape ca. 20 cm long and 4 cm wide, had a volume of 209 cc, with a dead space of ca. 1 cc, and was placed in a cylindrical copper block. It was heated by the use of two independent coils of Nichrome wire, the currents adjusted by powerstats, and one coil controlled by means of an on-off controller actuated by a thermoelement sensing the temperature of the copper block. The temperature of the reaction vessel was measured with a thermocouple placed into a finger-like increscence pointed toward the center of the vessel and could be read on a potentiometer (model MiniMite). The temperature could be controlled as well as measured to within a range of 0.5° , the reaction temperature being established within a uncertainty range of 1° .

Acetaldehyde was stored in F_3 in a water bath kept at a temperature between 10° and 15° C. NO was stored in B_1 over mercury, which could be condensed onto the walls of the trap to provide a large surface. Any NO_2 would thus be removed by the mercury. When a

Figure 1

Schematic diagram of the vacuum apparatus.

High Vac



run was being carried out a sufficient amount of acetaldehyde was transferred to T_1 and pumped through the auxiliary vacuum line Vac for 5 sec while being kept at -78°C . This was repeated three times. Then the acetaldehyde was transferred from T_3 into MIX, until the manometer M_1 showed the desired pressure. Nitric oxide was then introduced into V, the manometer M_2 showing the NO pressure. The nitric oxide was then condensed into MIX at -196° . After 30 min. the transfer was considered complete (p_{NO} at $-196^\circ = 0.08$ torr (56)), the coolant removed, and the mixture allowed to stand for the desired length of time; this was usually one hour, except in those experiments in which the effect of longer mixing times was to be studied. From the mixing vessel the mixture was allowed to expand into the reaction vessel. The products of the reaction were determined gas-chromatographically, with the exception of the CH_4 and CO, which are the major products, and the NO; these were measured by means of the gas buret on Toepler pump P_1 . The products were separated into three fractions: the "noncondensables" CH_4 , CO, N_2 , H_2 ; the "light condensables" NO, CO_2 , N_2O , C_2H_4 , C_2H_6 ; the "heavy condensables" comprised all the other products. The separation was accomplished as follows: the reaction mixture was expanded through the spiral traps ST at -196° where the "heavy condensables" and most of the "light condensables", including some NO, were retained, through the solid nitrogen trap T_4 at -210° where the rest of the NO and remaining traces of the other "light condensables" condensed, into the Toepler pump P_1 . There the "noncondensables" were collected and their volume measured; they were then transferred by means of the Toepler pump P_2 into the sampling tube U_2 , whence they were carried by a helium stream into the gas chromatograph. The valves in the Toepler pumps could be magnetically controlled by

means of the solenoids S_1 and S_2 . Sufficient time having been allowed for the NO trapped in ST to pass into T_4 (the larger the amount of NO, the longer the transfer takes), T_4 was warmed up (stopcock 21 having been closed), and the NO was collected by P_1 and measured in the gas burette. The "heavy condensables" and the "light condensables" still trapped in ST were subsequently condensed into U_1 at -196° . U_1 was then warmed up to and kept at -78° so that the "light condensables" could be drawn off into P_1 . There they were combined with the NO, transferred to U_2 by means of P_2 , and gas-chromatographed. The "heavy condensables" were gas-chromatographed from U_1 .

The transfer of gases into the Toepler pump P_1 was facilitated by the mercury diffusion pump P_3 .

The acetaldehyde was prepared from paraldehyde (BDH Laboratory Grade) which was distilled from F_1 into F_2 where the middle cut was received. Subsequently this was converted into acetaldehyde by the use of a few drops of concentrated H_2SO_4 as a catalyst. The middle cut of the acetaldehyde, which was easily separated from the paraldehyde by fractional distillation through column Fr_2 , was collected in F_3 . Once the flask F_1 with the paraldehyde had been attached the aldehyde no longer came in contact with air. Before the distillation was started, the air in the conversion system was evacuated and replaced by N_2 introduced through N , and throughout the distillation the system remained connected to the N_2 source to ensure the absence of O_2 .

The nitric oxide, obtained from Matheson, was introduced from the cylinder into B_4 via trap T_6 , kept at -78° . There most of the contaminating NO_2 condensed, as evidenced by the deep blue color of the condensate. From B_4 the NO was then passed through the trap

T₅ into B₁. T₅, a tube filled with silica gel, was kept at -98° (m. p. of methanol) to retain the rest of the contaminants, such as NO₂, CO₂, N₂O. Traces of N₂ could be removed by pumping the condensed NO at -196°. The NO so purified had only a slight bluish color when liquid. Since the color did not change in intensity or hue even after long storage over mercury it is concluded that pure liquid NO is not quite colorless, but is bluish.

Other compounds, for the purpose of comparison or calibration, were introduced through the gas inlet (so marked) or through the inlet for condensed substances (I).

The Gas Chromatograph.

The detector was a tungsten-wire thermal conductivity cell (Gow-Mac, model 9285), fed by a power supply (Trygon, model HR 40-750), whose signal was recorded with an automatic compensator (Philips, model PR 2216 A/21). Helium was used as the carrier gas at a flow rate of 35 cc/min. Four chromatographic columns were employed, made of 1/4" copper tubing:

1. for the "noncondensables"
Silica gel 60/80 mesh, L = 1.8 m, at -78°C;
2. for the "light condensables"
Porapak S 80/100 mesh, L = 2 m, at 0°C;
3. for H₂O, C₃H₆, and HCN
Porapak Q 80/100 mesh, L = 3 m, at 35°C;
4. for the other "heavy condensables" comprising all the remaining products, Teflon powder 40/60 mesh, coated with tetraethyleneglycoldimethylether (CH₃-(OCH₂CH₂)₄-OCH₃) (4% by weight),
L = 3 m, at 35°C.

Several other columns were also tried, but under conditions of isothermal operation as employed here did not work satisfactorily. Because there was such a variety of products, the "heavy condensable" fraction could not be analyzed on one single column. Two runs had to be made, one for the H_2O , C_3H_6 , and HCN, one for the rest. An additional difficulty was caused by the fact that the reactant acetaldehyde tended to swamp products having similar retention times, i. e., most of the other condensables. Those products which had nearly the same retention time would not be detectable at all. Attempts were made to find stationary phases which would alter the sequence of elution. It was possible to reverse the order of elution of H_2O and HCN with respect to acetaldehyde, but the relative retention times of the organic substances could only be affected slightly. To circumvent an excessive interference by the acetaldehyde it was decided to eliminate it (see Figure 2) by passing the products into the column, allowing the acetaldehyde to be eluted just beyond its peak maximum, and then reversing the flow and collecting at -196° what had not yet emerged. The reverse flow was maintained for twice as long as the regular flow. The flow through the column was then restored to its original direction, the collected substances warmed up and again injected into the column. Repetition of this cycle of operations by three times was sufficient to allow the determination of the compounds eluted after the acetaldehyde. Before the final injection to obtain the chromatogram the collector was partially evacuated (while still at -196°) in order to prevent unnecessary spreading of the sample owing to expansion of the cold gas contained in it.

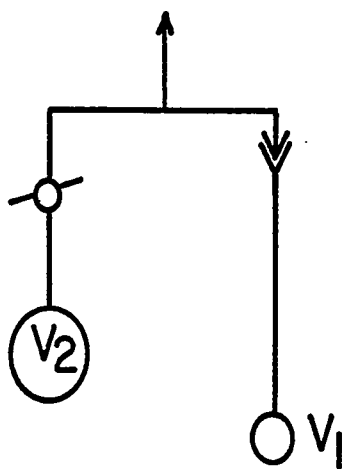
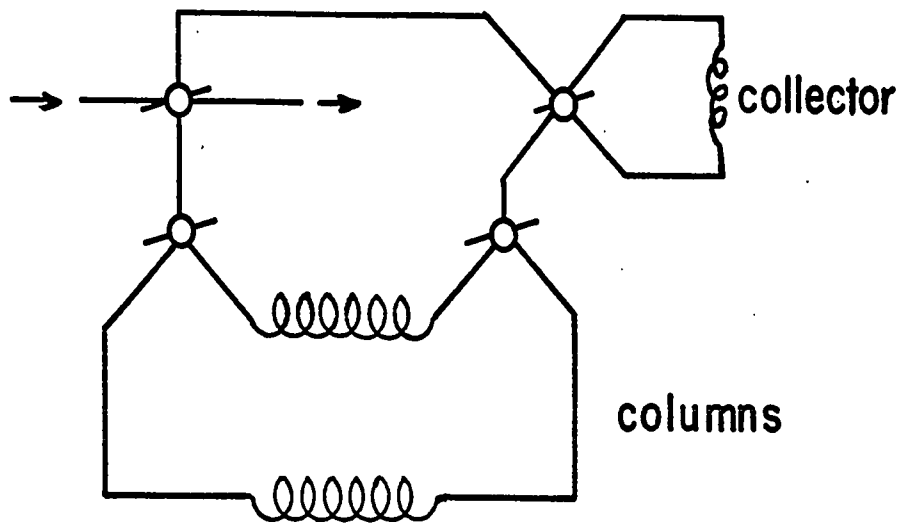
In order not to contaminate the product condensate with extraneous substances the helium, being slightly moist, was passed

Figure 2

Auxiliary devices

above: Arrangement for the elimination of excessive acetaldehyde from the product mixture.

below: Measuring device used for some calibrations.



through a spiral trap filled with crushed glass kept continuously at -196° for drying. The helium stream could be switched to flow through a sampling device situated downstream from the detector. In this way a compound, while giving its chromatographic signal, could be trapped for mass-spectrometric analysis.

RESULTS.

I. Products.

Beside the customary problems met in the investigation of a pyrolysis reaction, an additional difficulty was encountered in this work with mixtures of acetaldehyde and nitric oxide. It was found that the length of the mixing period prior to pyrolysis had an influence on the rate of product formation. The reason for this phenomenon must be a slow reaction in the gaseous mixture at room temperature. In the absence of light, which was ensured by wrapping the mixing vessel completely in aluminium foil, the process was found to occur undiminished, which proves that this "cold" reaction is not of a photochemical nature. In an attempt to determine its cause unpyrolyzed mixture was left standing for various lengths of time and then analyzed. Thus, because of this complication, the products, which are described in this section, have a very different origin, namely,

a) the pyrolysis

b) the cold reaction.

a) The kinetics of the pyrolysis depended on several experimental variables, among which are temperature, nitric oxide and acetaldehyde pressures, and mixing time. The reaction was explored over a broad range of the first two variables; for lack of time the others were only occasionally changed, rather as a matter of testing the trend. The results are collected in Tables 1, 2, and 3 at the end of this section. Furthermore, in a few tests several chemical compounds,

among them some of those discovered in the "cold" reaction, were added to and copolyolyzed with the acetaldehyde-nitric oxide mixture to study their influence on the product yield. These tests are summarized in Table 4.

Compounds identified as pyrolysis products were:

N_2	CO	CH_3NCO	C_3H_6
N_2O	CO_2	C_2H_4	CH_3COCH_3
H_2	HCN	C_2H_6	C_2H_5CHO
H_2O	CH_4	C_2H_5NCO	$CH_3CO_2C_2H_3$

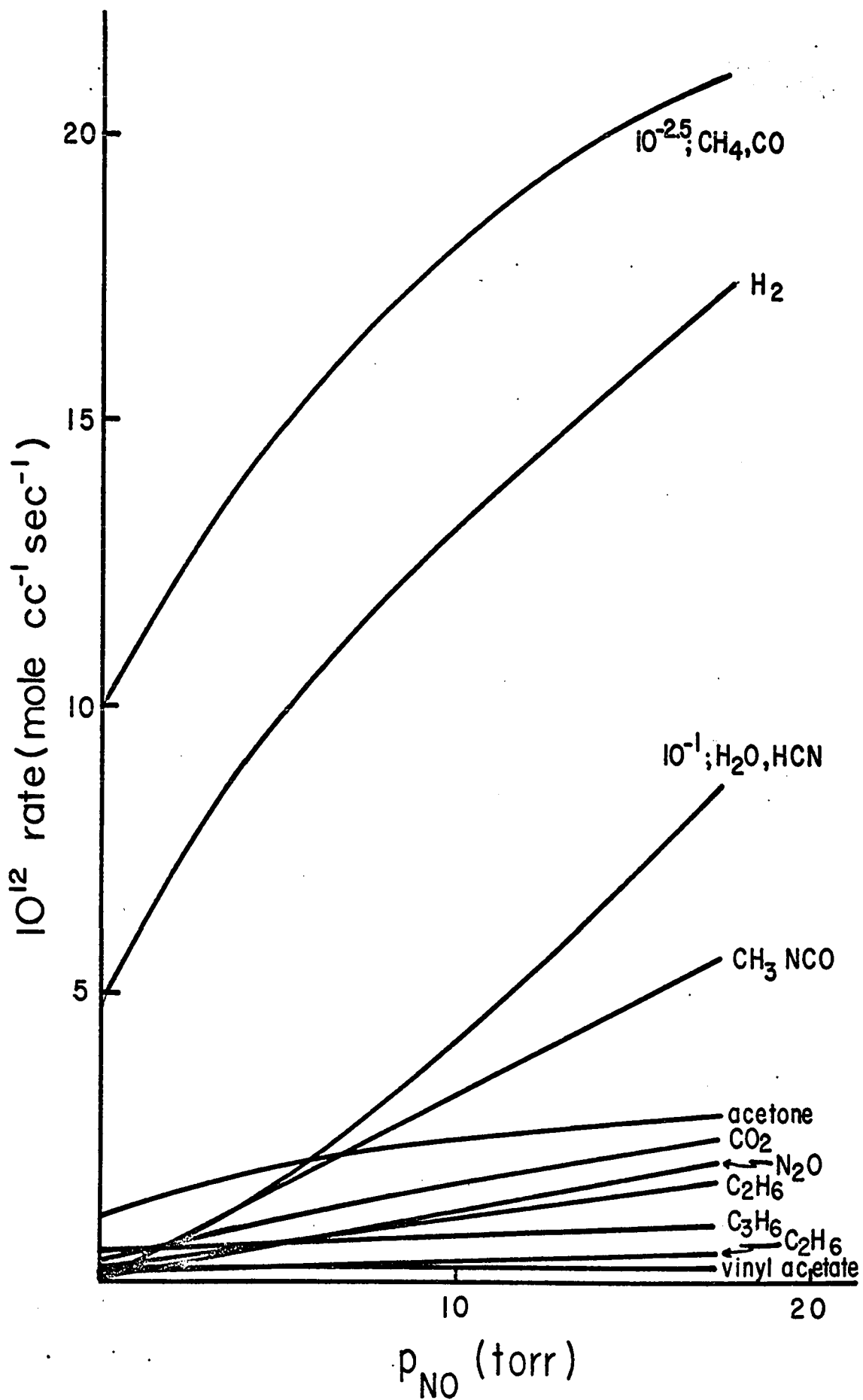
The rates of all except C_2H_5CHO could be measured throughout the range of $[NO]$ investigated. C_2H_5CHO , present in very small amounts, was measurable in the absence of NO ; however, in the presence of NO it is swamped by CH_3NCO , whose gas-chromatographic retention time is very similar. A small amount of a compound was found which was assumed to be crotonaldehyde, having the same retention time as the latter and showing a molecular weight of 70 when analyzed in the mass spectrometer. The rates of formation of all products except N_2 , C_2H_5NCO , and C_2H_5CHO are schematically shown in Figure 3 as functions of p_{NO} at $500^\circ C$.

Various compounds were tested on the gas-chromatograph in the presence of an excess of acetaldehyde. In this way it was found that the following could be analyzed, but were not detected as products:

CH_2O	CH_3ONO_2	CH_3CN	$(CH_3)_2CHOH$
CH_3ONO	CH_3OH	C_2H_5OH	$CH_3CO-COCH_3$
CH_3NO_2	CH_2CO	$C_2H_3OCH_3$	

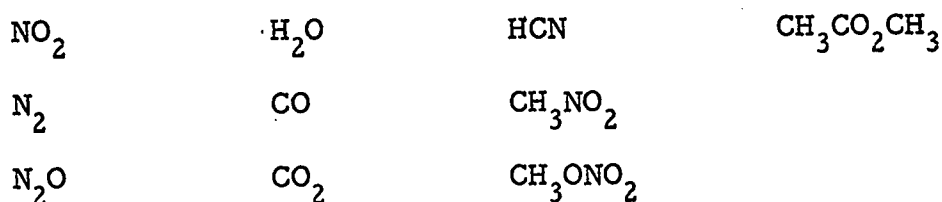
Figure 3

The rates of formation of various pyrolysis products ($p_a = 176.0$ torr, $T = 500^\circ\text{C}$).



In an effort to find an additional reaction that produced hydrogen atoms, important in the explanation of the NO-free pyrolysis (see Discussion), the compound $\text{CH}_3\text{CO}-\text{CH}=\text{CHOH}$ (tautomeric with $\text{CH}_3\text{CO}-\text{CH}_2\text{CHO}$) was tested, set free from its sodium salt by sulfuric acid. The salt had been prepared from sodium, acetone, and ethyl formate in a Claisen condensation reaction (57). Although gas chromatograms of β -ketobutyraldehyde could be obtained in the absence of acetaldehyde, the substance is apparently sufficiently reactive that it will quickly disappear when mixed with CH_3CHO . The pure compound is unstable and will polymerize (57).

b) The "cold" reaction, which was not studied in any great detail, neither kinetically nor product-wise, was found to give rise to the following products:



The behavior of a cold mixture in the course of several hours is shown in Figure 4.

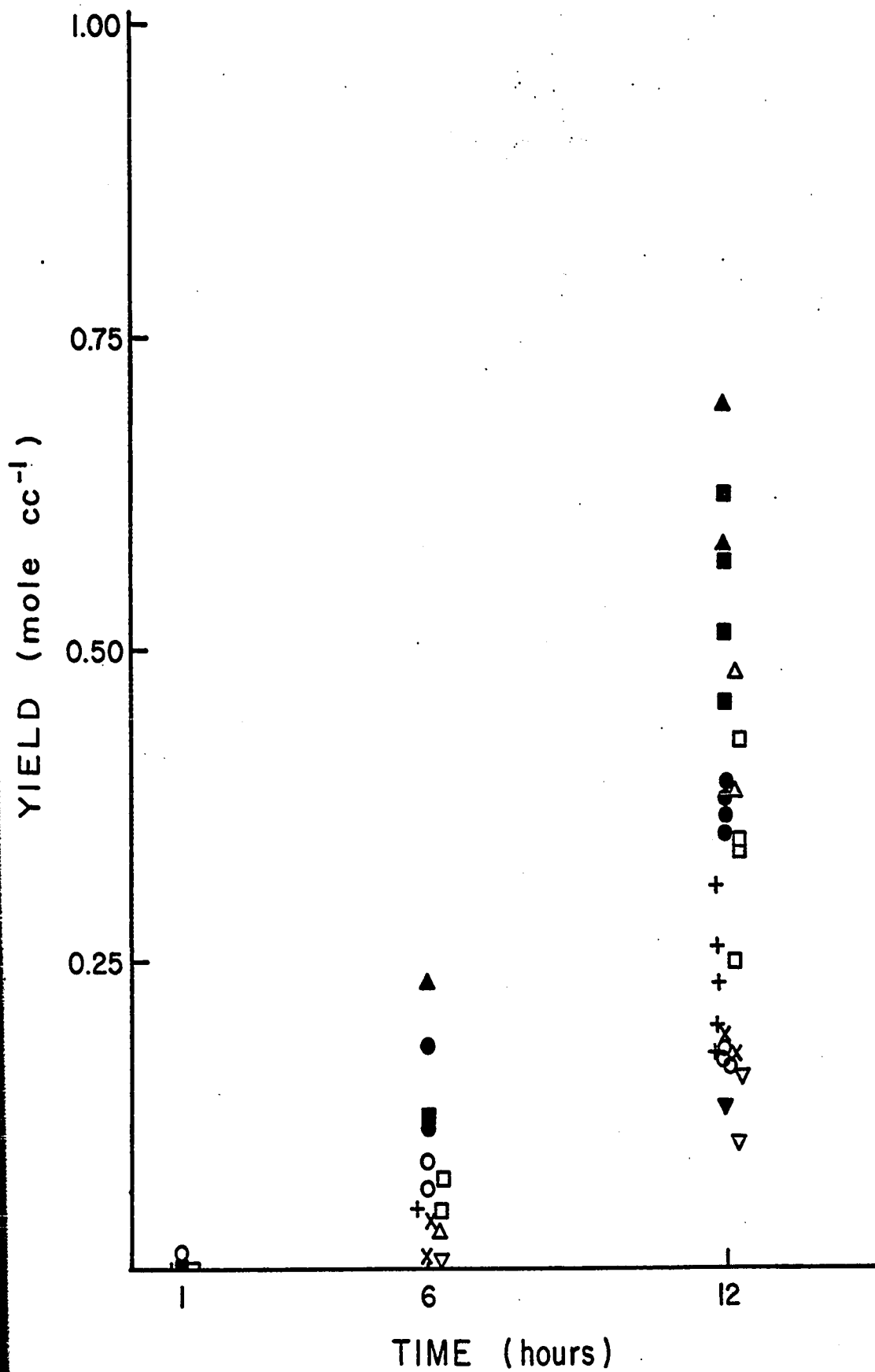
II. Identification of Products.

The "noncondensables" and "light condensables" were identified by gas-chromatographic comparison with the commercially available gases. In the same way were recognized H_2O , acetone, HCN, and propionaldehyde. It is noted that in the search for gas-chromatographic columns best suited for analysis, these compounds were identified on different columns so that spurious identification

Figure 4

Yield of various products of a slow reaction between acetaldehyde vapour and nitric oxide occurring at room temperature ($p_a = 200$ torr, $p_{NO} = 14$ torr).

Symbol	Compound	Scale factor to be applied
▽	H ₂ O	10 ⁻⁷
▼	CO	10 ⁻⁹
○	NO	10 ⁻⁶
×	N ₂ O	10 ⁻⁸
+	methyl acetate	10 ⁻⁹
□	CO ₂	10 ^{-7.7}
●	N ₂	10 ⁻⁷
△	HCN	10 ⁻⁸
■	CH ₃ NO ₃	10 ⁻⁹
▲	CH ₃ NO ₂	10 ⁻⁹



can be ruled out. The HCN was prepared in a small amount from sodium cyanide and concentrated phosphoric acid and repeatedly distilled at low temperatures to eliminate the water. All the remaining products, except nitrogen dioxide, in addition to gas-chromatographic identification, were subjected to mass-spectrometric analysis. In some cases the lower part of the spectrum was obscured to some extent by acetaldehyde contaminating the sample which was usually quite a small amount between 10^{-7} and 10^{-8} mole. CH_3ONO (58) and CH_3ONO_2 (59) were synthesized to measure their gas-chromatographic retention times.

Nitrogen dioxide could not be analyzed gas-chromatographically in the presence of acetaldehyde. A distinct blue colour was observed, however, when the cold mixtures of CH_3CHO and NO were condensed after long standing, suggesting the presence of N_2O_3 . Furthermore, a mixture which had been left for about two days acquired a slight brownish tinge characteristic of NO_2 . No such clear evidence was obtained concerning the formation of NO_2 in the pyrolysis, but it was noted that a small deposit of a mercury-containing substance slowly formed in the course of this study, explicable if one assumes oxidation of Hg condensed with the sample in U_1 by a higher oxide of nitrogen leading either to mercury nitrite or nitrate, which in its turn may react with HCN to form $\text{Hg}(\text{CN})_2$. For testing purposes NO_2 was made by decomposing dry $\text{Pb}(\text{NO}_3)_2$ and distilling and pumping it repeatedly to remove the contaminating O_2 .

III. Calibration.

The "noncondensables" and "light condensables" were introduced into the vacuum system via the gas inlet (Figure 1). Suitable amounts were measured out in the gas buret using the ideal gas law, transferred to U_2 , and passed into the gas chromatograph. The "heavy condensables" were introduced through an inlet near U_1 marked I by means of a measuring device shown schematically in Figure 2. A few drops of the compound were put into V_1 , repeatedly degassed at -196° and then thermostatted at the desired temperature. The previously evacuated device was then left for at least 30 min while the vapour pressure became established in V_2 , whose volume was known. A well-defined amount of the compound calculated according to the ideal gas law would thus be contained in V_2 at room temperature. The gas-chromatographic signals were evaluated by measuring peak heights or by determining the peak areas using an "Aristo" portable planimeter. Vapour pressure data were taken from ref. 56. For CH_3NCO , C_2H_5CHO , C_2H_5NCO , and CH_3ONO_2 such data were not available, but their amounts could be estimated in the following way: Considering that they differ not very much from acetone as far as molecular weight and size is concerned, one may assume that their influence on the thermal conductivity of He to which they are admixed is of similar magnitude. Thus the ratio of the peak area to concentration in the He will be about the same. For Gaussian curve peaks the relationship holds: $Area = const \cdot Height \cdot Half\ width$. The half widths of similar compounds on the same column are proportional to their retention times (60). Therefore the amount n , which is proportional to the area, must also be proportional to both peak height and retention time, $n = c \cdot h \cdot t_R$. From the acetone calibration one gets $c = (n/h \cdot t_R)_{acetone}$, so that n can be calculated.

IV. Rates of Product Formation.

In Table 1 rates of pyrolysis product formation are given as functions of temperature and nitric oxide pressure. The temperature ranges from 450°C to 525°C; the nitric oxide pressures employed go from zero up to 47 torr, the acetaldehyde pressure being always 176 torr. The mixing time is always one hour. The rates of nitric oxide disappearance are fraught with rather large uncertainties, the amounts of NO consumed having been obtained as the small difference of two larger quantities. With some products, e. g. H₂O, HCN, and CH₃NCO, results from a group of runs repeated after several months show a considerable divergence, indicating an uncontrollable surface effect. Rates of propionaldehyde formation could only be measured in the absence of NO, since its gas-chromatographic signal was almost completely swamped by that of methyl isocyanate, present in a relatively larger amount, even at the lowest nitric oxide pressures employed.

In Table 2 the rates are given as functions of the acetaldehyde pressure, which ranges from 88 torr to 264 torr, with $p_{\text{NO}} = 12.38$ torr, $T = 475^\circ\text{C}$, and the mixing time one hour. Comments on v_{NO} , $v_{\text{H}_2\text{O}}$, v_{HCN} , and $v_{\text{CH}_3\text{NCO}}$ have been made in connection with Table 1.

Table 3 gives some information about the dependence of various rates on mixing time. In this and the following table the rates are not meant to be initial rates, but are defined in the following way:

$$\text{rate} = \frac{\text{yield, after one hour of mixing}}{\text{reaction time} \cdot \text{reaction volume}}$$

In the last column of Table 3 are listed the derivatives of the rates with respect to mixing time, obtained from plots like those in Figure 5 and Figure 6.

Figure 5

Dependence of v_{acetone} on reactant mixing time

$$P_{\text{CH}_3\text{CHO}} = 176.0 \text{ torr}$$

$$P_{\text{NO}} = 12.38 \text{ torr}$$

$$T = 450^\circ \text{C}$$

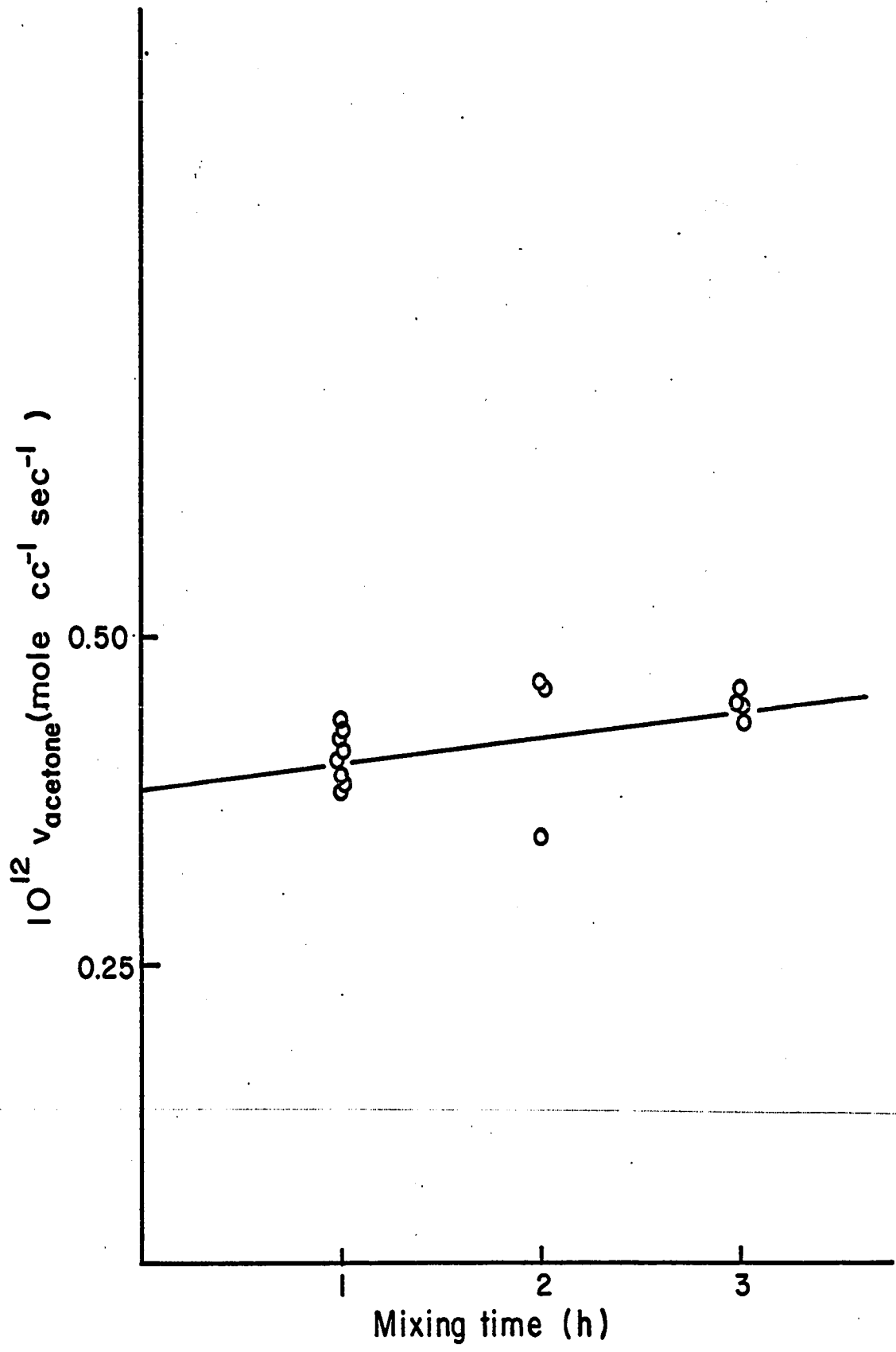


Figure 6

Dependence of v_{N_2} on reactant mixing time

$$P_{CH_3CHO} = 176.0 \text{ torr}$$

$$P_{NO} = 18.57 \text{ torr}$$

$$T = 525^{\circ}C$$

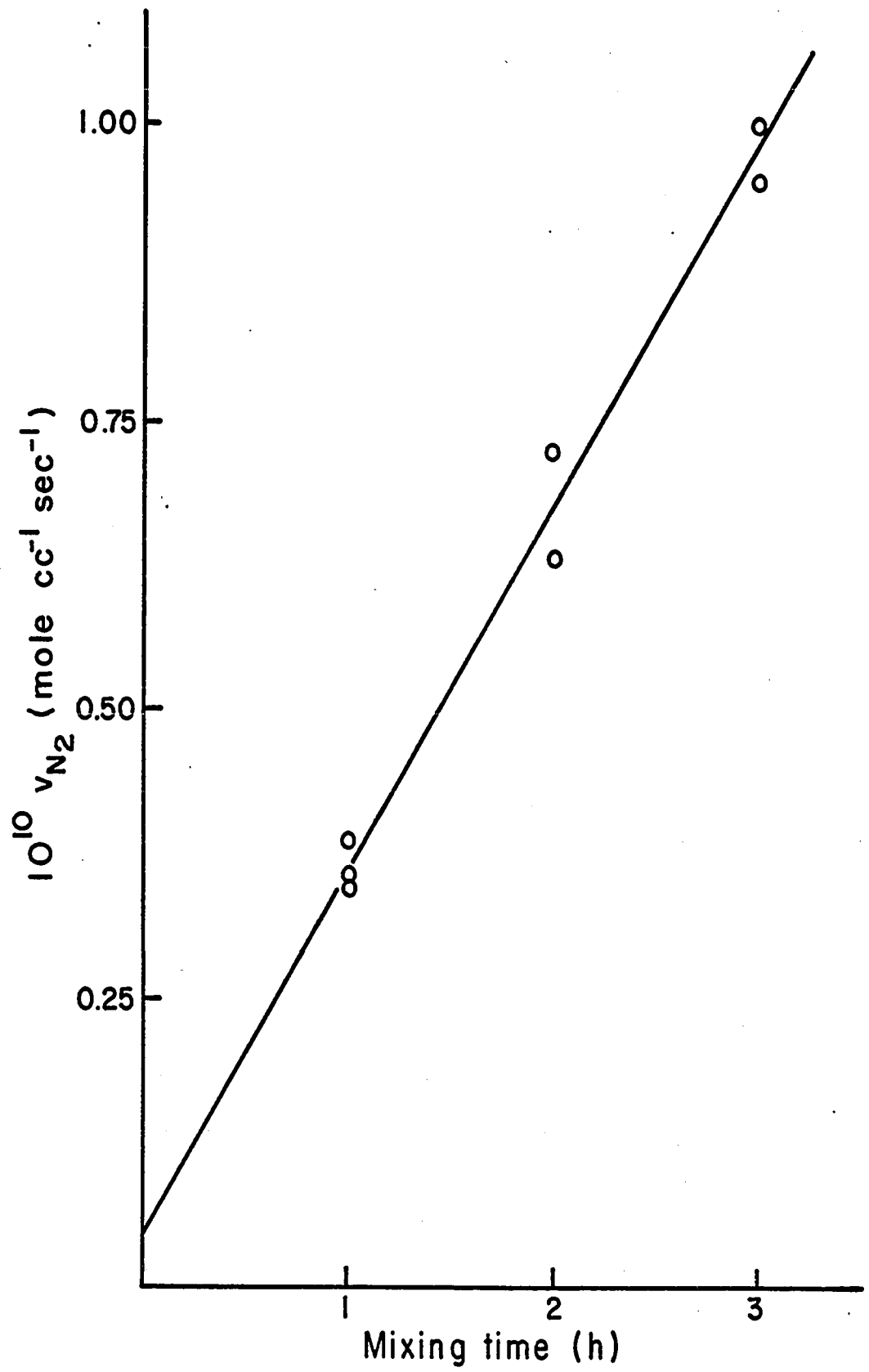


Table 4 shows the results of some tests where NO_2 , methyl acetate, CH_3NO_2 , CH_3ONO , and CH_3ONO_2 were copyrolyzed with the acetaldehyde-nitric oxide mixture. The first column contains the rate values (defined as in Table 3) of the pyrolysis without additive. The numbers at the top of the first column are rather putative, having been obtained from Figure 4, with the NO_2 pressure assumed to be about equal to the N_2 pressure.

Table 1. Rates of pyrolysis product formation as functions of temperature and nitric oxide pressure (acetaldehyde pressure 176.0 torr, mixing time one hour).

Rate (mole cc ⁻¹ sec ⁻¹)	Nitric oxide pressure in torr →									
	T(°C)	0.0	3.09	6.19	9.28	12.38	18.57	22.59	35.34	47.20
10 ⁹ v CH ₄ , 10 ⁹ v CO	450	0.443	0.755	0.875	1.03	1.30				
	475	1.17	1.90	2.20	2.39	2.58		3.23	3.78	4.12
	500	2.99		5.15	5.95	6.00	6.75			
	525	7.55		11.25		12.05	15.65			
-10 ¹¹ v NO	450		0.469	1.05	1.79	2.34				
	475		0.479	1.75	2.92	3.97		4.31	8.61	20.1
	500			1.91	7.18	8.13	17.7			
	525			6.22		14.4	27.3			
10 ¹² v N ₂	450		0.239	0.766	1.96	3.25				
	475		0.589	1.72	3.21	4.88		14.4	26.8	32.5
	500			3.16	6.22	10.8	19.1			
	525			6.22		16.7	36.4			
10 ¹² v H ₂	450									
	475	2.11	4.16	4.02	3.92	4.98		7.18	9.57	19.1
	500	4.79		11.5	13.4	14.4	18.2			
	525	21.1		30.6		31.6	43.1			

Table 1 continued

Rate (mole cc ⁻¹ sec ⁻¹)	T(°C)	Nitric oxide pressure in torr →												
		0.0	3.09	6.19	9.28	12.38	18.57	22.59	35.34	47.20				
¹³ vCO ₂	450	0.67	1.00	2.25	3.73	5.93								
	475	1.58	3.16	4.12	5.93	9.47					16.3	25.4	36.8	
	500	3.34		9.09	14.1	17.2	28.2							
	525	8.13		21.5		35.9	53.6							
¹³ vN ₂ O	450		0.718		2.82	4.83								
	475		1.24	4.49	4.88	8.61				44.0	71.8	134.0		
	500			3.83	12.4	13.9	20.1							
	525			10.5		17.2	37.3							
¹³ vC ₂ H ₄	450	0.211	0.278	0.536	0.603	0.766								
	475	0.516	1.04	1.14	1.51	1.85					2.58	3.83	5.26	
	500	0.765		3.11	3.73	4.30	4.74							
	525	4.88		7.27		9.86	12.4							
¹³ vC ₂ H ₆	450	0.263	0.670	0.957	1.44	2.15								
	475	0.861	2.11	3.06	3.73	4.31					6.22	9.09	8.61	
	500	3.35		9.57	12.9	13.9	20.6							
	525	11.0		29.7		40.2	56.0							
¹¹ vH ₂ O	450		0.186	0.402	0.723	1.22								
	475		1.12	1.09	1.67	2.13					5.74	10.5	13.8	
	500			1.96	3.97	5.31	9.52							
	525			4.21		9.19	19.5							

Table 1 continued

Rate (mole cc ⁻¹ sec ⁻¹)	T(°C)	Nitric oxide pressure in torr →												
		0.0	3.09	6.19	9.28	12.38	18.57	22.59	35.34	47.20				
¹³ C ₃ H ₆	450		1.29	1.24	1.15	1.05								
	475	2.25	2.78	2.78	2.78	2.78								
	500	5.02		10.0	14.8	10.0	8.61							
	525	19.1		22.0		22.0	24.9							
¹¹ VHCN	450		0.134	0.450	0.880	1.36								
	475		0.316	0.938	1.63	2.23		5.74	9.76	10.5				
	500			1.77	2.39	5.89	9.95							
	525			3.54		9.86	19.1							
¹² VCH ₃ NCO	450		0.426	0.847	1.19	1.72								
	475		0.435	1.10	1.65	2.32		5.26	7.37	8.85				
	500			1.72	1.96	4.83	6.51							
	525			3.35		5.36	11.5							
¹³ C ₂ H ₅ CHO	450	0.120												
	475	0.479												
	500	1.44												
	525	5.07												

Table 1 continued

Rate (mole cc ⁻¹ sec ⁻¹)	Nitric oxide pressure in torr →									
	T(°C)	0.0	3.09	6.19	9.28	12.38	18.57	22.59	35.34	47.20
¹² VCH ₃ COCH ₃	450	0.158	0.273	0.321	0.359	0.416				
	475	0.426	0.852	0.967	1.07	1.08		1.34	1.44	1.48
	500	1.24		2.34	2.68	2.78	3.25			
	525	3.64		5.17		6.03	6.79			
¹³ V ₂ C ₂ H ₅ NCO	450		0.507	0.715	1.20	1.87				
	475		0.572	1.08	1.44	2.21		3.25	3.51	3.90
	500			2.08	1.82	4.29	4.81			
	525			2.86		4.42	9.36			
¹³ VCH ₃ CO ₂ C ₂ H ₃	450		0.174	0.244	0.322	0.296				
	475		0.592	0.905	0.696	0.783				
	500			2.09	1.65	1.57	2.18			
	525			7.48		7.66	7.66			

Table 2. Rates of pyrolysis product formation as functions of acetaldehyde pressure (nitric oxide pressure 12.38 torr, T = 475°C, mixing time one hour).

Rate (mole cc ⁻¹ sec ⁻¹)	Acetaldehyde pressure (torr)		
	88.0	176.0	264.0
$10^9 v_{\text{CH}_4} = 10^9 v_{\text{CO}}$	0.835	2.58	4.98
$10^{11} v_{\text{NO}}$	1.91	3.97	5.74
$10^{12} v_{\text{N}_2}$	3.35	4.88	6.27
$10^{12} v_{\text{H}_2}$	2.11	4.98	9.57
$10^{13} v_{\text{CO}_2}$	4.40	9.47	10.8
$10^{13} v_{\text{N}_2\text{O}}$	8.61	8.61	10.8
$10^{13} v_{\text{C}_2\text{H}_4}$	3.83	18.5	21.5
$10^{13} v_{\text{C}_2\text{H}_6}$	1.72	4.31	7.66
$10^{11} v_{\text{H}_2\text{O}}$	1.29	2.13 2.97	3.68
$10^{13} v_{\text{C}_3\text{H}_6}$	1.24	2.78	5.65
$10^{11} v_{\text{HCN}}$	1.36	2.23 2.97	3.68
$10^{12} v_{\text{CH}_3\text{NCO}}$	1.40	2.32 3.59	6.32
$10^{12} v_{\text{CH}_3\text{COCH}_3}$	0.306	1.08	2.02
$10^{13} v_{\text{C}_2\text{H}_5\text{NCO}}$	0.455	2.21	5.20
$10^{13} v_{\text{CH}_3\text{CO}_2\text{C}_2\text{H}_3}$		0.783	0.696

Table 3. Rates of pyrolysis product formation as functions of reactant mixing time (acetaldehyde pressure 176.0 torr).

Compound	T(°C)	P _{NO} (torr)	v(mole cc ⁻¹ sec ⁻¹)*	dv/dt _{mix} (mole sec ⁻¹ cc ⁻¹ h ⁻¹)
CH ₄ +CO	450	12.38	2.01·10 ⁻⁹	0.11·10 ⁻⁹
	475	12.38	5.12·10 ⁻⁹	0.43·10 ⁻⁹
	475	22.59	8.88·10 ⁻⁹	0.96·10 ⁻⁹
	525	18.57	25.6 ·10 ⁻⁹	-
NO	450	12.38	-2.78·10 ⁻¹¹	-0.43·10 ⁻¹¹
	475	12.38	-5.28·10 ⁻¹¹	-1.60·10 ⁻¹¹
	475	22.59	-6.00·10 ⁻¹¹	-5.52·10 ⁻¹¹
	525	18.57	-33.6 ·10 ⁻¹¹	-10.1 ·10 ⁻¹¹
N ₂	450	12.38	3.07·10 ⁻¹²	1.73·10 ⁻¹²
	475	12.38	4.80·10 ⁻¹²	4.30·10 ⁻¹²
	475	22.59	16.3 ·10 ⁻¹²	15.6 ·10 ⁻¹²
	525	18.57	35.5 ·10 ⁻¹²	31.8 ·10 ⁻¹²
CO ₂	450	12.38	5.76·10 ⁻¹³	1.06·10 ⁻¹³
	475	12.38	8.80·10 ⁻¹³	2.40·10 ⁻¹³
	475	22.59	19.2 ·10 ⁻¹³	19.2 ·10 ⁻¹³
	525	18.57	50.4 ·10 ⁻¹³	30.2 ·10 ⁻¹³

*

$$v = \frac{\text{yield, after one hour of mixing}}{\text{reaction time} \cdot \text{reaction volume}}$$

Table 3 continued

Compound	T(°C)	p _{NO} (torr)	v(mole cc ⁻¹ sec ⁻¹)*	dv/dt _{mix} (mole sec ⁻¹ cc ⁻¹ h ⁻¹)
N ₂ O	450	12.38	4.70 · 10 ⁻¹³	0.86 · 10 ⁻¹³
	475	12.38	14.1 · 10 ⁻¹³	1.92 · 10 ⁻¹³
	475	22.59	43.7 · 10 ⁻¹³	4.37 · 10 ⁻¹³
	525	18.57	55.1 · 10 ⁻¹³	5.30 · 10 ⁻¹³
C ₂ H ₆	450	12.38	1.73 · 10 ⁻¹³	0.48 · 10 ⁻¹³
	475	12.38	4.00 · 10 ⁻¹³	2.40 · 10 ⁻¹³
	475	22.59	6.72 · 10 ⁻¹³	7.20 · 10 ⁻¹³
	525	18.57	50.4 · 10 ⁻¹³	13.3 · 10 ⁻¹³
C ₂ H ₅ NCO	450	12.38	0.60 · 10 ⁻¹³	0.34 · 10 ⁻¹³ · t _{mix} **
	475	12.38	1.72 · 10 ⁻¹³	0.90 · 10 ⁻¹³ · t _{mix}
	475	22.59	3.25 · 10 ⁻¹³	3.90 · 10 ⁻¹³ · t _{mix}
	525	18.57	8.64 · 10 ⁻¹³	7.20 · 10 ⁻¹³ · t _{mix}

* $v = \frac{\text{yield, after one hour of mixing}}{\text{reaction time} \cdot \text{reaction volume}}$

** $v_{\text{C}_2\text{H}_5\text{NCO}}$ is approximately proportional to the square of the mixing time.

Table 4

Influence of various additives on the rates of formation of some pyrolysis products (acetaldehyde pressure 176.0 torr; nitric oxide pressure 12.38 torr; T = 475°C; mixing time 1 hour; reaction time 300 sec).

a) NO ₂ added	p(torr) (approx.)			
	rate (mole cc ⁻¹ sec ⁻¹)*	1·10 ⁻²	5·10 ⁻²	5·10 ⁻¹
10 ⁹ _v CH ₄		2.6	2.8	2.1
10 ¹¹ _v NO		-6.0	-6.0	-2.0
10 ¹² _v N ₂		4.8	5.8	5.6
10 ¹² _v CO ₂		1.1	6.4	21.0
10 ¹² _v N ₂ O		1.6	1.9	2.0
10 ¹³ _v C ₂ H ₄		1.4	2.8	2.1
10 ¹³ _v C ₂ H ₆		5.5	7.7	3.7
10 ¹² _v CH ₃ NCO		2.7	1.9	1.6
10 ¹² _v CH ₃ COCH ₃		1.1	1.1	0.9
10 ¹³ _v C ₂ H ₅ NCO		2.2	2.0	1.5

Table 4 continued

b) $\text{CH}_3\text{CO}_2\text{CH}_3$ added rate (mole $\text{cc}^{-1}\text{sec}^{-1}$)*	p(torr) (approx.)	
	$1 \cdot 10^{-4}$	$5 \cdot 10^{-1}$
$10^9 v_{\text{CH}_4}$	2.6	2.8
$10^{11} v_{\text{NO}}$	-6.0	-6.4
$10^{12} v_{\text{N}_2}$	4.8	5.0
$10^{12} v_{\text{CO}_2}$	1.1	1.3
$10^{12} v_{\text{N}_2\text{O}}$	1.6	1.7
$10^{13} v_{\text{C}_2\text{H}_4}$	1.4	1.7
$10^{13} v_{\text{C}_2\text{H}_6}$	5.5	4.8
$10^{12} v_{\text{CH}_3\text{NCO}}$	2.7	2.9
$10^{12} v_{\text{CH}_3\text{COCH}_3}$	1.1	1.0

Table 4 continued

c) CH ₃ NO ₂ added	p(torr) (approx.)			
	rate (mole cc ⁻¹ sec ⁻¹)*	1·10 ⁻⁴	2·10 ⁻¹	6·10 ⁻¹
10 ⁹ _v CH ₄		2.6	4.1	6.0
10 ¹¹ _v NO		-6.0	-8.3	-10.0
10 ¹² _v N ₂		4.8	8.0	13.1
10 ¹² _v CO ₂		1.1	1.9	4.2
10 ¹² _v N ₂ O		1.6	2.0	2.7
10 ¹³ _v C ₂ H ₄		1.4	5.0	15.0
10 ¹³ _v C ₂ H ₆		5.5	16.8	75.2
10 ¹² _v CH ₃ NCO		2.7	3.4	3.4
10 ¹² _v CH ₃ COCH ₃		1.1	1.6	2.2
10 ¹³ _v C ₂ H ₅ NCO		2.2	6.5	34.6

Table 4 continued

d) CH ₃ ONO added rate (mole cc ⁻¹ sec ⁻¹)*	p(torr) (approx.)	
	< 10 ⁻⁴	2·10 ⁻¹
10 ⁹ v _{CH₄}	2.6	3.1
10 ¹¹ v _{NO}	-6.0	-7.5
10 ¹² v _{N₂}	4.8	7.4
10 ¹² v _{CO₂}	1.1	1.3
10 ¹² v _{N₂O}	1.6	2.1
10 ¹³ v _{C₂H₄}	1.4	2.1
10 ¹³ v _{C₂H₆}	5.5	17.4
10 ¹² v _{CH₃COCH₃}	1.1	1.0
10 ¹³ v _{C₂H₅NCO}	2.2	18.6

Table 4 continued

e) CH ₃ ONO ₂ added	p(torr) (approx.)	
	rate (mole cc ⁻¹ sec ⁻¹)*	1·10 ⁻⁴
10 ⁹ v _{CH₄}	2.6	3.1
10 ¹¹ v _{NO}	-6.0	-7.5
10 ¹² v _{N₂}	4.8	7.4
10 ¹² v _{CO₂}	1.1	2.2
10 ¹² v _{N₂O}	1.6	2.3
10 ¹³ v _{C₂H₄}	1.4	2.2
10 ¹³ v _{C₂H₆}	5.5	15.4
10 ¹² v _{CH₃NCO}	2.7	3.5
10 ¹² v _{CH₃COCH₃}	1.1	1.3
10 ¹³ v _{C₂H₅NCO}	2.2	43.4

*

$$v = \frac{\text{yield}}{\text{reaction time} \cdot \text{reaction volume}}$$

DISCUSSION.

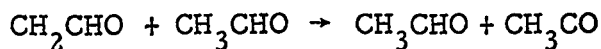
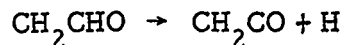
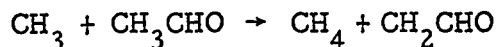
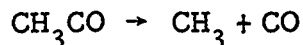
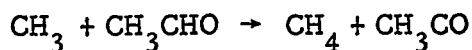
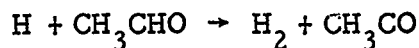
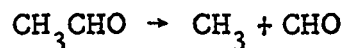
This work deals with the pyrolysis of acetaldehyde on three levels of complexity, namely

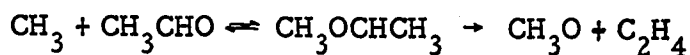
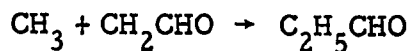
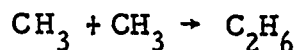
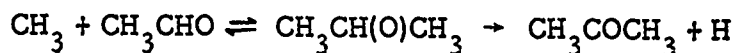
1. without NO;
2. with NO, extrapolated to zero mixing time;
3. with NO, after non-zero mixing time.

It is logical to start with the NO-free reaction, since it lies at the basis of the "inhibited" one. An important question is: which are the radicals arising in the system and what are their concentrations? These radicals, especially those present in relatively large concentrations, might combine with NO and lead to the formation of the minor products observed.

I. Intermediates in the NO-free Pyrolysis. Its Products and Mechanism.

In a recent study of the NO-free acetaldehyde pyrolysis by Liu and Laidler (61, 62, 55) the following mechanism was proposed:





They measured the rates of formation of CH_4 , CO , H_2 , CH_3COCH_3 , C_2H_6 , and $\text{C}_2\text{H}_5\text{CHO}$. The rates of formation of these products obtained in the present work agree with theirs to within a factor of two (Figure 7). However, their mechanism implies the formation of ketene, which they believe to be consumed, while in this work it has been shown that ketene is stable under the experimental conditions, but is nevertheless not found as a product. Thus the mechanism must be considered open to question as far as the fate of the CH_2CHO radicals and the origin of the H atoms is concerned. If the mechanism has indeed to be changed, other steps must replace these dubious ones. In the search for those, some important step, which does not give rise to a measurable product, might be overlooked. In order to try and avoid this a method was employed as discussed in the following.

A set of "basic" species has been assumed, namely

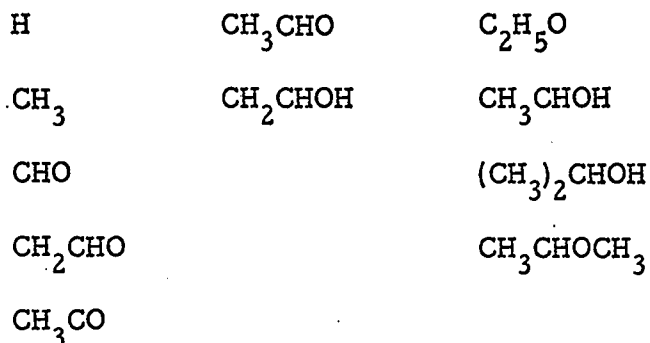


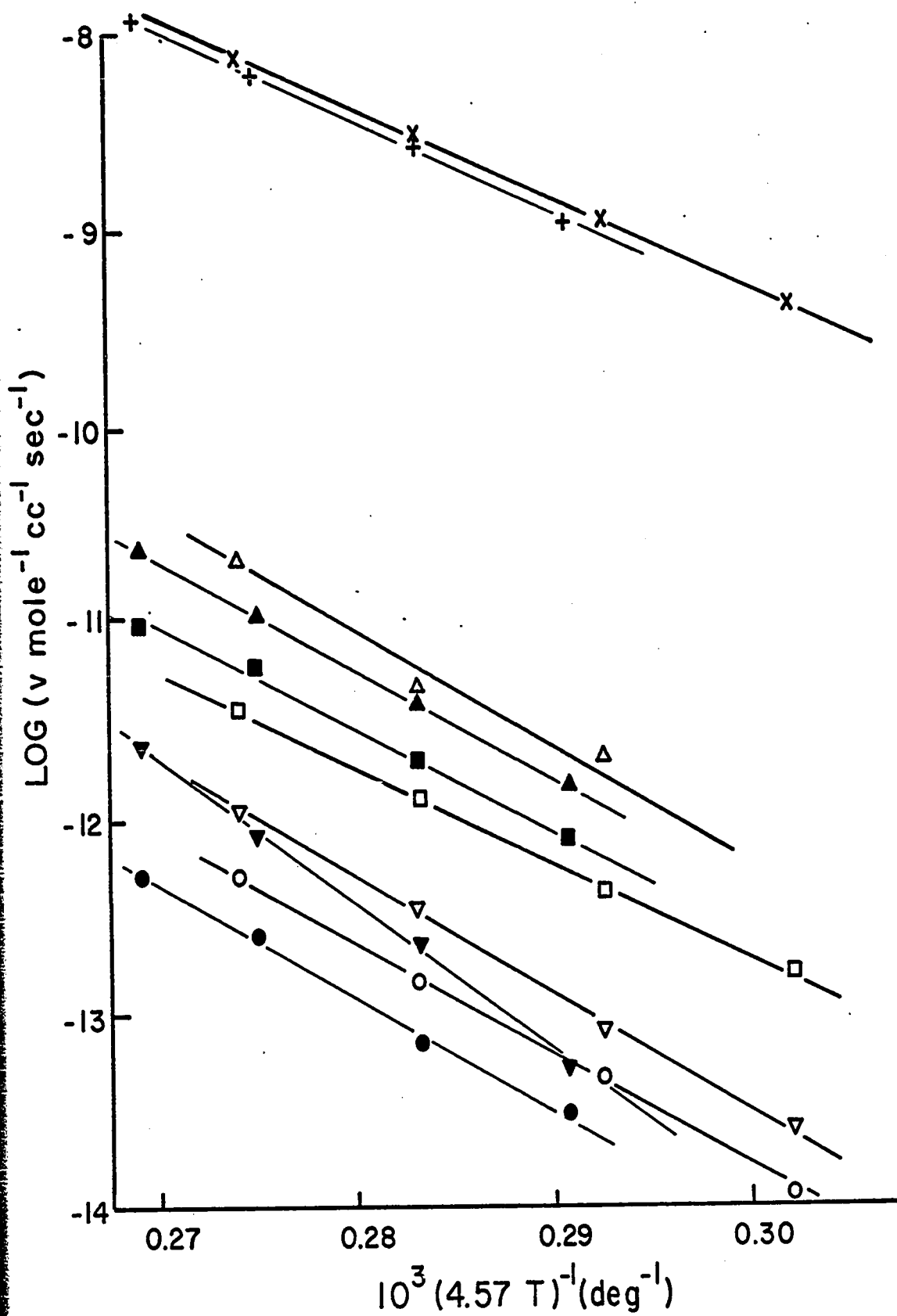
Figure 7

Arrhenius plots for several products of the nitric oxide-free
pyrolysis (acetaldehyde pressure 176.0 torr).

Open symbols and x refer to this work.

Other symbols refer to M. T. H. Liu's study (55).

Symbol	Compound
x +	CH_4
Δ \blacktriangle	H_2
\square \blacksquare	acetone
∇ \blacktriangledown	C_2H_6
\circ \bullet	$\text{C}_2\text{H}_5\text{CHO}$



They are basic in the sense that they are either the reactant itself (the aldo or the enol form), or they can in principle arise from the reactant in only one step, either through fragmentation of the acetaldehyde molecule, or through addition to it, of an H atom or a methyl radical. These species may undergo various unimolecular and bimolecular elementary reactions. Among all the conceivable ones, some fall into one of the following classes.

a) Decomposition (scission of one bond only)

- 1) splitting off H
- 2) splitting off CH_3
- 3) splitting off CHO

b) Combination

c) Abstraction

- 1) H transfer
- 2) CH_3 transfer
- 3) CHO transfer

These reactions have been listed (the list not being reproduced here since it contains several hundred), with the aim of removing from the scheme all those which occur only to a negligible extent. Ideally, the remaining ones would then represent precisely the mechanism of the NO-free pyrolysis. It must be emphasized, however, that the reactions on that list are only primary or secondary relative to the "basic" species. A reaction is called "primary", when its product(s) are "basic", and "secondary", when one or both products are not "basic". Product radicals or reactive intermediate molecules that are "non-basic" may subsequently react unimolecularly or bimolecularly in their turn. Such "tertiary" reactions, however, have

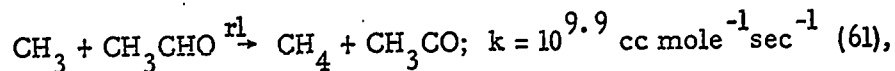
not been listed, as their number is quite large, certainly more than a thousand. Their omission implies the assumption that the larger aggregate radicals tend to fragment back into the smaller species rather than enter into bimolecular reactions, or that their formation through addition of medium large radicals to acetaldehyde molecules is comparatively slow, owing to a low steric factor.

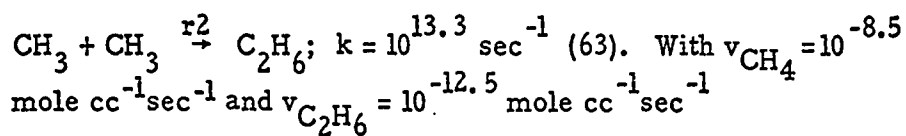
As a first step, the concentration of the "basic" radicals must be estimated. In the rate expressions

$$v_p = k_i [R_i]$$
$$v_p = k_{ik} [R_i] [R_k]$$

let R and P stand for reactant (a "basic" species) and product of an elementary unimolecular or bimolecular reaction characterized by the rate constant k_i or k_{ik} . Radical concentrations can then be estimated if the product P has been analyzed and if $[R_i]$ or $[R_k]$ and the rate constant are known or have been estimated, the rate constant perhaps on the basis of thermochemical considerations. Having obtained $[R_i]$ one can then further exclude from the scheme all those reactions involving R_i whose rates come out very small after substitution of k_{ik} , $[R_i]$, and $[R_k]$ into the rate expression. If P is a "basic" radical, then one can consider all the possible modes of reaction in which it is involved, and estimate [P] by means of the steady state hypothesis. The following estimates apply to conditions of 500°C and $[CH_3CHO] = 10^{-5.5}$ mole cc⁻¹.

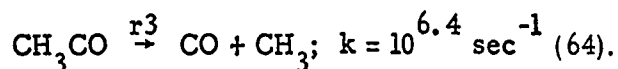
CH₃. $[CH_3]$ can be calculated in two different ways, as it forms directly both CH₄ and C₂H₆, most of which must arise from





$$\begin{aligned} [\text{CH}_3] &= 10^{-12.9} \text{ mole cc}^{-1} \text{ (from CH}_4\text{),} \\ &= 10^{-12.9} \text{ mole cc}^{-1} \text{ (from C}_2\text{H}_6\text{).} \end{aligned}$$

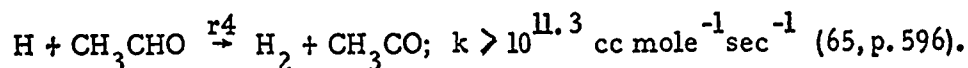
CH₃CO. Most of the CO must come from



$$\text{With } v_{\text{CO}} = 10^{-8.5} \text{ mole cc}^{-1}\text{sec}^{-1}$$

$$[\text{CH}_3\text{CO}] = 10^{-14.9} \text{ mole cc}^{-1}.$$

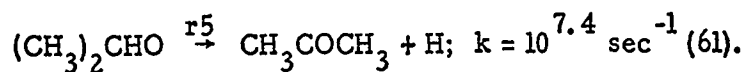
H. Most of the H₂ comes from



$$\text{With } v_{\text{H}_2} = 10^{-11.3} \text{ mole cc}^{-1}\text{sec}^{-1}$$

$$[\text{H}] = 10^{-17.1} \text{ mole cc}^{-1}.$$

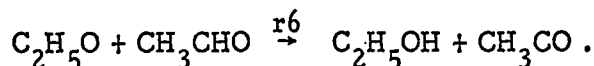
(CH₃)₂CHO. It has been shown (62) that the main source of acetone in this system is



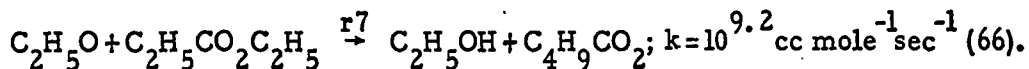
$$\text{With } v_{\text{CH}_3\text{COCH}_3} = 10^{-11.9} \text{ mole cc}^{-1}\text{sec}^{-1}$$

$$[(\text{CH}_3)_2\text{CHO}] = 10^{-19.3} \text{ mole cc}^{-1}.$$

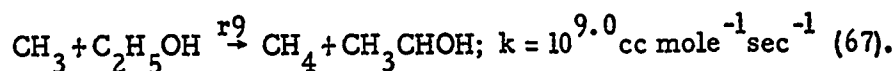
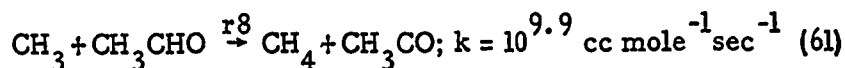
C₂H₅O. A likely product of this radical is ethanol, formed in



Arrhenius parameters for a similar reaction have been obtained:



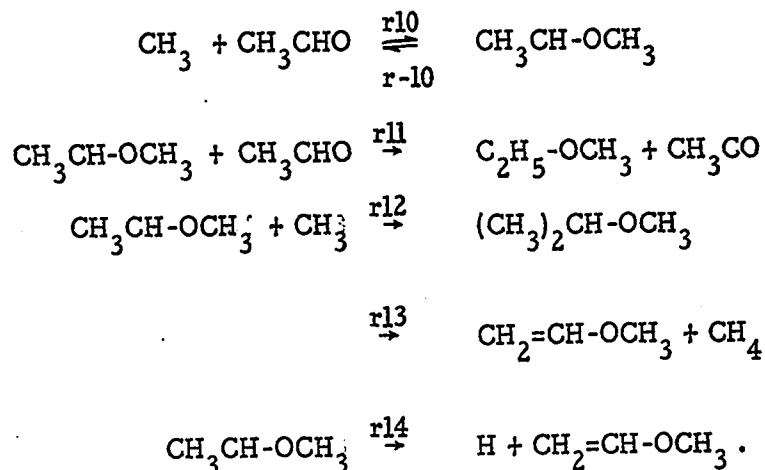
If ethanol was indeed formed, it would be more stable than acetaldehyde under the experimental conditions, judging from the rate constants of the two processes



Since ethanol has not been found among the products, its rate of formation must therefore be less than $10^{-14} \text{ mole cc}^{-1} \text{ sec}^{-1}$. Thus, if one assumes $k_{r6} \approx k_{r7}$,

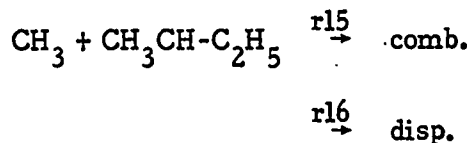
$$[\text{C}_2\text{H}_5\text{O}] < 10^{-17.7} \text{ mole cc}^{-1}.$$

$\text{CH}_3\text{CHOCH}_3$. The most important reactions involving this radical are probably



In this context it is recalled that it was impossible to analyze methyl ethyl ether and methyl isopropyl ether. Methyl vinyl ether, however,

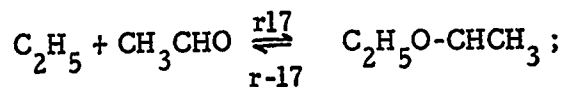
which could be analyzed, was not found as a product. Thus its rate of formation must be smaller than 10^{-14} mole cc⁻¹ sec⁻¹. The ratio of disproportionation to combination for the reactions



is given as lying between 0.07 and 0.30 (67). Assuming therefore $k_{\text{r12}}/k_{\text{r13}} \approx 0.1$ and $k_{\text{r12}} = 10^{12}$ cc mole⁻¹ sec⁻¹, one can put 10^{-14} mole cc⁻¹ sec⁻¹ $> v_{\text{CH}_2=\text{CH}-\text{OCH}_3}$, or

$$[\text{CH}_3\text{CH}-\text{OCH}_3] < 10^{-12.1} \text{ mole cc}^{-1}.$$

Another estimate is made using the steady-state condition. Consider the reactions



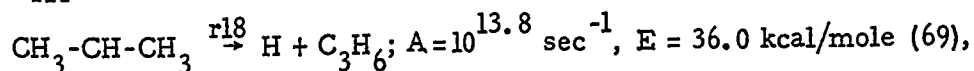
$$E_{\text{r17}} = 15 \text{ kcal/mole},$$

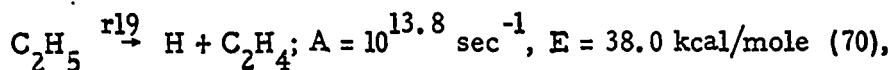
$$E_{\text{r-17}} = 19 \text{ kcal/mole} \quad (68),$$

similar to r10 and r-10. Putting $E_{\text{r17}} = E_{\text{r10}}$, $E_{\text{r-17}} = E_{\text{r-10}}$, $A_{\text{r10}} = 10^{13}$ cc mole⁻¹ sec⁻¹, $A_{\text{r-10}} = 10^{13}$ sec⁻¹, and further putting $k_{\text{r11}} \leq k_{\text{r1}} = 10^{9.9}$ cc mole⁻¹ sec⁻¹, one obtains

$$[\text{CH}_3\text{CH}-\text{OCH}_3] \leq 10^{-17.0} \text{ mole cc}^{-1}.$$

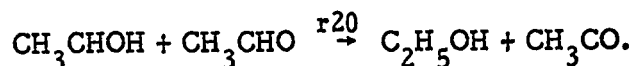
Similarly, based on reaction r14, assuming $A_{\text{r14}} = 10^{13}$ sec⁻¹ and $E_{\text{r14}} = 35$ kcal/mole, since





$$[\text{CH}_3\text{CH-OCH}_3] \leq 10^{-17} \text{ mole cc}^{-1}.$$

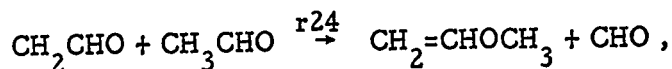
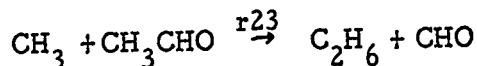
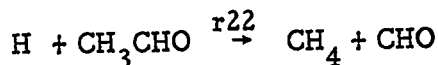
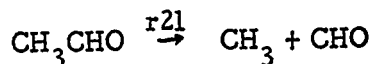
CH₃CHOH. Kinetic data on oxyalkyl radicals were not found, though it is known that these radicals are thermodynamically more stable than the isomeric alkoxy radicals (CH₃CHOH by 9.5 kcal/mole (71)). One of the reactions of the oxyethyl radical must be



Since the CH₃CHOH radicals are more stable than C₂H₅O· radicals, a larger activation energy will be required to abstract H. Thus if one puts E_{r20} = 10 kcal/mole > E_{r7} = 5.5 kcal/mole as well as A_{r20} = A_{r7} = 10^{10.7} cc mole⁻¹sec⁻¹, then, by the same argument as in the case of C₂H₅O,

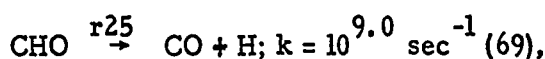
$$[\text{CH}_3\text{CHOH}] < 10^{-16.4} \text{ mole cc}^{-1}.$$

CHO. The formyl radical is a source of H atoms, but it cannot alone account for all the H₂. The reason is that the reactions generating CHO,



are too slow. Reaction r21, the initiation step, is slow: v_{r21} = 10^{-12.5} mole cc⁻¹sec⁻¹. Reaction r22, which has been found to occur at room temperature (72) with k_{r22} = (5.2 ± 1.2) 10¹⁰ cc mole⁻¹sec⁻¹, is not a contributor of H atoms to the system at all. Reaction r23 cannot be

important either, since otherwise v_{H_2} and $v_{C_2H_6}$ would be of the same order of magnitude, which is not the case ($v_{H_2} = 10^{-11.3}$ mole cc⁻¹ sec⁻¹, $v_{C_2H_6} = 10^{-12.5}$ mole cc⁻¹ sec⁻¹). Reaction r24 which involves the ethenoxy radical does not occur with a rate exceeding 10^{-14} mole cc⁻¹ sec⁻¹, which is the detectability threshold for methyl vinyl ether. It is seen that the combined v_{CHO} cannot exceed $2 \cdot 10^{-12.5}$ mole cc⁻¹ sec⁻¹. Considering the reaction

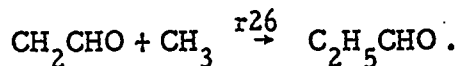


an upper limit can be placed on $[CHO]$, as $v_{H_2} \approx v_H > k_{r25} [CHO]$.

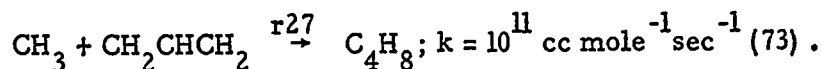
Thus

$$[CHO] < 10^{-20.3} \text{ mole cc}^{-1}.$$

CH₂CHO. Propionaldehyde is formed in the reaction (61)



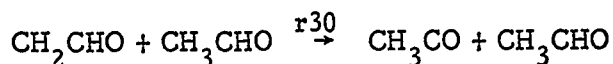
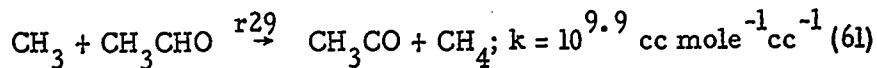
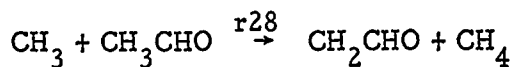
Ethenoxyl is isoelectronic with allyl.



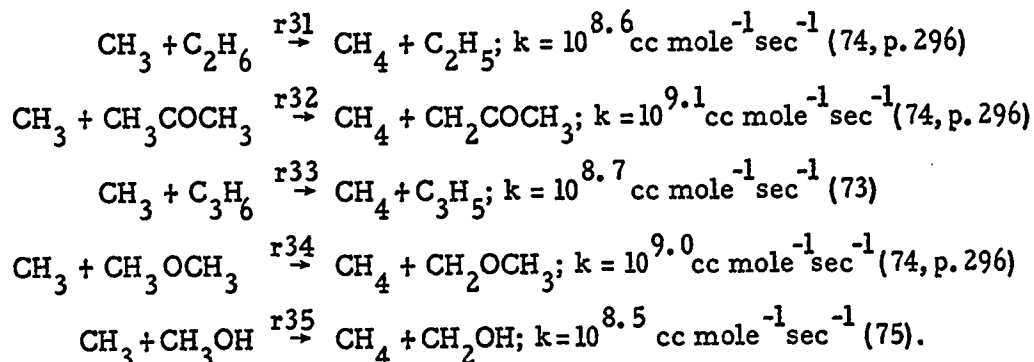
If $k_{r26} = k_{r27}$, then with $v_{C_2H_5CHO} = 10^{-12.8}$ mole cc⁻¹ sec⁻¹ and $[CH_3] = 10^{-12.9}$ mole cc⁻¹

$$[CH_2CHO] = 10^{-10.9} \text{ mole cc}^{-1}.$$

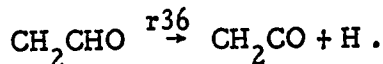
A different way to establish the importance of this radical is to find out how easily it is formed, and to compare it with CH₃ as far as its interaction with CH₃CHO is concerned.



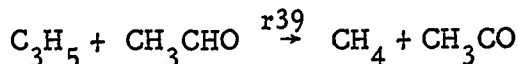
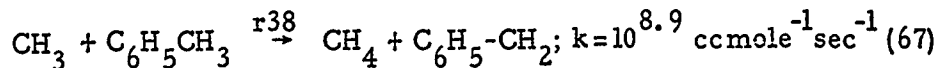
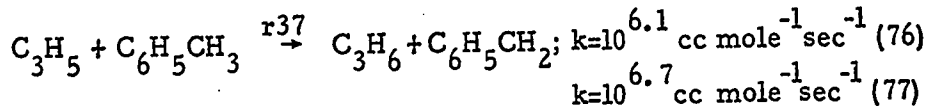
The Arrhenius parameters of r28 are not known, but a comparison with a series of similar abstraction reactions $\text{CH}_3 + \text{CH}_3\text{R} \rightarrow \text{CH}_4 + \text{CH}_2\text{R}$ suggests a value $k_{r28} \approx 10^9 \text{ cc mole}^{-1} \text{ sec}^{-1}$. For example,



$v_{\text{CH}_2\text{CHO}}$ is thus seen to be about one tenth of v_{CH_4} , and accordingly another process, or several processes, must operate removing the radical at the same rate. It has been suggested (62) that this occurs via



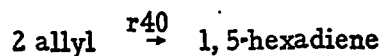
Apart from the fact that this would lead to a rate of hydrogen formation of about one tenth of that of CH_4 (whereas the experiment gave $v_{\text{H}_2}/v_{\text{CH}_4} = 10^{-2.8}$), ketene is not produced in the pyrolysis. The only other route of importance must therefore be r30. As before, the allyl radical may serve as a model to gauge the behavior of ethenoxyl:



Postulating that $k_{r37}/k_{r38} = 10^{-2.3} = k_{r39}/k_{r29}$ and $k_{r39} = k_{r30}$, one obtains $k_{r30} = 10^{7.6} \text{ cc mole}^{-1} \text{ sec}^{-1}$. Thus

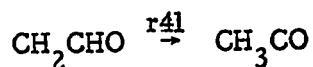
$$[\text{CH}_2\text{CHO}] \approx 10^{-11.6} \text{ mole cc}^{-1}.$$

In a very recent study (78) of the reaction



its rate constant was found equal to $7.4 \cdot 10^{12} \text{ cc mole}^{-1} \text{ sec}^{-1}$ (at 913°K), which was considered by the authors as an upper limit. Thus $k_{r_{26}} \approx 1 \cdot 10^{13}$ would be expected. If, furthermore, the ethenoxy radical were rather more reactive than allyl, owing to a much smaller resonance stabilization (79), its concentration would fall considerably short of the estimate given above (cf. 30, p.140).

It seems unlikely that the isomerization reaction



is important relative to r_{30} under these experimental conditions. The transition state for r_{41} would be a three-membered ring. It has been assumed by Benson (30, p. 65) that the ring strain for the transition state in hydrogen 1, 2-shifts in alkyl radicals is the same as in cyclopropane, namely 27 kcal/mole. The strain in cyclopropene is 56 kcal/mole (80). Accordingly it may be assumed that the ring strain in the transition state of r_{41} equals the average, 42 kcal/mole, considering that because of mesomery the bond order of the C-C bond in CH_2CHO may be about 1.5. It is of interest here to note that a very recent survey (80a) gives the ring strain of methylenecyclopropane as 41 kcal/mole. Together with an energy barrier for H abstraction of 5 kcal/mole one arrives thus at a total of 47 kcal/mole for $E_{r_{41}}$. Assuming $A_{r_{41}} = 10^{13} \text{ sec}^{-1}$, one obtains at 500°C $k_{r_{41}} = 10^0 \text{ sec}^{-1}$. Therefore $v_{r_{41}}/v_{r_{30}} = 10^0 / (10^{7.6} [\text{CH}_3\text{CHO}]) \approx 10^{-2}$.

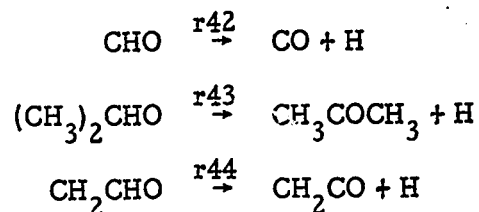
CH₂CHOH. The enol form of the acetaldehyde molecule is more energetic than the aldo form by about 10 kcal/mole (81). Assuming that both forms are in equilibrium, and that $\Delta S = 0$,

$$[\text{CH}_2\text{CHOH}] = 10^{-8.3} \text{ mole cc}^{-1}.$$

The conclusion to be drawn from this survey of the simpler radicals derived from the aldo form is that the ethenoxy radical may play an important role in the kinetics of the "inhibited" pyrolysis of acetaldehyde, as it may be up to a hundred times more numerous than the methyl radical.

Another point must be discussed here, relating to the generation of H atoms, which has already been briefly touched upon.

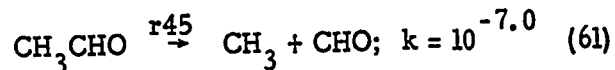
The reactions



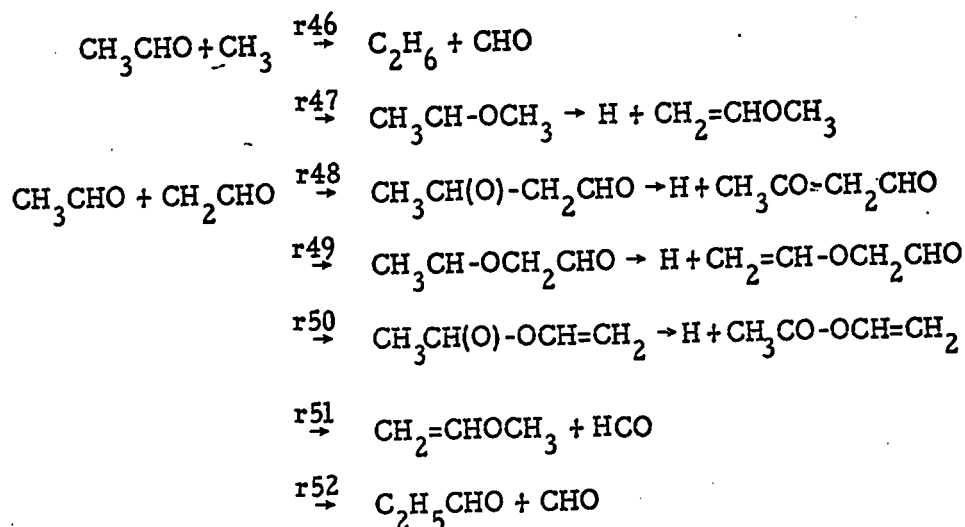
have been proposed as hydrogen sources (61, 62), but doubt is cast on reaction r44 by results of the present work, which are recalled here:

1. Ketene could be analyzed, as proven by means of a sample of pure ketene used to establish its retention time.
2. Ketene was not found among the products.
3. Small, identical amounts of ketene were copyrolyzed with acetaldehyde, with the reaction time varying between 10 and 400 sec. The amounts of ketene found were essentially the same after each of these runs.

An alternative to r44 must therefore exist, since r42 and r43 alone are insufficient. If

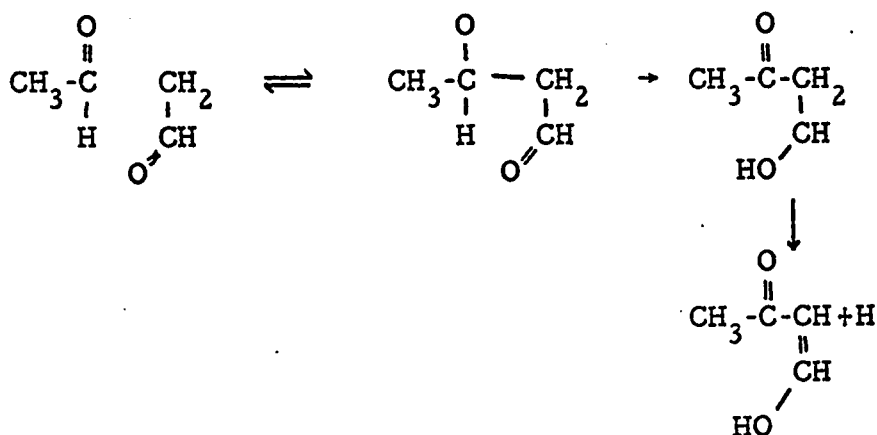


is the only process leading to CHO then $v_{r42} = k_{r42} [\text{CHO}] = [\text{CH}_3\text{CHO}] \cdot k_{r45}$
 $10^{-12.5} \text{ mole cc}^{-1} \text{ sec}^{-1}$. Thus $v_{r42} + v_{r43} = 10^{-12.5} + 10^{-11.9} = 10^{-11.8}$
 $\text{mole cc}^{-1} \text{ sec}^{-1} = 0.3 v_{\text{H}_2}$. To account for the rest of the H_2 a reaction must be found which converts, as it were, a methyl or ethenoxy radical into a hydrogen atom. Several such could be imagined:



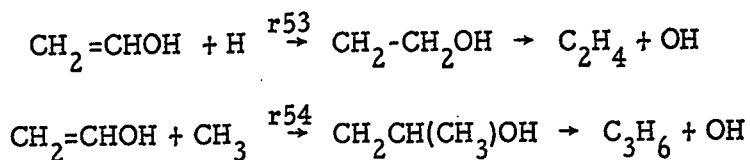
It is unlikely that any radical with a concentration of less than $10^{-14} \text{ mole cc}^{-1}$ could serve as a promoter of H atoms. This may be inferred from the fact that C-H bonds tend to be stronger than both C-C and C-O bonds. Reactions r46 and r52 can be excluded because $v_{\text{C}_2\text{H}_6} + v_{\text{C}_2\text{H}_5\text{CHO}} \ll v_{\text{H}_2}$; similarly, reactions r47 and r51 can be excluded owing to the absence of methyl vinyl ether. Reaction r50 leads to vinyl acetate which, though somewhat more unstable than acetaldehyde under pyrolysis conditions, shows a marked increase with increasing reaction time, i. e., its steady-state concentration is far above any ever attained in a run. But $v_{\text{C}_2\text{H}_3\text{O-COCH}_3} \leq 10^{-12.8} \text{ mole cc}^{-1} \text{ sec}^{-1}$,

which is far below v_{H_2} . Processes r48 and r49 remain. Formyl-methyl vinyl ether which would arise from r49 has not been investigated. Regarding r48, it is recalled that β -keto-butyraldehyde cannot be analyzed in the presence of acetaldehyde. This compound is known to be unstable in its pure form at room temperature; it polymerizes to form 1,3,5-triacetylbenzene (57). In the absence of a better alternative, r48 is assumed to furnish the H atoms required to explain the full H_2 yield:



The tendency to form conjugated double bonds would aid the elimination of the H atom.

Minor products which have not yet been explained are C_2H_4 , C_3H_6 , CO_2 , and crotonaldehyde. Previous investigations also have revealed C_2H_4 (61), CO_2 (61), and C_3H_6 (82, 83). Crotonaldehyde has been postulated (82). A displacement reaction similar to the one leading to acetone could be responsible for C_2H_4 and C_3H_6 :



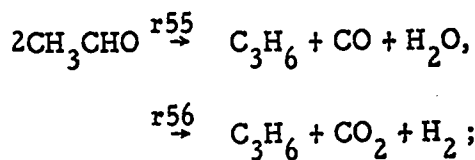
That the rates of formation $v_{C_2H_4}$ and $v_{C_3H_6}$ differ by a lesser factor than the concentrations $[H]$ and $[CH_3]$ is plausible since the addition of H to a double bond is much faster than that of CH_3 (cf. 69, table).

The orders with respect to acetaldehyde were not obtained for the NO-free pyrolysis; with $p_{NO} = 12.38$ torr the order of $v_{C_2H_4}$ is about 1.5, that of $v_{C_3H_6}$ about 1.3, agreeing fairly well with expectation:

$$v_{H_2} = k[CH_3CHO][H] \sim [CH_3CHO]^{1.4}, \quad v_{CH_4} = k[CH_3CHO][CH_3] \sim [CH_3CHO]^{1.5} \quad (61),$$

which means $[H] \sim [CH_3CHO]^{0.4}$, $[CH_3] \sim [CH_3CHO]^{0.5}$.

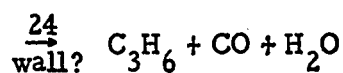
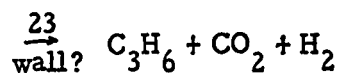
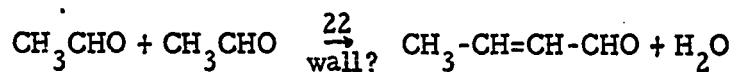
The picture for C_3H_6 , however, may be more complicated if there are other paths leading to it, e. g.



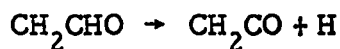
which would at the same time explain the CO_2 . While the order of v_{CO_2} in the NO-free pyrolysis was not determined, there is little doubt that CO_2 is a primary product. Reactions r55 and r56 would seem to contradict the principle of least motion (84), unless one assumes they are surface-catalyzed.

Crotonaldehyde could be attributed to the process $2CH_3CHO \xrightarrow{r57} CH_3CH=CHCHO + H_2O$. The small amounts of water arising from r53, r54, r55 and r57 would not produce a signal strong enough to be detected. The hypothesis that some of these processes are influenced by the surface is supported by earlier work (82) where it was found that packing increases $v_{C_3H_6}$. It is also supported by the fact that propylene production rates differed considerably when reaction vessels made of different materials were used (83).

The following mechanism can account for the results of the present NO-free work, and it will serve as the basis from which to discuss the NO-influenced reaction.



The important difference between this mechanism and the one put forward by Liu and Laidler (1) lies in the rejection of



and the acceptance instead of reaction 8 as an additional source of H atoms.

On the basis of this mechanism it is possible to estimate k_7 and $k_8 k_{18}/(k_{-8} + k_{18})$. With the usual approximations and the abbreviations $[\text{CH}_3\text{CHO}] = a$, $[\text{CH}_3] = y$, $(k_7 + k_8 k_{18}/(k_{-8} + k_{18})) = P_1$,

$$P_1 a[\text{CH}_2\text{CHO}] = k_3 a[\text{H}] + k_5 a y - k_{16} y [\text{CH}_2\text{CHO}]$$

$$= v_{\text{H}_2} k_3/(k_2 + k_3) + v_{\text{CH}_4} k_5/(k_4 + k_5) - v_{\text{C}_2\text{H}_5\text{CHO}} \quad [1]$$

A comparison of k_2 and k_3 is attempted in the following manner.

Consider the reactions $\text{H} + \text{RH} \xrightarrow{k_{\text{H}}} \text{R} + \text{H}_2$ and $\text{CH}_3 + \text{RH} \xrightarrow{k_{\text{CH}_3}} \text{R} + \text{CH}_4$.

E_{H} and E_{CH_3} as functions of the bond dissociation energy $D(\text{R-H})$ run roughly parallel (see Figure 8), with $E_{\text{CH}_3} - E_{\text{H}} \approx 2.5$ kcal/mole.

If one assumes $D(\text{HCOCH}_2\text{-H}) = D(\text{CH}_3\text{COCH}_2\text{-H})$, then $E_5 - E_4 =$

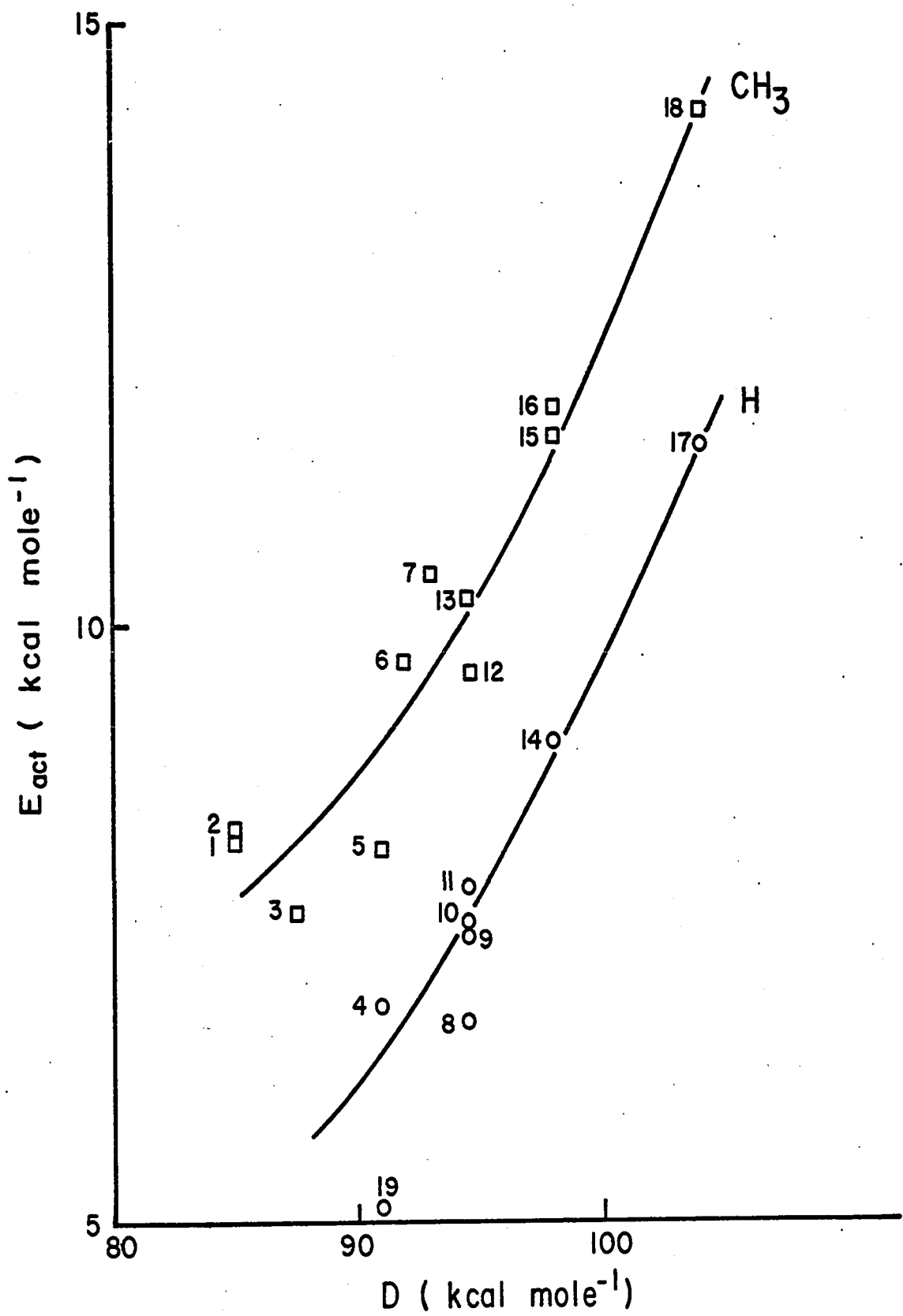
$E_3 - E_2 \approx 2$ kcal/mole. If it is further assumed that the pre-exponential factor are about equal, then $k_2/k_3 = e^{+2/RT} \approx 2$ (in the temperature range studied). Therefore

$$k_3/(k_2 + k_3) \approx 0.3 \quad [2]$$

Figure 8

The activation energies for various hydrogen abstraction reactions, by CH_3 and by H , as functions of the bond dissociation energy of the hydrogen atoms abstracted.

Symbol No.	Reaction	Reference for E	Reference for D
1	$\text{CH}_2=\text{CH}-\text{CH}_2-\text{H} + \text{CH}_3$	75	85
2	$\text{C}_6\text{H}_5\text{CH}_2-\text{H} + \text{CH}_3$	75	85
3	$\text{CH}_3\text{CO}-\text{H} + \text{CH}_3$	75	85
4	$(\text{CH}_3)_3\text{C}-\text{H} + \text{H}$	75	85
5	$(\text{CH}_3)_3\text{C}-\text{H} + \text{CD}_3$	75	85
6	$\text{CH}_3\text{COCH}_2-\text{H} + \text{CH}_3$	74, p. 296	86
7	$\text{CH}_2(\text{OH})-\text{H} + \text{CH}_3$	75	85
8	$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)-\text{H} + \text{H}$	75	86
9	$(\text{CH}_3)_2\text{CH}-\text{H} + \text{H}$	75	85
10	$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)-\text{H} + \text{H}$	75	86
11	$(\text{CH}_3)_2\text{CH}-\text{H} + \text{H}$	75	85
12	$\text{C}_2\text{H}_5\text{CH}(\text{CH}_3)-\text{H} + \text{CD}_3$	75	86
13	$(\text{CH}_3)_2\text{CH}-\text{H} + \text{CD}_3$	75	85
14	$\text{C}_2\text{H}_5-\text{H} + \text{H}$	75	85
15	$(\text{CH}_3)_2\text{CD}-\text{CH}_2-\text{H} + \text{CH}_3$	75	86
16	$\text{C}_2\text{H}_5-\text{H} + \text{CD}_3$	75	85
17	$\text{CH}_4 + \text{H}$	75	85
18	$\text{CH}_4 + \text{CD}_3$	75	85
19	$(\text{CH}_3)_3\text{C}-\text{H} + \text{H}$	75	85



In a similar way k_4 and k_5 can be compared, with the assumption as before that $D(\text{OCHCH}_2 - \text{H}) = D(\text{CH}_3\text{COCH}_2 - \text{H})$, i. e., $k_5 = 0.5 \cdot 10^{10.36} T^{1/2} e^{-9.7/RT}$ cc mole⁻¹ sec⁻¹ deg^{-1/2}, one half the value of the rate constant of $\text{CH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{COCH}_3$ (74, p. 296); one half because there is one methyl group in acetaldehyde, whereas acetone has two. Also $k_4 = 10^{12.2} e^{-8.4/RT}$ cc mole⁻¹ sec⁻¹ (61). Thus $k_5/k_4 = 10^{-2.1} T^{1/2} e^{-1.3/RT}$ deg^{-1/2} ≈ 0.1 (in the temperature range studied), and

$$k_5/(k_4 + k_5) \approx 0.1. \quad [3]$$

Noting that

$$v_{\text{C}_2\text{H}_5\text{CHO}} = k_{16} y [\text{CH}_2\text{CHO}] \quad [4]$$

$$v_{\text{acetone}} = k_{\text{ace}} a y \quad [5]$$

$$v_{\text{CH}_4} = k_{\text{CH}_4} a y, \quad [6]$$

where $k_{\text{CH}_4} = 10^{12.24} e^{-8.4/RT}$ cc mole⁻¹ sec⁻¹ and $k_{\text{ace}} = 10^{10.22} e^{-17.4/RT}$ cc mole⁻¹ sec⁻¹ (61), one has, combining equations 1, 2, 3, 4, 5

$$P_1 = \frac{(0.3 v_{\text{H}_2} + 0.1 v_{\text{CH}_4} - v_{\text{C}_2\text{H}_5\text{CHO}}) v_{\text{acetone}} k_{16}}{k_{\text{ace}} a^2 v_{\text{C}_2\text{H}_5\text{CHO}}}$$

whereas equations 1, 2, 3, 4, 6 together give

$$P_1 = \frac{(0.3 v_{\text{H}_2} + 0.1 v_{\text{CH}_4} - v_{\text{C}_2\text{H}_5\text{CHO}}) v_{\text{CH}_4} k_{16}}{k_{\text{CH}_4} a^2 v_{\text{C}_2\text{H}_5\text{CHO}}}$$

These expressions contain k_{16} which is estimated in the following way: CH_2CHO is isoelectronic with the allyl radical, i. e.,
 $\text{CH}_3 + \text{CH}_2\text{CHCH}_2 \rightarrow \text{C}_4\text{H}_8$ ($k = 5 \cdot 10^{11}$ cc mole⁻¹ sec⁻¹ (87);
 $k = 1 \cdot 10^{11}$ cc mole⁻¹ sec⁻¹ (73); average $3 \cdot 10^{11}$) corresponds to reaction 16. It is then assumed that $k_{16} = 3 \cdot 10^{11}$ cc mole⁻¹ sec⁻¹. On substituting two sets of values for P_1 (cc mole⁻¹ sec⁻¹) are obtained:

Table 5

Values of the parameter P_1 from equation 1.

T(°C)	450	475	500	525
based on k_{ace}	$0.39 \cdot 10^7$	$0.57 \cdot 10^7$	$1.16 \cdot 10^7$	$1.97 \cdot 10^7$
based on k_{CH_4}	$0.65 \cdot 10^7$	$1.00 \cdot 10^7$	$1.92 \cdot 10^7$	$3.20 \cdot 10^7$

The term $k_8 k_{18} / (k_{-8} + k_{18}) \equiv P_1$, can be estimated by means of the steady-state assumption applied to H atoms:

$$v_{\text{H}_2} - v_{\text{acetone}} - k_{18} [\text{CH}_3\text{CH}(\text{O})\text{CH}_2\text{CHO}] - k_{14} [\text{CHO}] = 0 \quad [7]$$

Since $k_{14} [\text{CHO}] = k_1 a = v_{\text{C}_2\text{H}_6} + v_{\text{C}_2\text{H}_5\text{CHO}}$, one obtains, using also [4] and [5],

$$P_1' = \frac{(v_{\text{H}_2} - v_{\text{acetone}} - v_{\text{C}_2\text{H}_6} - v_{\text{C}_2\text{H}_5\text{CHO}}) k_{16} v_{\text{acetone}}}{a^2 k_{\text{ace}} v_{\text{C}_2\text{H}_5\text{CHO}}}$$

Using [4] and [6] one obtains

$$P_1' = \frac{(v_{\text{H}_2} - v_{\text{acetone}} - v_{\text{C}_2\text{H}_6} - v_{\text{C}_2\text{H}_5\text{CHO}}) k_{16} v_{\text{CH}_4}}{a^2 k_{\text{CH}_4} v_{\text{C}_2\text{H}_5\text{CHO}}}$$

On substitution, two sets of values for P_1 , ($\text{cc mole}^{-1} \text{sec}^{-1}$) result:

Table 6
Values of the term P_1

$T(^{\circ}\text{C})$	450	475	500	525
based on k_{ace}	-	$0.8 \cdot 10^5$	$1.2 \cdot 10^5$	$4.3 \cdot 10^5$
based on k_{CH_4}	-	$1.4 \cdot 10^5$	$2.0 \cdot 10^5$	$6.8 \cdot 10^5$

II. The Pyrolysis of "Clean" Mixtures of Acetaldehyde and Nitric Oxide.

The presence of NO leads to several products in addition to those of the pure pyrolysis. All the products found, namely CH_4 , CO , N_2 , H_2 , CO_2 , N_2O , C_2H_4 , C_2H_6 , H_2O , C_3H_6 , HCN , CH_3NCO , CH_3COCH_3 , $\text{C}_2\text{H}_5\text{NCO}$, and vinyl acetate, can be classed in two groups: those whose rate of formation depends only slightly on the duration of the pre-reaction mixing period (i. e., extrapolation to zero mixing time yields a rate of the same order of magnitude, see for example Figure 5), and those where extrapolation gives a rate smaller by about one order of magnitude than that observed after one hour of mixing (Figure 6). The first group, with which alone this section is concerned, comprises all products except N_2 and $\text{C}_2\text{H}_5\text{NCO}$. Since their dependence on mixing time is small, and because the effect has not been studied systematically, the results obtained after one hour of mixing are taken, instead of the extrapolated ones, to reflect the pyrolysis of "clean" mixtures of CH_3CHO and NO . (A mixture is

called "clean" if it is uncontaminated by any compounds which arise in it owing to a slow reaction occurring at room temperature.)

In order to develop the mechanism it is proposed to proceed in the following manner: First, probable elementary reactions will be postulated, with the relative rates of formation of the products and their dependence on $[\text{NO}]$ and $[\text{CH}_3\text{CHO}]$ being taken into account. Second, the mathematical consequences of the resulting mechanism will be explored.

A. Probable Elementary Reactions.

The foremost fact that must be explained is the catalytic effect of the NO. Several possible reasons can be advanced:

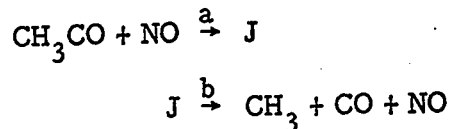
1. Additional initiation through hydrogen abstraction by NO (cf. 6).
2. "Stabilization" of radicals, i. e., the stabilized chain carrier has a smaller termination/propagation ratio than the free one (27, 28).
3. Provision of an alternative and faster route for the $\dot{\text{C}}\text{-C}$ -radical to decompose into product and the chain carrier.
4. Additional initiation through a displacement reaction, where NO adds to a double bond, and subsequent cleavage of a C-C bond occurs with a small probability, furnishing a radical.
5. Chain branching or additional initiation through a splitting of unstable molecules into radicals.

1) This assumption promises to hold a partial explanation of the catalytic effect, to the extent that there is unimolecular decomposition

of HNO, which could account for the increase by NO of the hydrogen production. It does not afford a complete explanation, however, since the chemical net effect of the reaction sequence $\text{CH}_3\text{CHO} + \text{NO} \rightarrow \text{HNO} + \text{CH}_3\text{CO}$, $\text{CH}_3\text{CO} \rightarrow \text{CO} + \text{CH}_3$, $\text{CH}_3 + \text{HNO} \rightarrow \text{CH}_4 + \text{NO}$ is the same as without the participation of NO, namely $\text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CO}$. If HCN and H_2O result from $\text{CH}_3 + \text{NO} \rightarrow \text{CH}_3\text{NO} \rightarrow \text{CH}_2=\text{NOH} \rightarrow \text{HCN} + \text{H}_2\text{O}$, then a process is needed whose net effect is to furnish methyl radicals. The reaction $\text{CH}_3\text{CHO} + \text{NO} \rightarrow \text{HNO} + \text{CH}_3\text{CO}$ does this only insofar as the HNO splits according to $\text{HNO} \rightarrow \text{NO} + \text{H}$. The chemical net result is in this case $2\text{CH}_3\text{CHO} \rightarrow \text{H}_2 + 2\text{CH}_3\text{CO}$. But the part of v_{H_2} that is due to the influence of NO is less than one fifth of v_{HCN} .

2) The concept of the stabilized radical has lost its appeal in organic pyrolyses since the advent of gas-chromatographic analysis, which demonstrated that NO is irreversibly consumed, forming a variety of nitrogeous substances. Thus, in order to account for the not inconsiderable amounts of HCN and H_2O found in this work, any mechanism based on that concept would have to be supplemented to such an extent as to render the concept itself useless.

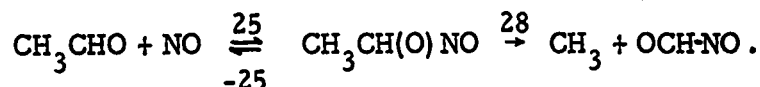
3) The μ -radical which regenerates the main chain carrier in the acetaldehyde pyrolysis is CH_3CO , which decomposes much faster than e. g., C_2H_5 ; at 500°C the ratio $k_{\text{CH}_3\text{CO}}/k_{\text{C}_2\text{H}_5} \approx 10^3$ (cf. 69, 70).
An indirect route



would be faster if $k_a[\text{NO}] > k_{\text{CH}_3\text{CO}}$, i. e., if (at 500°C and $[\text{NO}] \approx 10^{-7}$ mole cc^{-1}) $k_a > 10^{13}$ $\text{cc mole}^{-1}\text{sec}^{-1}$. This seems possible, but it is

hard to imagine an intermediate J which will readily break up again. A process leading to a radical different from CH_3 would have to lead to another major product comparable in quantity with CH_4 , contrary to the experimental evidence.

4) Consider the reaction sequence



It may be assumed that $E_{-25} < E_{28}$. The rate with which CH_3 radicals are produced equals

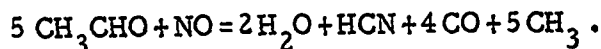
$$v_{\text{CH}_3} = \frac{k_{25} k_{28}}{k_{-25} + k_{28}} [\text{CH}_3\text{CHO}][\text{NO}] = \frac{A_{25} A_{28}}{A_{-25}} e^{-(\Delta H + E_{-28})/RT} [\text{CH}_3\text{CHO}][\text{NO}],$$

where $\Delta H = \Delta H_{\text{CH}_3} + \Delta H_{\text{CHO-NO}} - \Delta H_{\text{CH}_3\text{CHO}} - \Delta H_{\text{NO}}$, and at the same time $\Delta H = E_{25} + E_{28} - E_{-25} - E_{-28}$. To estimate the enthalpy of formation $\Delta H_{\text{CHO-NO}}$ of nitroso formaldehyde it is assumed that its C-N bond dissociation energy is equal to 40 ± 5 kcal/mole, similar to that of CH_3NO (41 ± 2.5 kcal/mole (85)). Accordingly, $\Delta H_{\text{CHO-NO}} = \Delta H_{\text{CHO}} + \Delta H_{\text{NO}} - (40 \pm 5)$ kcal/mole. With $\Delta H_{\text{CH}_3} = +34 \pm 1$, $\Delta H_{\text{CH}_3\text{CHO}} = -39.7$, $\Delta H_{\text{CHO}} = +6.3$ kcal/mole (85) $\Delta H = 39 \pm 6$ kcal/mole. Further assuming $E_{-28} = 3 \pm 2$ kcal/mole, $A_{28} = A_{-25}$, and $A_{25} = 10^{10 \pm 2}$ cc mole⁻¹ sec⁻¹ (for $\text{CH}_3 + \text{CH}_3\text{COCH}_3 \rightarrow (\text{CH}_3)_3\text{CO}$, $A = 10^{9.2}$ cc mole⁻¹ sec⁻¹ (69)),

$$v_{\text{CH}_3} = 10^{-14 \pm 4} \text{ mole cc}^{-1} \text{ sec}^{-1}.$$

The rate of CH_3 production due to $\text{CH}_3\text{CHO} \rightarrow \text{CH}_3 + \text{CHO}$ under the same conditions equals $10^{-12.5}$ mole cc⁻¹ sec⁻¹. It is apparent that the possibility of additional initiation by displacement of CH_3 through NO may be a real one.

5) Oxime-like compounds may arise in the system and undergo a split into two radicals (cf. 46). On the basis of radicals involved in the NO-free pyrolysis, $\text{CH}_2=\text{NOH}$, $\text{OCH}-\text{CH}=\text{NOH}$ (from CH_3NO and $\text{OCH}-\text{CH}_2\text{NO}$), and $\text{CH}_3\text{CO}-\text{NO}$ must be considered. However, the only possible mode of splitting for the formaldoxime seems to be into OH and CH_2N , a radical which would either lose an H atom, in which case the H_2 and HCN yields would be comparable, or abstract H from CH_3CHO to form methylene imine, which would probably react further. But such secondary products have not been found. Similar arguments apply for C-formyl formaldoxime: $v_{\text{H}_2}/v_{\text{HCN}} < 1/5$ at moderate $[\text{NO}]$, decreasing with increasing $[\text{NO}]$. CH_3CONO finally seems incapable of easy rearrangement and subsequent split. Generally speaking, if possibility 5 is to be realized at all, a way has to exist generating more radicals than have entered into the unstable intermediate, and which must not ultimately lead to the formation of H_2 . $\text{CHO}-\text{NO}$ has been mentioned above. It may be able to rearrange into the oxime-like compound $\text{OC}=\text{NOH}$. If this splits into OCN and OH , HOCN and H_2O will result. If in turn HOCN splits into OH and CN , which will abstract H, the following stoichiometry holds:



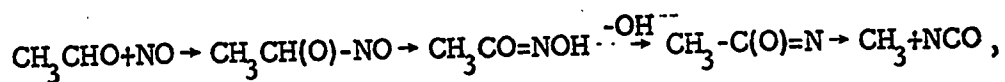
This hypothesis suffers from two weaknesses. First it seems unexpected that $\text{OCH}-\text{NO} \rightarrow \text{OC}=\text{NOH}$ rather than $\text{OCH}-\text{NO} \rightarrow \text{NO} + \text{HCO}$ should predominate. Second, the reaction $\text{HOCN} \rightarrow \text{OH} + \text{CN}$ must be strongly endothermic. A comparison of bond dissociation energies (Table 7) suggests an energy well above 100 kcal/mole which precludes a homogeneous mode. Only if surface catalysis is assumed can the scheme be maintained.

Table 7

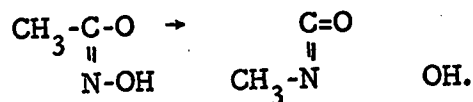
Some bond dissociation energies (30).

Compound	CH ₃ -Cl	CH ₃ -OH	CH ₃ -F	Cl-CN	HO-CN	F-CN
D(kcal/mole)	84	92	108	107	?	130

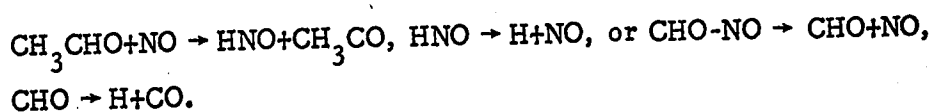
A reaction path involving an isomer of methyl isocyanate may also be capable of furnishing additional radicals,



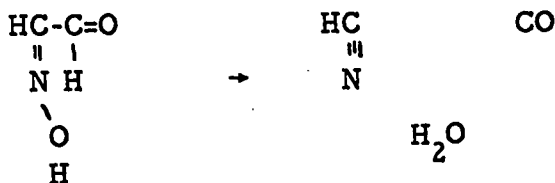
the stoichiometry being the same as before. In fact, CH₃NCO itself is a product of the pyrolysis, and it may form in a process similar to a Beckmann rearrangement:



In this case the increased H₂ production could be caused by

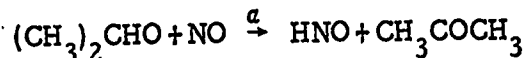


The question of additional initiation having been dealt with, additional termination reactions due to NO, besides those already mentioned will now be considered. It has been suggested (e. g. 6, 46) that alkyl radicals react with NO to form nitroso alkanes which eliminate H₂O with the formation of the nitrile. CH₂CHO is assumed here to undergo a similar process; the oxime could fragment in a concerted reaction

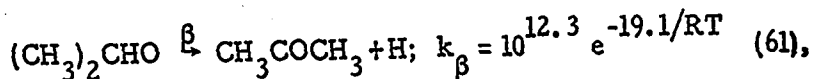


The effect of the conjugated double bonds would be to render more planar the 5-membered ring leading to the transition state and thus increase the frequency factor. The terminations $\text{CH}_3 + \text{CH}_3\text{NO} \rightarrow \text{C}_2\text{H}_6 + \text{NO}$, and $\text{CH}_3 + \text{OCH-CH}_2\text{NO} \rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{NO}$ also cannot be ruled out. The reaction $\text{CH}_2\text{CHO} + \text{OCHCH}_2\text{NO} \rightarrow (\text{CH}_2\text{CHO})_2 + \text{NO}$ is disregarded because it probably has a comparatively low frequency factor.

The reaction



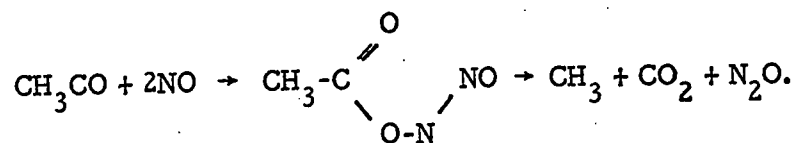
can be omitted because $E_a = 1 \pm 1$ kcal/mole (88) and $A_a \leq 10^{10}$ cc mole⁻¹ sec⁻¹ (the reaction $\text{C}_2\text{H}_5\text{O} + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{HNO}$ has $k = 10^{10}$ cc mole⁻¹ sec⁻¹ (89)). Taking into consideration the rate constant of



one obtains, at 500°C, $v_a/v_\beta \approx 10^3 [\text{NO}]$. Under the conditions of this study $[\text{NO}] \leq 10^{-6}$ mole cc⁻¹. Thus $v_a/v_\beta \leq 10^{-3}$.

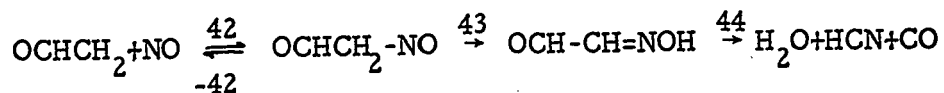
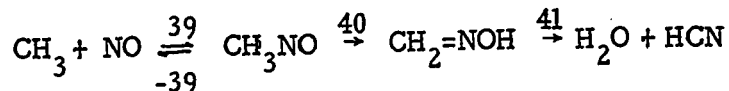
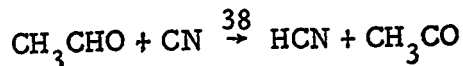
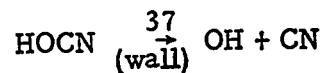
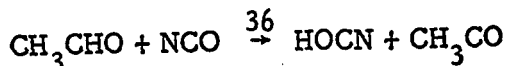
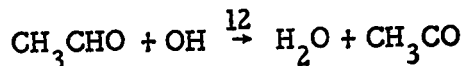
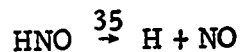
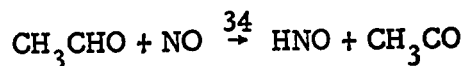
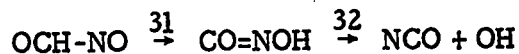
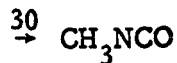
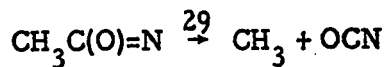
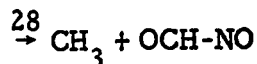
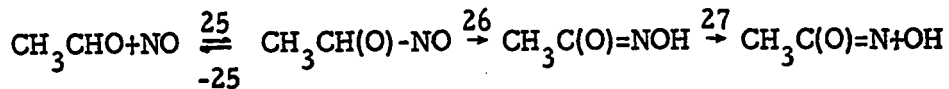
Finally, N_2O and CO_2 are formed in about equal amounts, allowance having been made for the NO-free contribution of CO_2 .

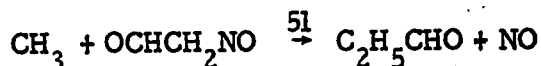
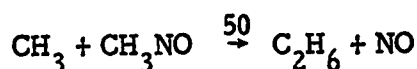
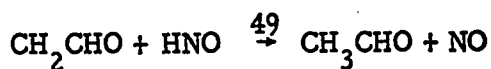
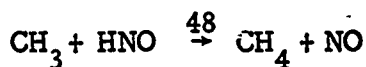
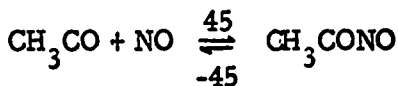
This fact can be rationalized assuming the sequence



B. The Overall Mechanism.

In view of the above conclusions, the following reactions are added to the NO-free mechanism, and the resulting tentative mechanism is tested mathematically:





Since the yield-time curves are non-sigmoid, the steady-state assumption is justified, i. e., radical formation equals radical annihilation. The term "radical" signifies any odd-electron species except NO. Replacing for convenience $[\text{CH}_3\text{CHO}]$, $[\text{NO}]$, and $[\text{CH}_3]$ by a , x , and y , one can write

$$\begin{aligned} & 2k_1a - k_{15}y^2 - k_{16}y[\text{CH}_2\text{CHO}] + k_{25}ax - k_{25}[\text{CH}_3\text{CH}(\text{O})\text{-NO}] + \\ & 2k_{29}[\text{CH}_3\text{C}(\text{O})=\text{N}] + 2k_{32}[\text{CO}=\text{NOH}] + k_{33}[\text{OCH}\text{-NO}] + k_{34}ax + \\ & k_{35}[\text{HNO}] + 2k_{37}[\text{HOCN}] - k_{39}xy + k_{39}[\text{CH}_3\text{NO}] - k_{42}x \\ & [\text{CH}_2\text{CHO}] + k_{42}[\text{OCH}\text{-CH}_2\text{-NO}] - k_{45}x[\text{CH}_3\text{CO}] + k_{45} \\ & [\text{CH}_3\text{CONO}] + k_{46}x[\text{CH}_3\text{CONO}] - k_{46}[\text{CH}_3\text{CO}(\text{NO})_2] - k_{50}y \\ & [\text{CH}_3\text{NO}] - k_{51}y[\text{CH}_2(\text{NO})\text{CHO}] - k_{48}y[\text{HNO}] - k_{49}[\text{CH}_2\text{CHO}][\text{HNO}] = 0. \end{aligned}$$

With the usual approximations this expression transforms into an implicit function of the concentrations of acetaldehyde, nitric oxide, and methyl only:

$$F(a, x, y) = 2k_1 a - 2k_{15} y^2 - \frac{2k_{16} k_5 a y^2}{P_1 a + P_2 x} G + P_3 a x = P_4 x y + H -$$

$$\frac{P_2 k_5 a x y}{P_1 a + P_2 x} G - \frac{2P_5 k_5 a x y^2}{P_1 a + P_2 x} G - 2P_6 x y^2 = 0,$$

with

$$G = \frac{k_5 a y + P_2 x y}{k_5 a y + P_2 x y + P_7 a x}, \quad H = \frac{P_8 (P_1 a + P_2 x)}{(k_5 a + P_2 x) y}.$$

(To obtain a manageable expression for CH_2CHO ,

$$[\text{CH}_2\text{CHO}] = \frac{k_5 a y}{P_1 a + P_2 x} G,$$

it has been assumed that $k_{48} = k_{49}$, $4P_1 \approx 4k_7 < k_5$, and $(k_5 a y + P_2 x y + P_7 a x)^2 > 4P_7 k_5 a^2 x y$.

The parameters P are functions of rate constants:

$$P_1 = k_7 + \frac{k_8 k_{18}}{k_{-8} + k_{18}}$$

$$P_2 = \frac{k_{43} k_{42}}{k_{43} + k_{-42}}$$

$$P_3 = \frac{k_{25}}{k_{-25} + k_{28} + k_{26}} \left[\frac{k_{26} (5k_{29} + k_{30})}{k_{29} + k_{30}} + \frac{k_{28} (5k_{31} + 2k_{33})}{k_{31} + k_{33}} \right]$$

$$P_4 = \frac{k_{40} k_{39}}{k_{40} + k_{-39}}$$

$$P_5 = \frac{k_{42} k_{51}}{k_{43} + k_{-42}}$$

$$P_6 = \frac{k_{39} k_{50}}{k_{40} + k_{-39}}$$

$$P_7 = k_{34}$$

$$P_8 = \frac{2k_{34} k_{35}}{k_{48}}$$

Having converted v_{CH_4} into $[\text{CH}_3]$ according to $v_{\text{CH}_4} = k_{\text{CH}_4} [\text{CH}_3] [\text{CH}_3\text{CHO}]$ (Figure 9), and v_{acetone} into $[\text{CH}_3]$ according to $v_{\text{acetone}} = k_{\text{ace}} [\text{CH}_3] [\text{CH}_3\text{CHO}]$ (Figure 10) (k_{CH_4} and k_{ace} from (61)), $F(a, x, y)$ has been fitted to the experimental data with P_7 and P_8 zero, the reason being that the limited accuracy of the data did not permit investigation of all eight parameters at the same time.

The fitting was done by means of a digital computer. For n experimental points values of the parameter P_i were sought such that

$$\sum_{v=1}^n F(a, x_v, y_v)^2 = \text{Min.}$$

Data from ref. 90, converted into $[\text{CH}_3]$ versus $[\text{NO}]$ diagrams, were treated in the same way (Figures 11 and 12). It is apparent that the mechanism explains well the inhibition observed at the lower acetaldehyde and low nitric oxide pressures. Those values of the parameters which lead to a good fit are listed in Table 8.

The success of the mechanism rests on the fact that it allows for two radicals of major mechanistic importance, CH_3 and CH_2CHO , whose concentrations are affected by NO in different ways. Whereas CH_3 is removed as well as generated directly through NO , CH_2CHO is removed directly, but generated by NO only indirectly, via the CH_3 . With some simplification, this state of affairs can be looked at in the following way:

Suppose that the CH_2CHO radical were absent. Then, disregarding reaction 50,

$$F(a, x, y) = 2k_1 a - 2k_{15} y^2 + P_3 a x - P_4 x y = 0,$$

(cont'd on p. 81)

Figure 9

$[\text{CH}_3]$ as a function of $[\text{NO}]$ and temperature, calculated from the methane data on the basis of k_{CH_4} , the rate constant of the reaction $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$. ($p_a = 176.0$ torr).

○ experimental

— calculated fit; the values of the parameters used are given in Table 8.

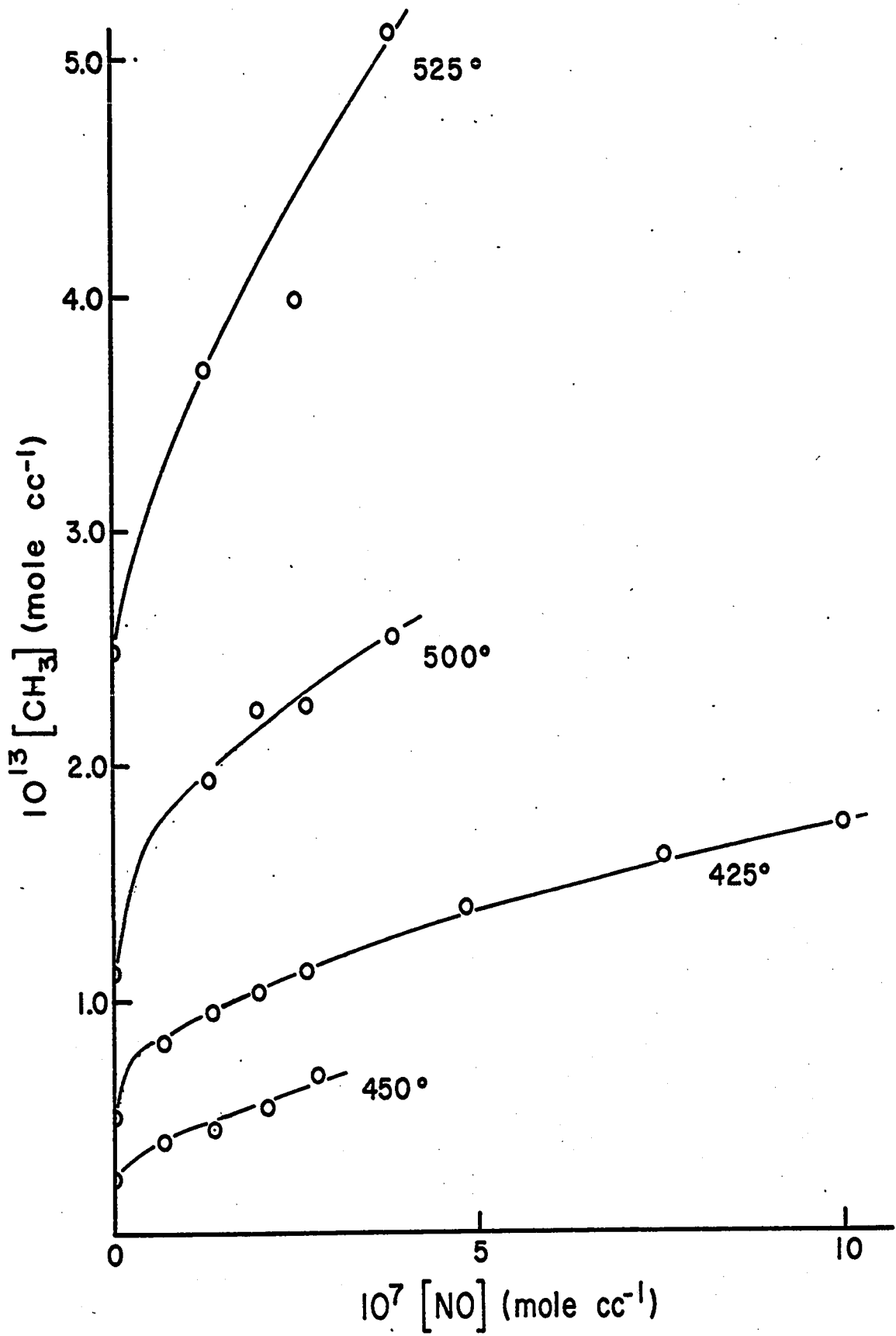


Figure 10

$[\text{CH}_3]$ as a function of $[\text{NO}]$ and temperature, calculated from the acetone data on the basis of k_{ace} , the rate constant of the reaction $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{COCH}_3 + \text{H}$, ($p_a = 176.0$ torr).

o

experimental

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calculated fit; the values of the parameters used are given in Table 8.

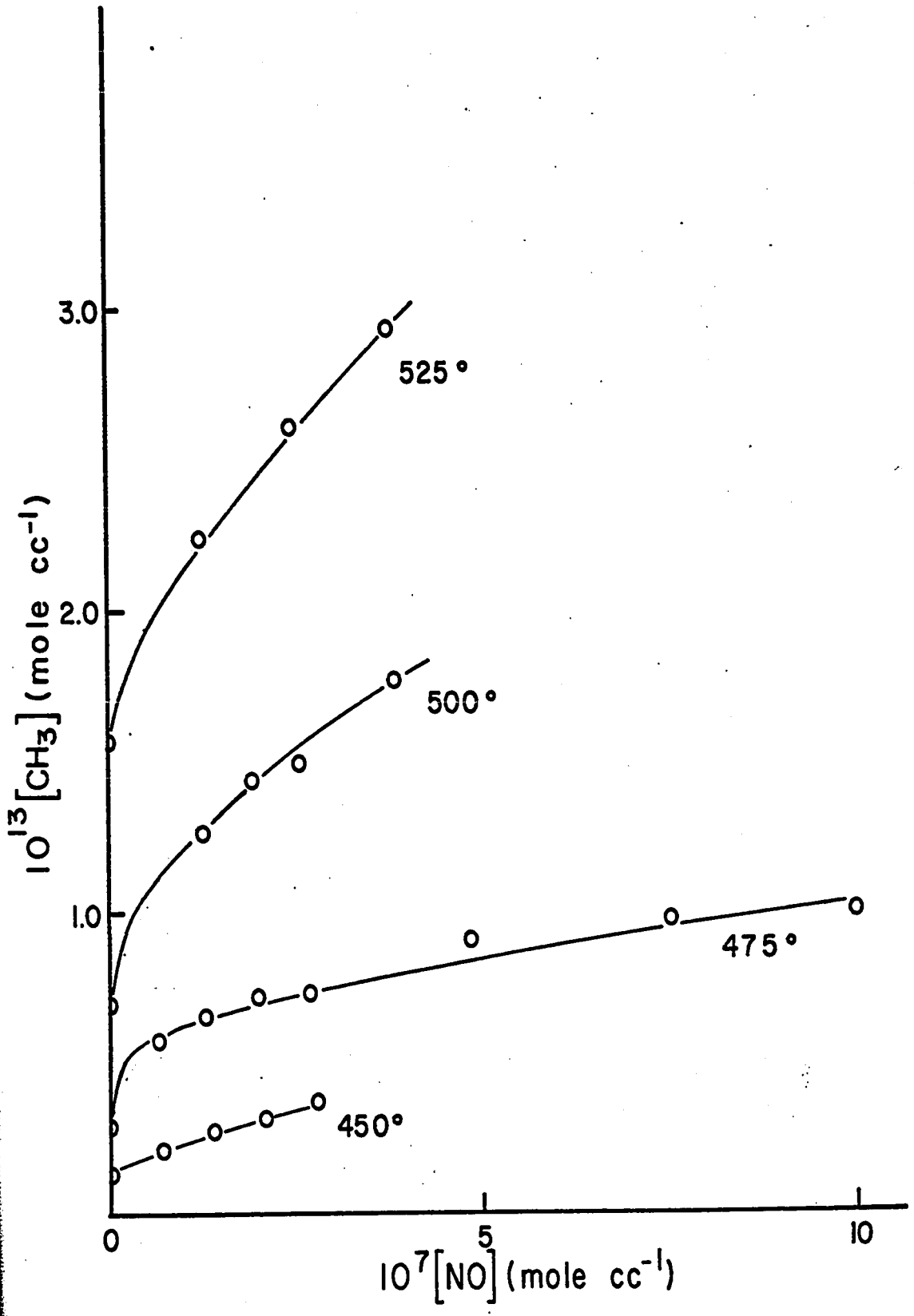


Figure 11

$[\text{CH}_3]$ as a function of $[\text{NO}]$ and the acetaldehyde pressure, calculated from data in reference 90, based on k_{CH_4} , the rate constant of the reaction $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$, ($T = 505^\circ\text{C}$). Behaviour at lower $[\text{NO}]$.

○ experimental

— The function was fitted to the data for $p_a = 52$ torr, and the parameters thus obtained were used to calculate the curves corresponding to the other aldehyde pressures. For parameter values used see Table 8.

The results from ref. 90 shown are not mutually consistent, for at $[\text{NO}] = 0$, if $[\text{CH}_3]$ (52 torr) is taken as the basis, $[\text{CH}_3]$ (70 torr) and $[\text{CH}_3]$ (100 torr) are considerably too low, while $[\text{CH}_3]$ (200 torr) is too high. If $[\text{CH}_3]$ (52 torr) is assumed to be correct, then the others should lie on the curves, in agreement with the $3/2$ order kinetics of the pure pyrolysis.

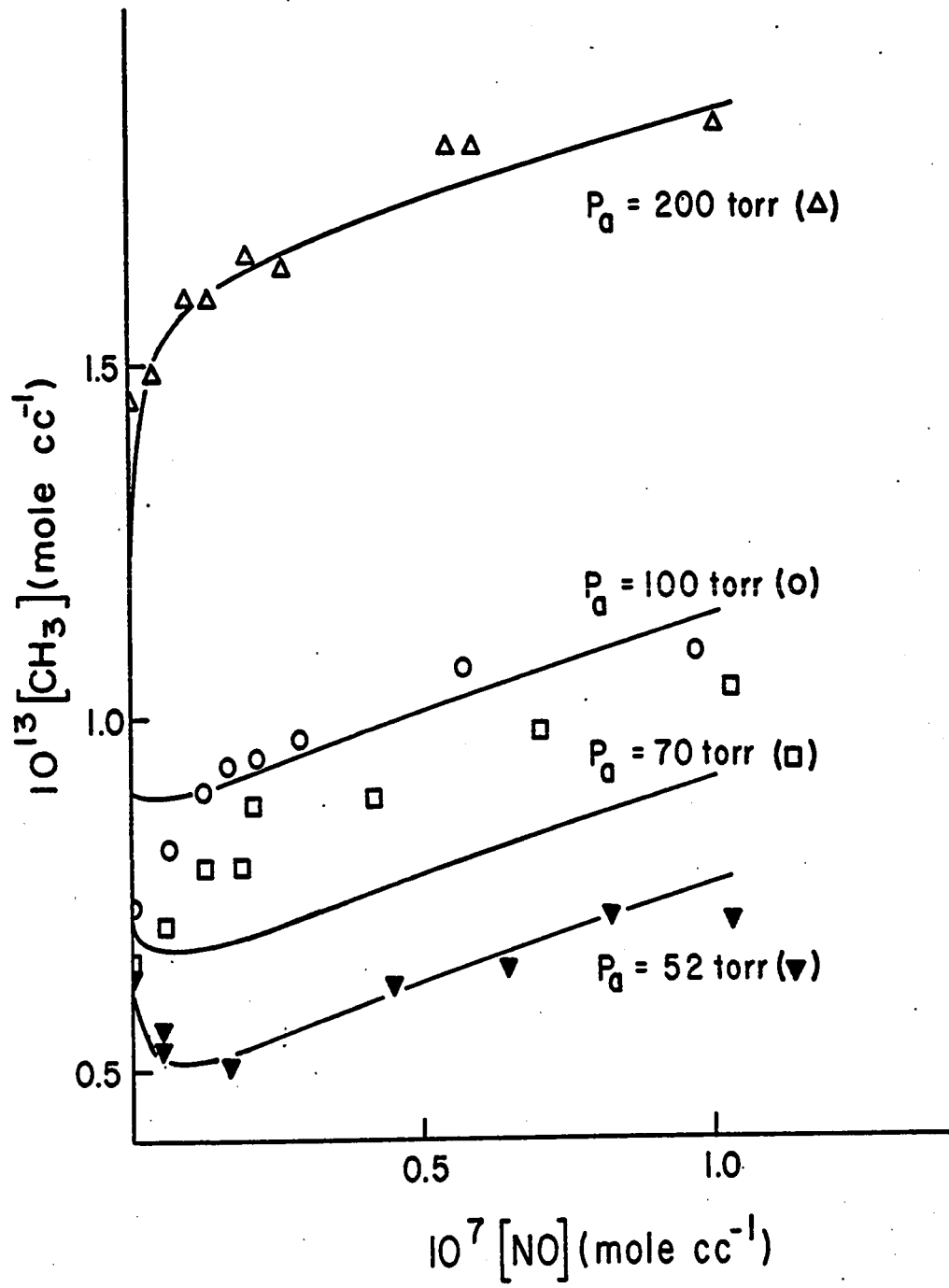


Figure 12

$[\text{CH}_3]$ as a function of $[\text{NO}]$ and p_a , calculated from data in reference 90, based on k_{CH_4} , the rate constant of the reaction $\text{CH}_3 + \text{CH}_3\text{CHO} \rightarrow \text{CH}_4 + \text{CH}_3\text{CO}$. ($T = 505^\circ\text{C}$). Behaviour over a wider range of $[\text{NO}]$.

- experimental
- calculated; the parameter values obtained through fitting the function to the data for $p_a = 52$ torr were used to calculate the other curves. For the parameter values used see Table 8.

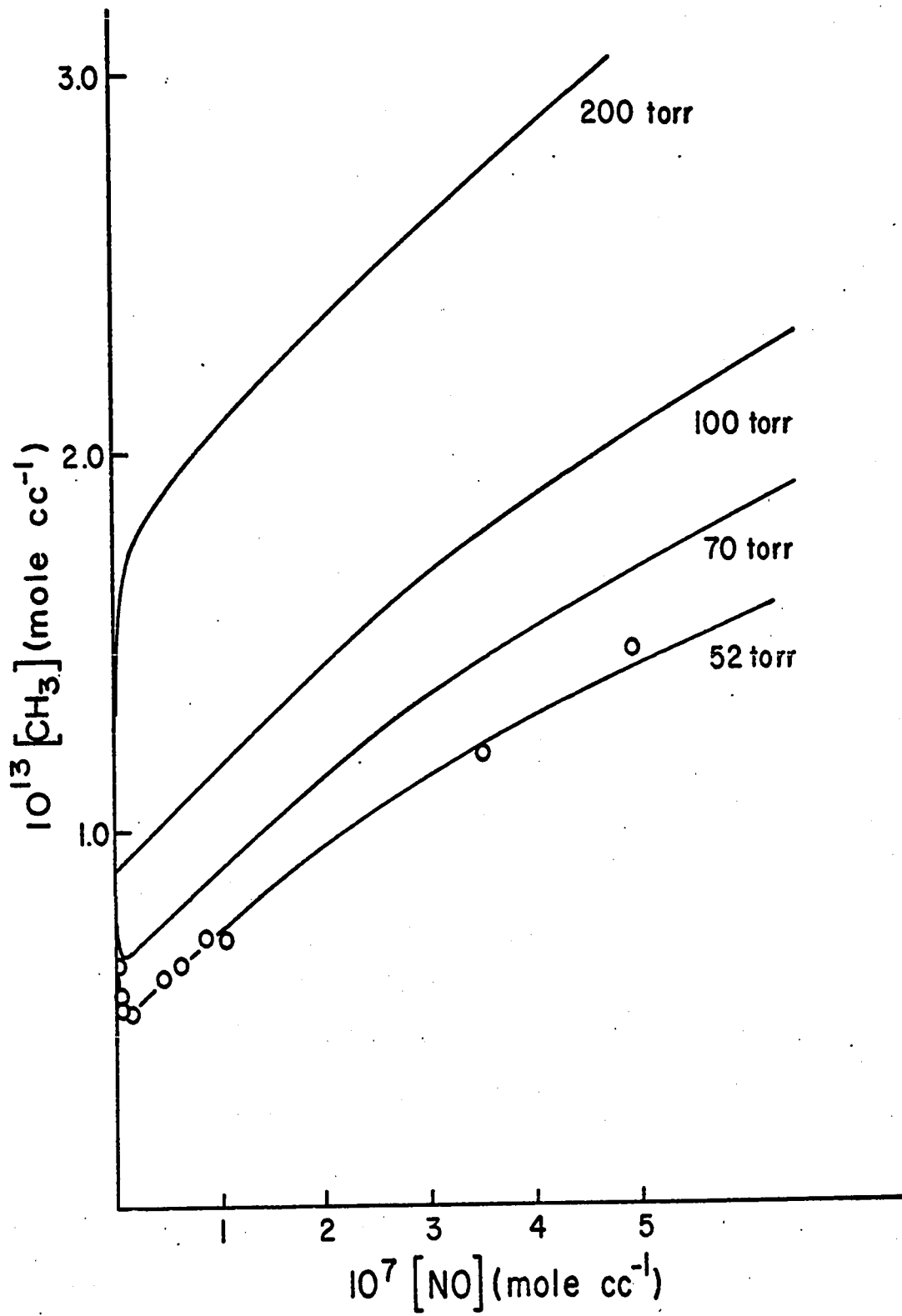


Table 8
Parameter values fitting $F(a, x, y)$ to data derived from
the methane and acetone productions,

Fig.	T(°C)	P ₁	P ₂	P ₃	P ₄	P ₅ *	P ₆ *	P ₇	P ₈
based on k _{CH₄}	450	0.60·10 ⁸	0.87·10 ⁹	0.63·10 ²	0.13·10 ⁹	0.2·10 ¹⁹	0.2·10 ¹⁹	0	0
	475	0.79·10 ⁸	0.52·10 ⁹	0.10·10 ³	0.62·10 ⁹	0.1·10 ²⁰	0.1·10 ¹⁹		
	500	0.37·10 ⁸	0.26·10 ⁹	0.29·10 ³	0.10·10 ¹⁰	0.0	0.0		
	525	0.45·10 ⁸	0.69·10 ⁹	0.13·10 ⁴	0.37·10 ¹⁰	0.1·10 ²⁰	0.1·10 ¹⁹		
based on k _{ace}	450	0.40·10 ⁷	0.70·10 ⁸	0.40·10 ²	0.33·10 ⁹	0.9·10 ⁹	0.5·10 ²⁰	0	0
	475	0.44·10 ⁷	0.27·10 ⁸	0.75·10 ²	0.12·10 ¹⁰	0.0	0.0		
	500	0.50·10 ⁷	0.62·10 ⁸	0.32·10 ³	0.24·10 ¹⁰	0.1·10 ²⁰	0.2·10 ²⁰		
	525	0.50·10 ⁷	0.53·10 ⁸	0.60·10 ³	0.28·10 ¹⁰	0.0	0.0		
based on k _{CH₄}	505	0.20·10 ⁸	0.17·10 ⁹	0.34·10 ³	0.88·10 ⁹	0.1·10 ²¹	0.1·10 ²¹	0	0
	505	0.20·10 ⁸	0.16·10 ⁹	0.31·10 ³	0.10·10 ¹⁰	0.0	0.0		

*It was found that P₅ and P₆ affect the feature of the dip only marginally, unless they are given values exceeding 10²², and generally depress the [CH₃] versus [NO] curves progressively with increasing [NO]. In any case, judging from the C₂H₆ results, which give slightly concave rather than convex curves for vC₂H₆ versus [NO], reaction 50 is, even at the highest [NO] investigated, at the most about as frequent as reaction 15. Presumably this is true also for the analogous reactions involving the CH₂CHO. Thus if P₆xy² = k₁₅y², with x = 10⁻⁶ mole cc⁻¹ and k₁₅ = 0.22·10¹⁴ cc mole⁻¹ sec⁻¹, P₆ = 0.2·10²⁰ cc² mole⁻² sec⁻¹. Comparing further the parameter values relating to Figure 11 and 12, it is to be noted that the effect of a change of P₅ and P₆ can be offset by a corresponding change of P₂, P₃ and P₄.

or

$$y = -\frac{P_4 x}{4k_{15}} + \left[\frac{P_4 x}{4k_{15}}^2 + \frac{P_3 a x + 2k_1 a}{2k_{15}} \right]^{1/2}$$

y' can be zero only under two conditions, namely if

1. $\lim_{x \rightarrow \infty} y' = 0$ for any a

2. $y'' = 0$ for all x .
 $a = P_4^2 k_1 / P_3^2 k_{15}$

The second condition is equivalent to requiring that y be equal to $y_0 = (k_1 a / k_{15})^{1/2}$ for all x . Thus y either rises monotonically, if $a > P_4^2 k_1 / P_3^2 k_{15}$, or falls in the opposite case.

Consider now the ethenoxy radical, With the usual assumptions, one obtains

$$[\text{CH}_2\text{CHO}] \equiv z = \frac{k_5 a y}{P_1 a + P_2 x}$$

For small x , the region where the dip is found, one may write for y

$$y = y_0 + y_0' x$$

Then

$$\frac{dz}{dx} = \frac{k_5 a (P_1 a y_0' - P_2 y_0)}{(P_1 a + P_2 x)^2}$$

Thus z rises monotonically if $a > P_2 y_0 / P_1 y_0'$, and falls otherwise.

Now because of reaction 7 it can be said that, in the steady state, a certain fraction of the CH_2CHO radicals is continually being transformed

into methyl radicals; this fraction is called C. Thus the methyl radical concentration may be thought of as composed of two terms, y and Cz. The result of a superposition of y(x) and Cz(x) for "large" a ($a > P_2 y_0 / P_1 y'_0$) and "intermediate" a ($P_2 y_0 / P_1 y'_0 > a > P_4^2 k_1 / P_3^2 k_{15}$) is shown schematically in Figure 13.

The behaviour predicted at low acetaldehyde pressures is shown in Figure 14, the values of the parameters being the same as for Figure 12. It must be noted, however, that in the present mechanism it is assumed that all elementary reactions are in their high-pressure region, which compromises its applicability at low pressures.

Besides CH_4 and acetone, the results for HCN, H_2 , CO_2 , C_2H_6 , and CH_3NCO were also mathematically analyzed. Thereby the rates were treated as functions v(a, x, y), into which instead of the experimental values of $[\text{CH}_3]$ (obtained via v_{CH_4} and v_{acetone}) calculated values y(x), read off Figures 9 and 10, were substituted.

HCN

Making the usual assumptions, one can express

$$v_{\text{HCN}} = Q_1 a x + P_4 x y + \frac{P_2 k_5 a x y}{P_1 a + P_2 x} \cdot G,$$

$$\text{with } Q_1 = \frac{k_{25}(k_{28} + k_{26})}{k_{-25} + k_{28} + k_{26}},$$

and the other symbols having the same meaning as above. It is seen that $P_3/5 \leq Q_1 < P_3$, i. e., $Q_1 \geq 10$. It was found, however, that the best fits were obtained with very small, essentially zero, Q_1 .

(cont'd on p. 85)

Figure 13

Schematic diagram showing $[CH_3]$, which is proportional to v_{CH_4} ,
as the sum of two terms.

above: "large" $a(= [CH_3CHO])$

below: "intermediate" $a(= [CH_3CHO])$

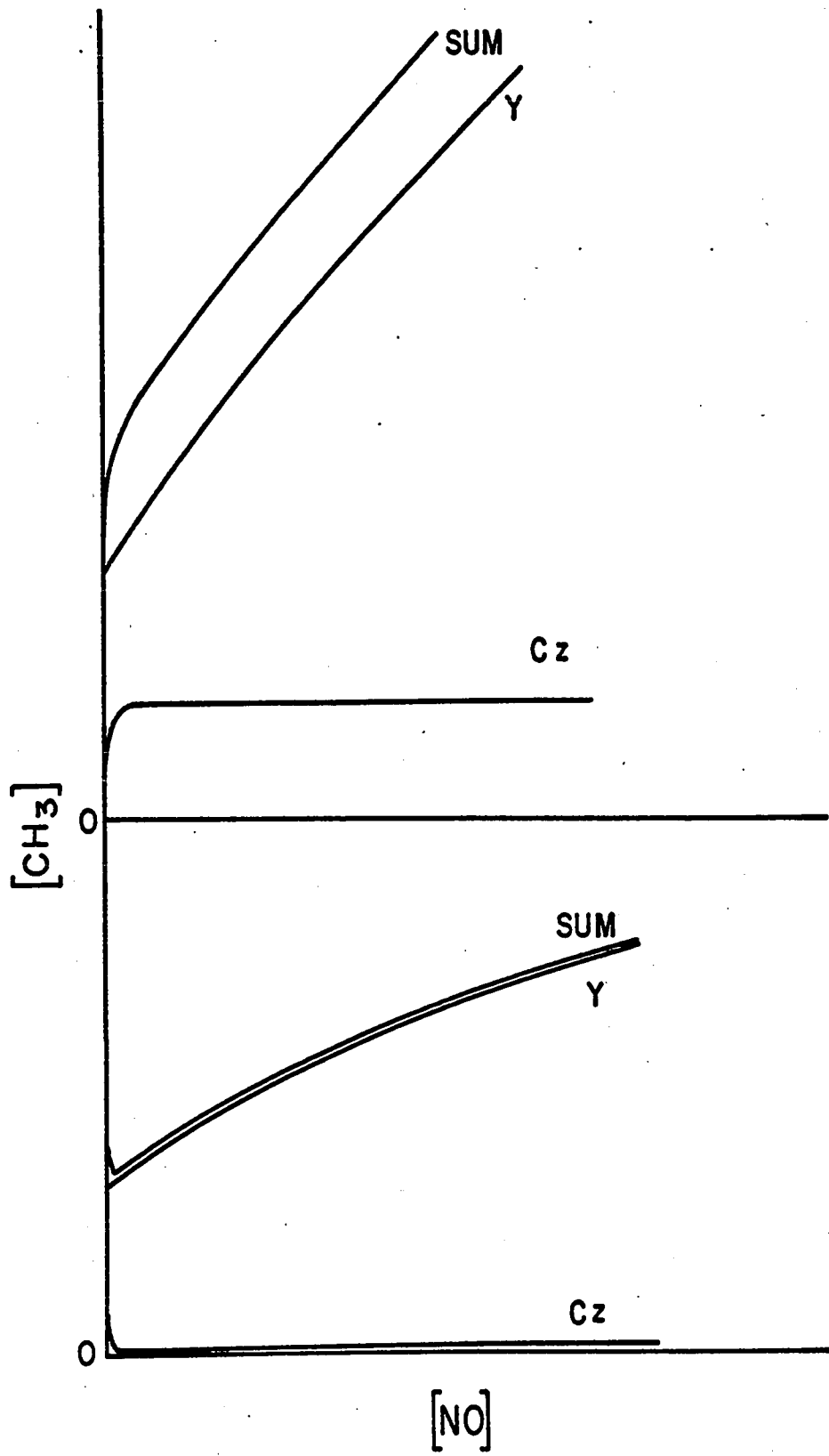
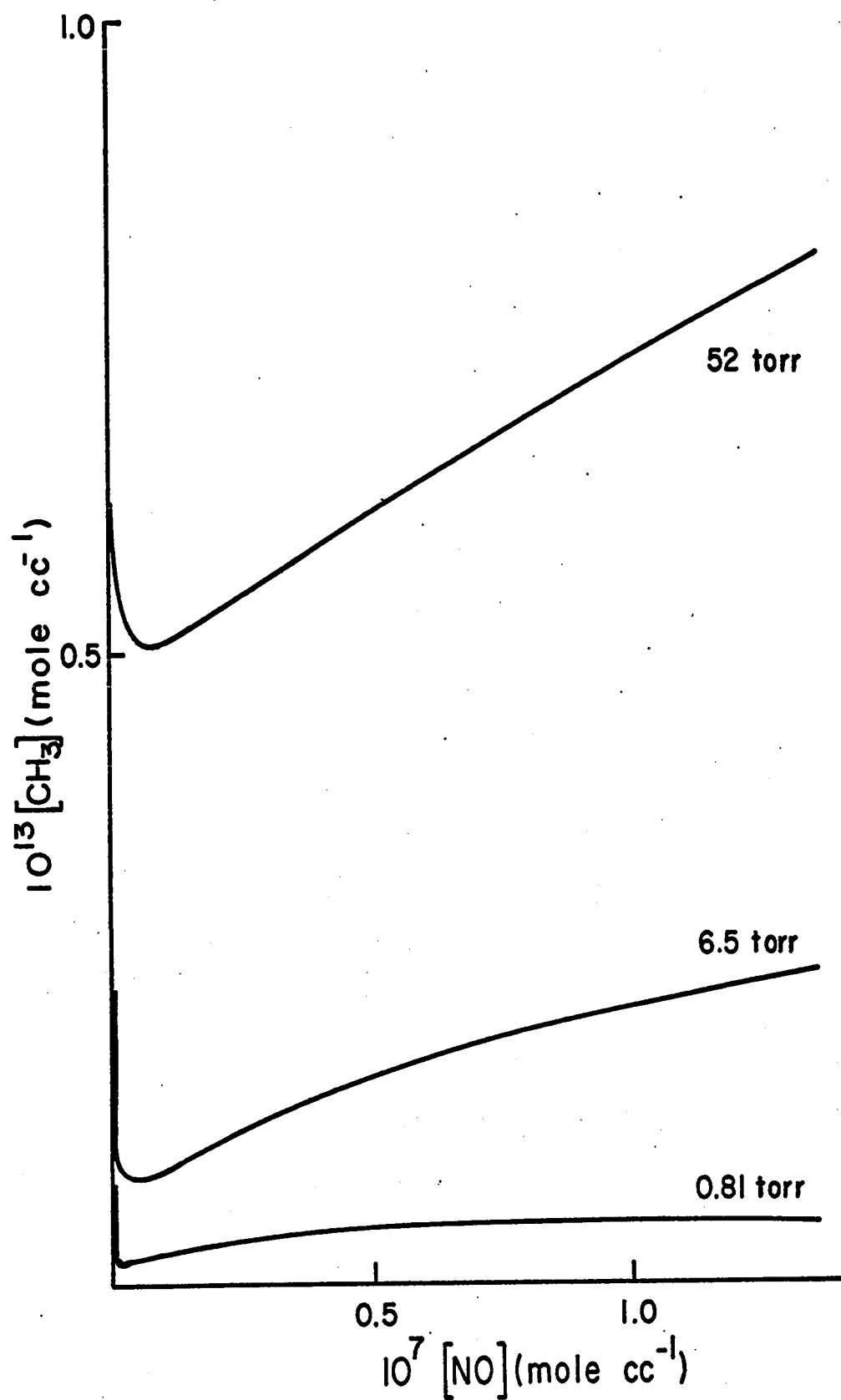


Figure 14

[CH₃] as a function of [NO] at low acetaldehyde pressures. (T = 505° C).



This would indicate that all of the HCN results from termination, which is at variance with the analytical constraint (namely, that products connected with the generation of radicals must balance those coming from the annihilation of radicals), according to which only part of the HCN can derive from termination reactions. The best values of the parameters are listed in Table 9, and the calculated function $v_{\text{HCN}}(a, x, y)$ compared with the experiment in Figure 15.

H₂

The rate of production of H₂ can be expressed thus:

$$v_{\text{H}_2} = R_1 a y + \frac{R_2 k_5 a^2 y}{P_1 a + P_2 x} G + k_1 a + R_3 a x + H a x / 2,$$

with

$$R_1 = \frac{k_6 k_{17}}{k_{-6} + k_{17}}$$

$$R_3 = \frac{k_{25} k_{28} k_{33}}{(k_{-25} + k_{28} + k_{26})(k_{31} + k_{33})}$$

$$R_2 = \frac{k_8 k_{18}}{k_{-8} + k_{18}},$$

and the other symbols as above. The accuracy of the data did not warrant varying R₃, P₇, and P₈ simultaneously, as P₇ and P₈ together can act in a very similar way to R₃ alone. Putting R₃ = 0 means that P₇ and P₈ are at their maximum possible value; their upper limit is thus calculated. The best parameter values are listed in Table 10. Experimental results and calculations are shown in Figure 16.

(cont'd on p. 90)

Table 9
Parameter values fitting v_{HCN} to the experimental data for HCN.

	$T(^{\circ}\text{C})$	P_1	P_2	Q_1	P_4	P_7
Based on k_{CH_4}	450	$0.60 \cdot 10^8$	$0.18 \cdot 10^7$	0	$0.74 \cdot 10^9$	$0.65 \cdot 10^1$
	475	$0.79 \cdot 10^8$	$0.30 \cdot 10^8$	0	$0.70 \cdot 10^9$	$0.13 \cdot 10^3$
	500	$0.37 \cdot 10^8$	$0.29 \cdot 10^7$	0	$0.90 \cdot 10^9$	$0.58 \cdot 10^1$
	525	$0.45 \cdot 10^8$	$0.45 \cdot 10^7$	0	$0.90 \cdot 10^9$	$0.14 \cdot 10^2$
Based on k_{ace}	450	$0.40 \cdot 10^7$	$0.23 \cdot 10^7$	0	$0.11 \cdot 10^{10}$	$0.42 \cdot 10^1$
	475	$0.44 \cdot 10^7$	$0.11 \cdot 10^6$	0	$0.13 \cdot 10^{10}$	$0.93 \cdot 10^1$
	500	$0.50 \cdot 10^7$	$0.57 \cdot 10^7$	0	$0.65 \cdot 10^9$	$0.18 \cdot 10^1$
	525	$0.50 \cdot 10^7$	$0.40 \cdot 10^7$	0	$0.10 \cdot 10^{10}$	$0.53 \cdot 10^1$

Figure 15

v_{HCN} as a function of [NO] and temperature. ($p_a = 176.0$ torr)

Symbols: : experimental

— calculated fit; for parameter values used see
Table 9.

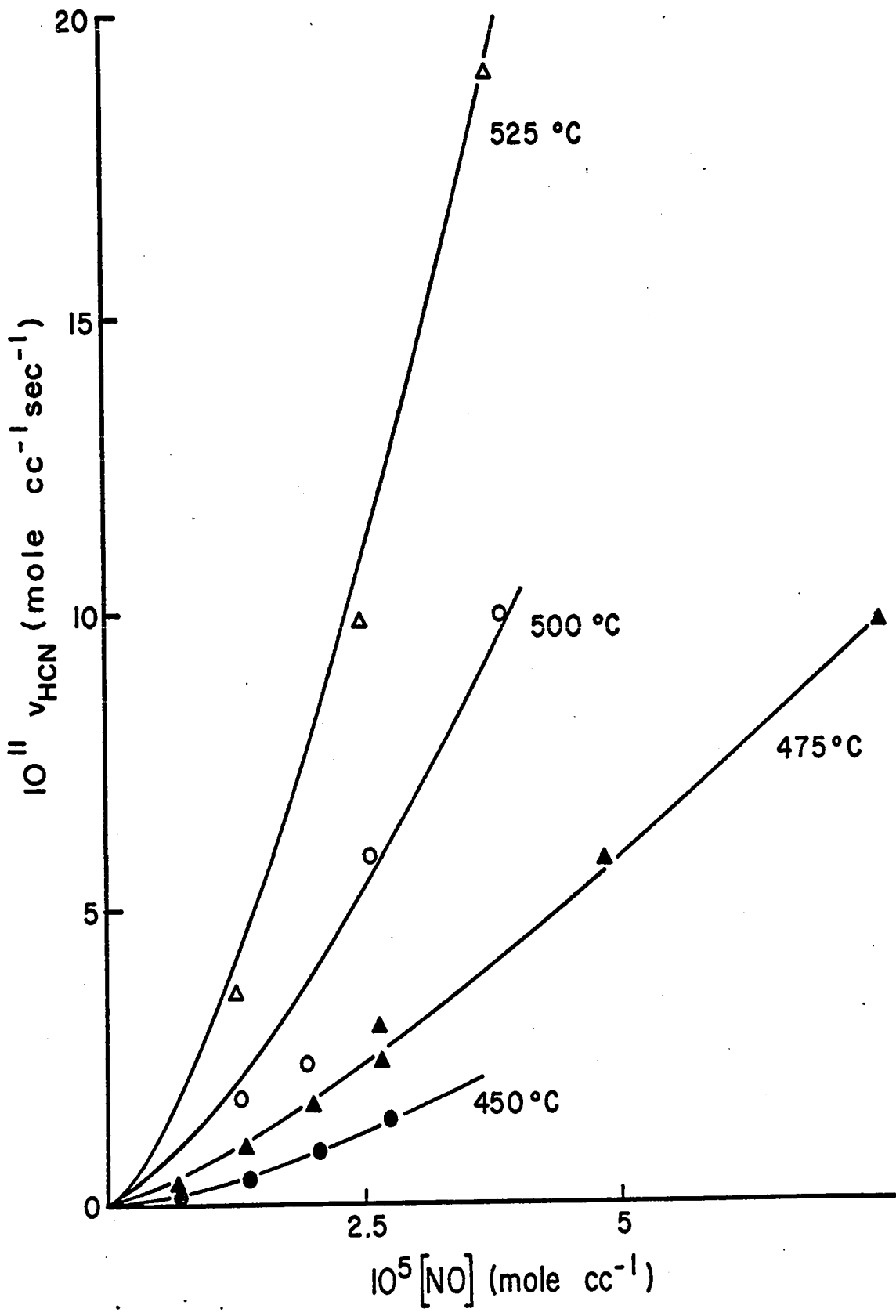


Table 10

Parameter values fitting v_{H_2} to the experimental data for H_2

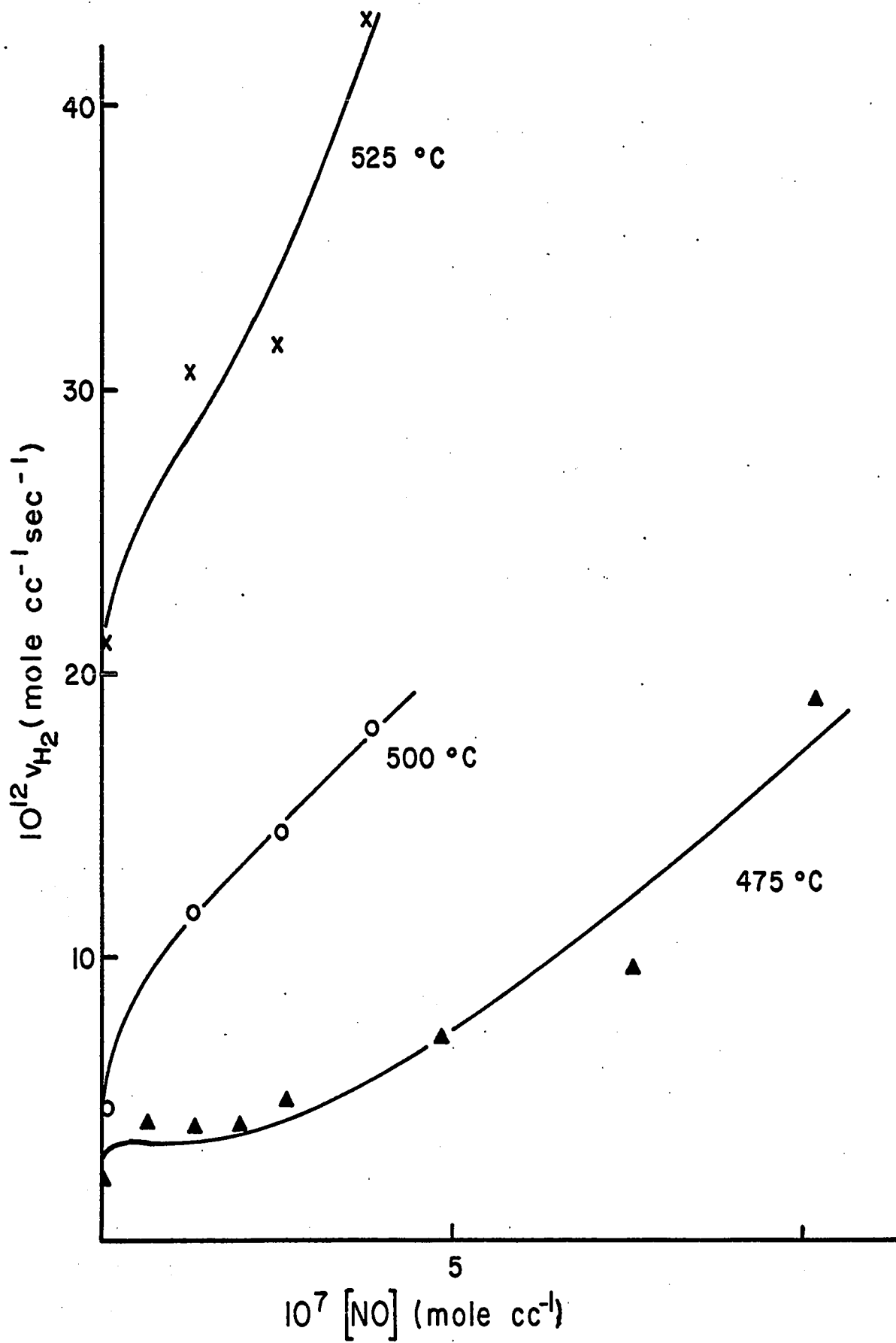
	$T(^{\circ}C)$	P_1	P_2	R_1	R_2	R_3	P_7	P_8
Based on k_{CH_4}	475	$0.26 \cdot 10^8$	$0.83 \cdot 10^9$	$0.88 \cdot 10^6$	$0.49 \cdot 10^6$	0	$0.89 \cdot 10^2$	$0.25 \cdot 10^{-11}$
	500	$0.44 \cdot 10^8$	$0.61 \cdot 10^8$	$0.46 \cdot 10^7$	$0.40 \cdot 10^6$	0	$0.13 \cdot 10^3$	$0.25 \cdot 10^{-10}$
	525	$0.62 \cdot 10^8$	$0.58 \cdot 10^9$	$0.13 \cdot 10^8$	$0.69 \cdot 10^6$	0	$0.55 \cdot 10^3$	$0.32 \cdot 10^{-9}$
Based on k_{ace}	475	$0.24 \cdot 10^7$	$0.42 \cdot 10^8$	$0.37 \cdot 10^7$	$0.63 \cdot 10^5$	0	$0.20 \cdot 10^3$	$0.20 \cdot 10^{-10}$
	500	$0.59 \cdot 10^7$	$0.21 \cdot 10^8$	$0.51 \cdot 10^7$	$0.11 \cdot 10^6$	0	$0.27 \cdot 10^2$	$0.10 \cdot 10^{-9}$
	525	$0.50 \cdot 10^7$	$0.54 \cdot 10^8$	$0.66 \cdot 10^7$	$0.17 \cdot 10^6$	0	$0.15 \cdot 10^3$	$0.40 \cdot 10^{-9}$

Figure 16

v_{H_2} as a function of [NO] and temperature. ($p_a = 176.0$ torr).

Symbols: experimental

— calculated fit. For parameter values used
see Table 10.



It is recalled that values for $R_1 = k_6 k_{17} / (k_{-6} + k_{17}) = k_{ace}$ and $R_2 \equiv P_{1'} = k_8 k_{18} / (k_{-8} + k_{18})$ have been obtained from the NO-free work (see (61) for k_{ace} , and Table 6 for $P_{1'} \equiv R_2$): at 500°C , $R_1 \approx 0.5 \cdot 10^7$ cc mole⁻¹ sec⁻¹ and $R_2 \approx 0.2 \cdot 10^6$ cc mole⁻¹ sec⁻¹.

CO₂

The function

$$v_{\text{CO}_2} = \frac{S_1 a x^2 y}{S_2 + x} + v_{\text{CO}_2}(0),$$

based on $[\text{CH}_3\text{CO}] = k_4 a y / k_{13}$, has been fitted to the data obtained for CO₂ (Figure 17), where

$$S_1 = \frac{k_{45} k_4}{k_{13}} \qquad S_2 = \frac{k_{-45} (k_{-46} + k_{47})}{k_{46} k_{47}}$$

Values of the parameters are shown in Table 11.

C₂H₆

The rate of formation of C₂H₆ has been fitted by the expression

$$v_{\text{C}_2\text{H}_6} = U_1 k_{15} y^2 \quad (y = v_{\text{CH}_4} / k_{\text{CH}_4} \cdot a \text{ or } v_{\text{acetone}} / k_{\text{ace}} \cdot a).$$

As Figure 18 shows, a single quadratic term is quite adequate. However, the parameter U_1 differs from unity (Table 12).

(cont'd on p. 94)

Figure 17

v_{CO_2} as a function of [NO] and temperature. ($p_a = 176.0$ torr).

o experimental

— calculated fit; for parameter values used
see Table II.

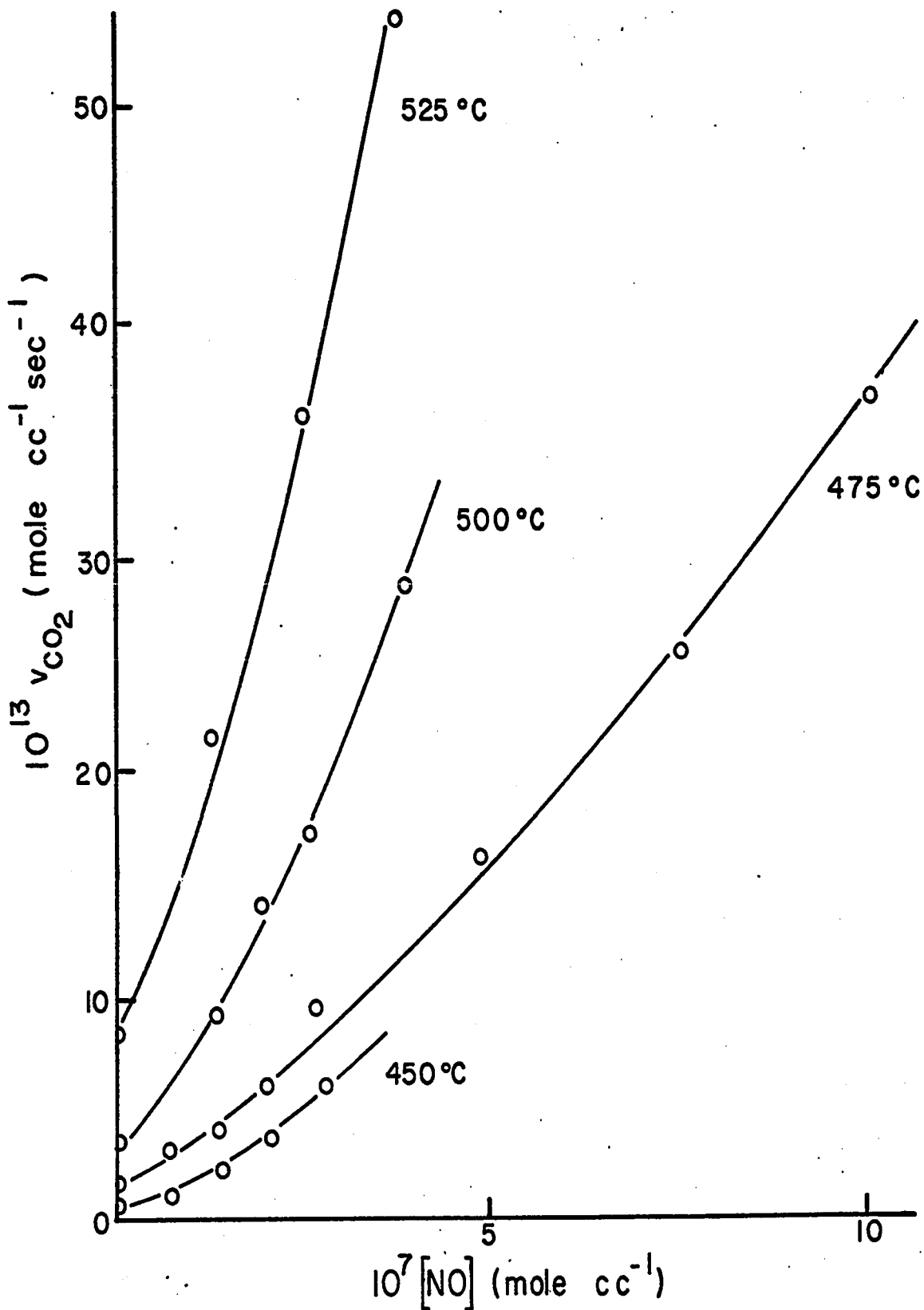


Table II
Parameter values fitting v_{CO_2}
to the experimental data for CO_2 .

	$T(^{\circ}C)$	S_1	S_2
Based on k_{ace}	450	$0.16 \cdot 10^{14}$	$0.56 \cdot 10^{-7}$
	475	$0.88 \cdot 10^{13}$	$0.14 \cdot 10^{-8}$
	500	$0.10 \cdot 10^{14}$	$0.38 \cdot 10^{-8}$
	525	$0.17 \cdot 10^{14}$	$0.20 \cdot 10^{-9}$
Based on k_{CH_4}	450	$0.92 \cdot 10^{13}$	$0.65 \cdot 10^{-7}$
	475	$0.53 \cdot 10^{13}$	$0.20 \cdot 10^{-9}$
	500	$0.71 \cdot 10^{13}$	$0.84 \cdot 10^{-8}$
	525	$0.20 \cdot 10^{13}$	$0.17 \cdot 10^{-9}$

Figure 18

$v_{C_2H_6}$ as a function of [NO] and temperature. ($p_a = 176.0$ torr).

Symbols: experimental

— calculated fit; for parameter values used
see Table 12.

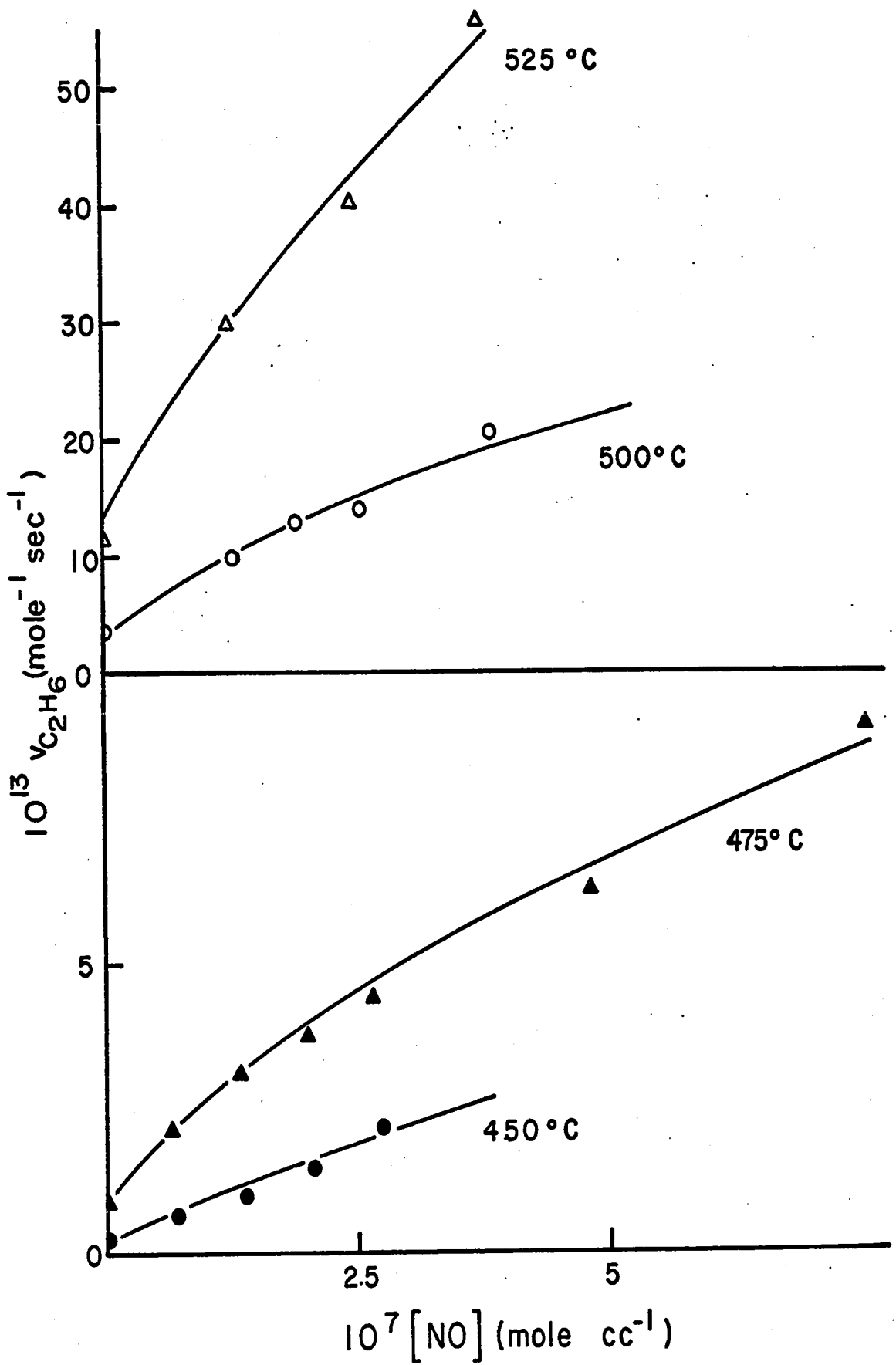


Table 12

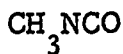
Parameter values fitting $v_{C_2H_6}$ to the experimental data for C_2H_6 .

$T(^{\circ}C)$	450	475	500	525
U_1 (based on k_{CH_4})	2.2	1.6	1.3	1.0
U_1 (based on k_{ace})	6.9	3.8	2.9	2.8

If k_{15} is correct, then this would seem to indicate that $[CH_3]$ can be more accurately calculated on the basis of v_{CH_4} , and that there is a systematic error in both k_{CH_4} and k_{ace} . Calling k_{15}^o the "true" constant (such that $U_1 = 1$) one has $k_{15}/k_{15}^o = (U_1(T))^{-1}$. The relationship between k_{15} and k_{15}^o is found graphically to be

$$k_{15}^o = 30 \cdot e^{-5.9/RT} \cdot k_{15} ,$$

representing an adjustment of the rate constants which is unacceptably large. It is therefore concluded that the apparent trend of U_1 with temperature is not real.



The rate of formation of CH_3NCO is given by

$$v_{CH_3NCO} = U_2 a x ,$$

with

$$U_2 = \frac{k_{25} k_{30} k_{27}}{(k_{29} + k_{30})(k_{-25} + k_{28} + k_{26})}$$

U_2 was obtained graphically from Figure 19, and values are given in Table 13.

Table 13

Values of U_2 , the slope of lines in Figure 19.

$T(^{\circ}C)$	450	475	500	525
U_2	0.8	2.6	4.6	9.0

No attempt was made to treat the rates of formation of the other products in a similar quantitative way, because the accuracy of the data does not warrant this.

To sum up, the following set of reactions seems sufficient to explain the effect of the NO in the pyrolysis of a "clean" mixture of acetaldehyde and nitric oxide:

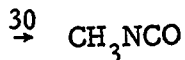
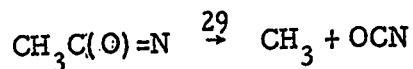
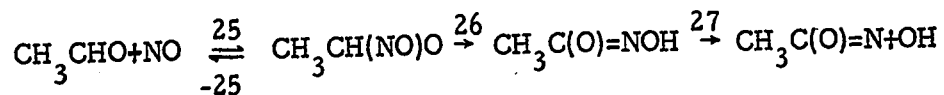
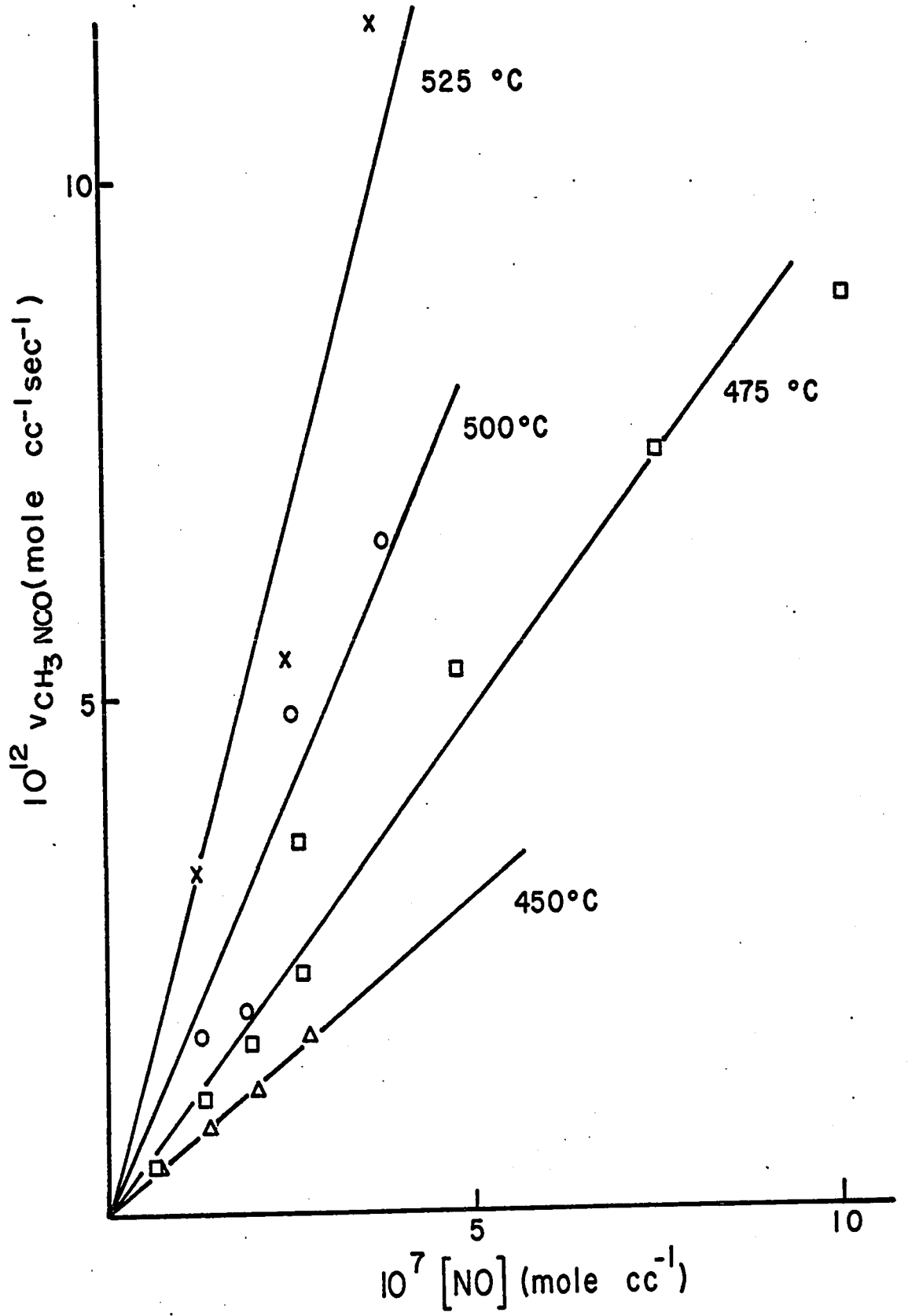
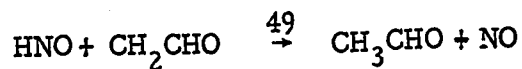
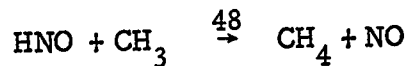
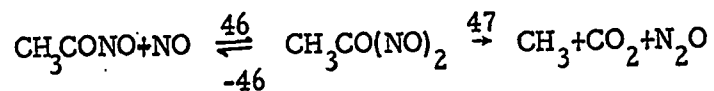
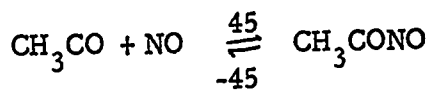
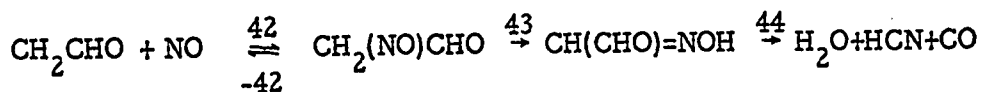
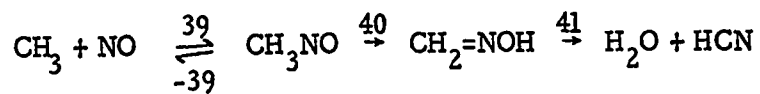
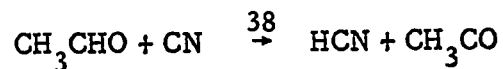
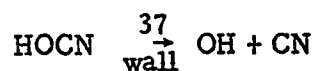
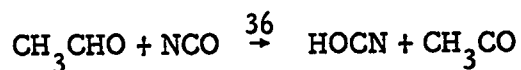
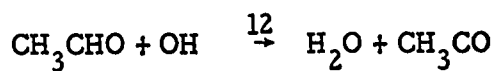
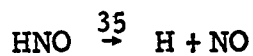
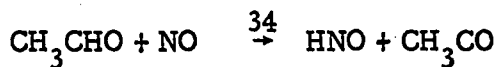


Figure 19

$v_{\text{CH}_3\text{NCO}}$ as a function of [NO] and temperature. Best straight lines drawn by eye.





III. The "Unclean" Pyrolysis.

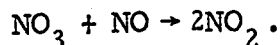
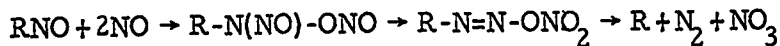
This section is devoted to the pyrolysis of "unclean" mixtures of CH_3CHO and NO . A mixture is called "unclean" if it is contaminated by compounds which arise owing to a slow reaction at room temperature ("cold" reaction). The dependence of the kinetics of the pyrolysis on the length of the mixing period must be due to one or several such compounds accumulating prior to pyrolysis. In order to explain this dependence, in particular the strong enhancement of the rates of nitrogen and ethyl isocyanate formation, the "cold" reaction, which produced N_2 , NO_2 , H_2O , CO_2 , N_2O , HCN , CH_3NO_2 , CH_3NO_3 , methyl acetate, CO , (see Figure 4) and quite probably others which escaped detection, will be discussed first.

A. Processes at Room Temperature.

Dark reactions at room temperature have been observed in previously photolyzed mixtures of C_2H_6 and NO (91), and of CH_3CHO and NO (92). In the latter case the reacting species is assumed to be triplet acetaldehyde:

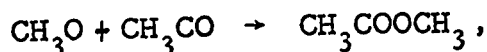


Acetaldehyde vapour reacts with NO and NO_2 at room temperature forming N_2 and NO_2 (93). It has been assumed by Christie and others that the reactive species in such systems are nitroso compounds which are also able to catalyze the disproportionation of NO into N_2 and NO_2 (91, 92, 93, 94) in processes of the following type:

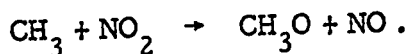


In the case of acetaldehyde, according to Christie, the role of R is largely played by the acetyl radical. Such processes, judging from the present work, must be limited to low temperature conditions.

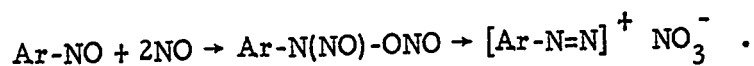
A variety of nitrogeous and nitrogen-free compounds have been identified as products of the photolysis at 25° C of mixtures of acetyl compounds with oxides of nitrogen. A mixture of CH₃CHO and NO₂ (95) yielded CO₂, methyl acetate, CH₃NO₂, and CH₃NO₃, while acetone plus NO (95) gave rise to methyl acetate, CH₃NO₂, CH₃NO₃, and formamide, among other nitrogen-free products. With biacetyl and NO (96) N₂, NO₂, CO₂, CO, CH₃NO₂, CH₃ONO, CH₃NO₃, methyl acetate, and other nitrogen-free products were observed. The most likely source of methyl acetate was considered (96) to be the reaction



with CH₃O produced by

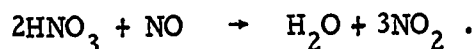
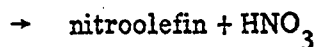
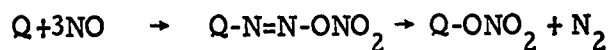
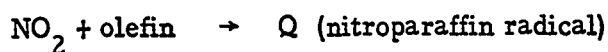


Studies have also been made in the liquid phase at or near room temperature. Acetaldehyde in cold soda solution was treated (97) with NO to see whether it would add on to the carbonyl group in a similar way as it does to the nitroso group in aromatic systems, which were known (98) to yield the diazonium nitrates by a reaction sequence assumed to be

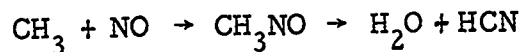
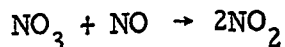
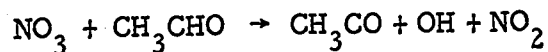
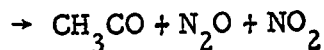
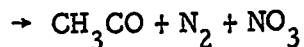
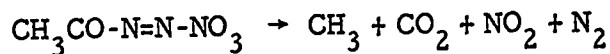
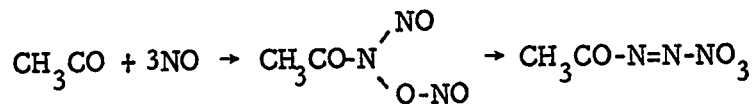


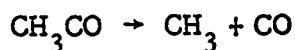
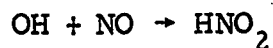
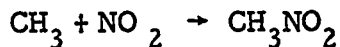
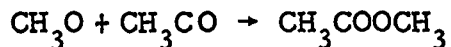
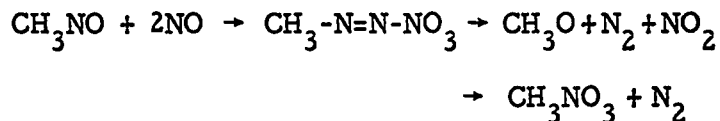
With the acetaldehyde, however, no evidence was found that a reaction had occurred. Liquid olefins have been found to react

smoothly with NO in the presence of minute traces of NO₂ (99,100), giving a variety of nitrogenous products and N₂; it was also found that in the complete absence of NO₂ there was no reaction. The mechanism suggested here with regard to the main features of the findings was



In the present system a variety of compounds were found (Figure 4), presumably fewer than were actually formed. To account for them, a branched-chain mechanism can be postulated:

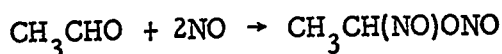




NO_2 may also have a catalytic effect (93):



If the branching outweighs the termination reactions, a progressive increase of product yield would be expected, as is indeed observed. At room temperature CH_3CO is less likely to dissociate than to associate with NO ; this is borne out by the fact that only traces of CO were found. The absence of CH_4 may be understood in a similar way: abstraction reactions must be strongly disfavoured in this system as compared to combinations. The chain could be initiated by



and subsequent disproportionation of NO by this nitroso compound; alternatively, traces of air, not entirely avoidable in a conventional high vacuum system, might start the chain.

B. Processes at High Temperatures.

It is thus seen that a mixture of various compounds undergoes the subsequent pyrolysis, not just CH_3CHO and NO . Of those compounds detected all but CH_3ONO_2 , CH_3NO_2 , and NO_2 may be considered inert. Nitrogen is not merely carried over from the cold reaction but mainly arises in the hot reaction, as evidenced by a linear dependence of yield on reaction time with a comparatively small intercept; N_2 must therefore owe its formation to some reactive species, about which several assertions can be made:

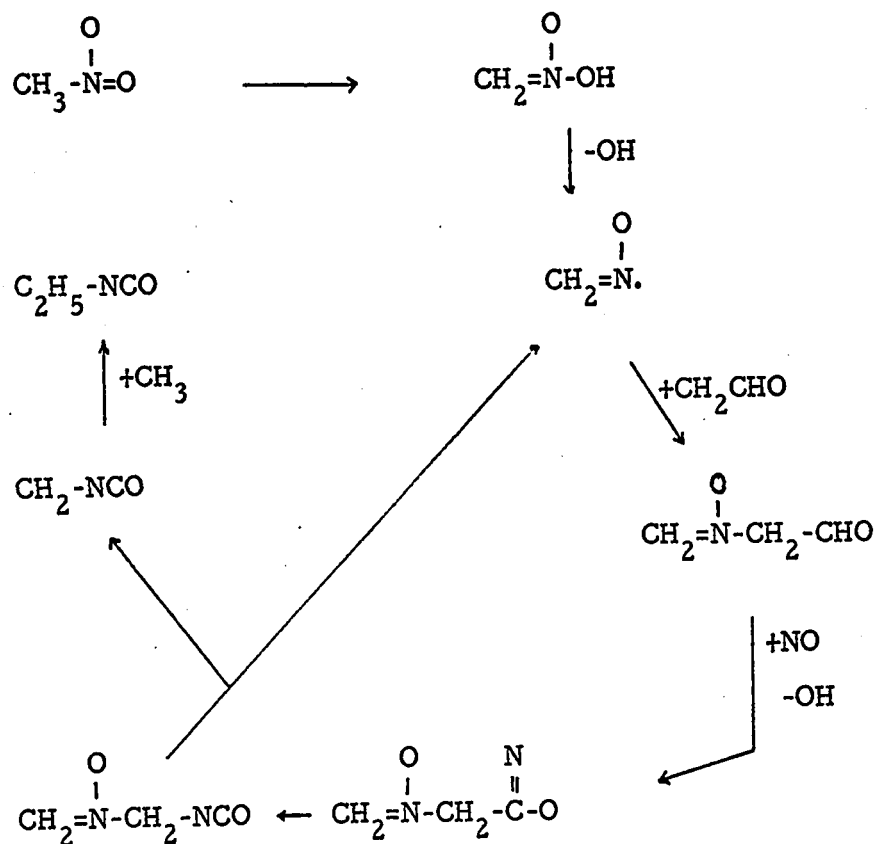
1. It is not formed in the pyrolysis of pure CH_3CHO and NO .
2. It accumulates in the cold mixture.
3. It does not produce N_2 by its irrevocable decomposition, but acts as a catalyst. (The N_2 yield-time curves are linear. Only if the species is sufficiently stable under pyrolysis conditions, and present in a high concentration, would this be compatible with a straightforward decomposition.)

Analogous statements can be made about the formation of $\text{C}_2\text{H}_5\text{NCO}$.

The tests carried out with NO_2 , CH_3NO_2 , CH_3ONO , CH_3ONO_2 , and $\text{CH}_3\text{COOCH}_3$ revealed that the latter is indeed quite inert. NO_2 seems to have a slight inhibiting effect; the CO_2 production is drastically enhanced while at the same time the loss of NO is diminished, which indicates that much of the NO_2 is simply reduced by CO . CH_3NO_2 , CH_3ONO , and CH_3ONO_2 boost the production of N_2 , C_2H_6 , and particularly $\text{C}_2\text{H}_5\text{NCO}$. The increase in N_2 production,

There are five elementary reactions involving NO; v_{N_2} is about second-order in NO. Unless $[CH_3CH(O)\cdot NO]$ builds up to a considerable extent (which is unlikely as the radical will tend to combine with NO), the rate of formation of α -nitrosoethyl nitrite will be first-order with respect to NO, and time independent. If a step in the pyrolysis involving NO is rate-determining, either in the cycle or in the sequence leading up to it, second-order behaviour will ensue. Reaction 7 might be that step.

A path via CH_3NO_2 leading to C_2H_5NCO might be as follows:



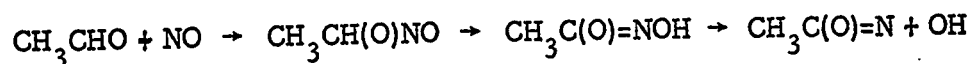
This scheme qualitatively agrees with the observation that $v_{C_2H_5NCO}$ depends on mixing time to some positive power, through CH_3NO_2 (Figure 4).

CONCLUSIONS.

The acetaldehyde-nitric oxide system is chemically rather complex at elevated temperatures, owing to the considerable number of different radicals and active species participating in the reaction. Thus the steady-state hypothesis leads to complicated expressions for the concentrations of the intermediates and a fortiori for the rates of product formation, so that the concept of order with respect to reactants loses its meaning. The overall activation energies associated with the rates of formation are also of little use, and so no attempt has been made to characterize the formation of the various products in this way. Because of this complexity, a large number of experiments is desirable to establish accurately the rates as functions of reactant concentration. Since the products found are fairly numerous and chemically variegated, the time required to analyze each run is considerable. In this work the dependence of the rate on two variables, $[\text{NO}]$ and T , has been studied in particular. Of the other variables, $[\text{CH}_3\text{CHO}]$, pre-reaction mixing time, S/V , surface material of the reaction vessel, and influence of various inert gases, only the first two were to some extent explored over a small range. That there is some surface effect seems to be quite certain since it was observed that when a new series of runs was started after a lapse of time, several experiments usually had to be done under identical conditions until a systematic trend of the results had subsided and the usual degree of reproducibility had been achieved. An exhaustive study based on the analytic methods employed would have taken a prohibitively long time, but such a study may yet be possible when a sensitive optical spectrometric method will have

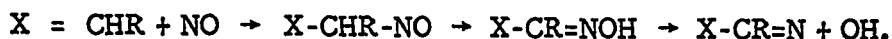
been developed which allows many compounds to be monitored at the same time, while the reaction is going on. It may also be desirable to discontinue completely the use of ordinary high vacuum stopcocks in the investigation of any non-combustive gas reaction. It had been found (101) that even 10^{-2} torr of O_2 accelerate noticeably the decomposition of 225 torr of acetaldehyde. In the present work the contamination of NO-free acetaldehyde by O_2 did not exceed $2 \cdot 10^{-3}$ torr after one hour standing, as evidenced by the absence of N_2 from the products (the detectability threshold of N_2 corresponded to about $5 \cdot 10^{-3}$ torr in the reaction vessel at $500^\circ C$, and $p_{O_2} = 1/4 p_{N_2}$ if the oxygen is due to leakage of air; however, the effect of O_2 on organic pyrolyses might be magnified in some way by NO. Very recent work on the NO-free acetaldehyde pyrolysis (102) seems to suggest that even smaller traces of O_2 change the kinetics substantially, the "ultraclean" reaction having an overall activation energy of about 57 kcal/mole as compared to results so far obtained by other workers, namely 46 (103), 48 (104), 49.1 (55), 47.6 (90), and 46 kcal/mole (this work).

The limitations as to the range of variables covered in this work having been pointed out, one may say that a pattern nevertheless suggests itself. It has been seen that the reactions

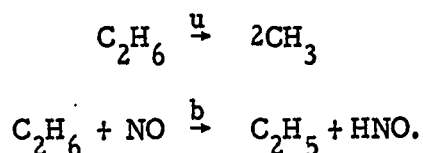


may well play a decisive role in the acetaldehyde pyrolysis in the presence of NO. In this context it is of interest to recall the features of various NO-influenced organic pyrolyses. Paraffins and ethers shows pronounced inhibition, with catalysis setting in after a deep and wide minimum. With aldehydes and various partially-substituted

ethylenes, as well as C_2H_4 itself, on the other hand, the minimum is either rather shallow and narrow or altogether absent (ketones seem to occupy an intermediate position; Table 14). The compounds of the latter group all have a hydrogen atom attached to a double-bonded carbon atom, making it possible to formulate the reaction sequence



No evidence was found for H abstraction by NO in the ethane pyrolysis in a very recent study (105), where the various products of the reaction and its acceleration at high $[NO]$ were explained by giving the radical $CH_3CH=N$ a central role. This fact seems to support indirectly the assumption that in pyrolyses of compounds with C-H bonds of similar strength as in CH_3CO-H , abstraction by NO may not be very important either. (In compounds with a much weaker C-H bond, of course, H abstraction by NO may be dominant, as for instance with the cyclohexadienes (106)). Consider



With $[NO] = 10^{-5}$ mole cc^{-1} it was found (105) that $k_b[NO] < k_u$, $k_u = 10^{16} e^{-86/RT}$ sec^{-1} (107). Thus at $600^\circ C$ $k_b < 10^0$ cc mole $^{-1}sec^{-1}$. Assuming a frequency factor $A_b = 10^{13}$ cc mole $^{-1}sec^{-1}$, one obtains $E_b > 52$ kcal/mole. Consider now

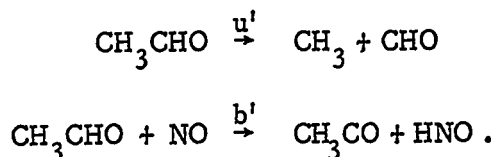


Table 14

Features of various NO-influenced organic pyrolyses.

Compound	p(torr)	T(°C)	onset of catalysis at approx. P _{NO} (torr)	approx.* v _o /v _{min}	Ref.
C ₂ H ₆	100	630	25	5	108
C ₃ H ₈	100	590	50	5	109
n-C ₄ H ₁₀	100	530	40	5	110
CH ₃ OCH ₃	100	520	10	16	111
C ₂ H ₅ OC ₂ H ₅	100	580	40	3	112
CH ₃ COCH ₃	100	570	20	1.4	113
C ₂ H ₅ COCH ₃	100	580	10	1.05	114
CH ₃ CHO	50	505 to 525	0 to 2	1 to 1.5	6
C ₂ H ₅ CHO	100	540	2	2	45
n-C ₃ H ₇ CHO	100	523	2	3	115
i-C ₃ H ₇ CHO	100	523	2	1.8	115
C ₂ H ₄	300	600	0	1	116
C ₃ H ₆	100	600	2	1	117
n-butene(1)	300	530	0	1	116
n-pentene(1)	75 to 150	530	0 to 70	1 to 1.1	116

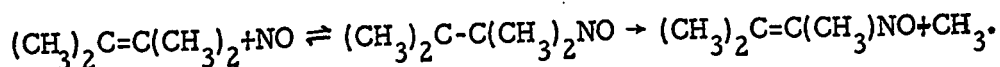
* v_o uninhibited rate

v_{min} rate at maximal inhibition

Since the relationship $E_b - E_{b'} < D(C_2H_5-H) - D(CH_3CO-H)$ can be expected to hold, one concludes (with $D(C_2H_5-H) = 98$ kcal/mole and $D(CH_3CO-H) = 88$ kcal/mole, (86)) that $E_{b'} > 42$ kcal/mole.

On the other hand, if it is true that with acetaldehyde, if $[NO] = 10^{-6}$ mole cc⁻¹, $k_{b'}[NO] \approx k_{u'}$, then at 500° C with $k_{u'} = 10^{15.3} e^{-79/RT}$ (61), and with the assumption that $A_{b'} = 10^{12}$ cc mole⁻¹ sec⁻¹, the activation energy will be $E_{b'} \approx 46$ kcal/mole.

The simplest olefin without olefinic hydrogen is tetramethylethylene. If the hypothesis advanced above is correct and the formation of an oxime-like radical is important in the NO-catalyzed olefin pyrolyses, then the pyrolysis of $(CH_3)_2C=C(CH_3)_2$ in the presence of NO should be markedly slower than the pyrolysis of trimethyl ethylene. These compounds would probably also hold their allylic hydrogen atoms more strongly bound than propylene ($D(C_3H_5-H) = 85$ kcal/mole, (86)), since in them the activating effect of the double bond is spread out over several methyl groups. If, however, their rates were found to be similar, it might be quite easy to decide on the basis of the products whether initiation occurs through H abstraction by NO, or through a displacement reaction, e. g.



In this case one would expect the methane formation to be enhanced by NO.

A general and at the same time simple theory of organic NO-influenced pyrolyses may well be impossible, each system having its own peculiarities. Whatever the NO does, however, its mode of action will be described by one or several of the following. It may

1. combine with a radical,
2. add to a double bond, thus generating a radical.

Then,

3. nitrogeneous species thus formed may break down quickly
 - a) unimolecularly (perhaps in a surface-catalyzed step), or
 - b) through radical attack.

Also,

4. NO may abstract a hydrogen atom from a radical, or
5. abstract a hydrogen atom from a molecule.

While the main tenets of the Hinshelwood school (existence of a kinetically important non-radical mode) and the Szabó school (entirely reversible interaction of NO with the chain radicals) have been abandoned, one may still say that each of the proposals discussed above carries part of the truth. Of all the different aspects of such pyrolyses the surface effects, whose importance was stressed especially by Voevodsky and other Russian workers, will likely prove the most difficult to unravel.

It may be useful to make a final general remark about the investigation of complicated systems such as the one under study.

1. Given sufficiently sensitive procedures, all reaction products can be measured and thus the exact stoichiometry of the reaction can be established (the products being the species which accumulate in the system without their concentration reaching a maximum while the reaction is allowed to proceed).

2. A mechanism can be devised consisting of n elementary steps, whose sum total reflects the stoichiometry, involving m ($m < n$) different intermediate species (the intermediates are those to which the steady-state hypothesis can be applied; their concentration reaches a maximum at very low conversions and is thereafter very much smaller than the concentration of the products).
3. If A and B are the reactants and k_1, \dots, k_n the rate constants of the elementary steps, then the rates of product formation depend on [A], [B], and on up to n rate constants (some of which may be already known),

$$v = v([A], [B], k_1, \dots, k_n).$$

v may be expanded into a Taylor series with respect to reactant concentration, e. g.

$$v = a_0 + a_1 f[B] + a_2 (f[B])^2 + \dots,$$

where the a_i can be functions of [A] and some or all of the rate constants, and $f[B]$ can be [B] itself or some function suitable to fit the experimental data easily with as small a number of terms as possible. If v has been sufficiently accurately measured, one may obtain n equations by taking the derivative n times at $f[B] = 0$:

$$\frac{\partial^n v}{\partial f[B]^n} = n! a_n,$$

and so in principle calculate all rate constants characterizing v .

This contrasts with a statement made elsewhere (118, p. 33) which asserts that "even if one analyses for all products, the mechanism cannot be deduced...if the number of free radicals exceeds two."

From a practical point of view, it is clear that the more accurately a quantity has been measured experimentally, the more useful are its derivatives with respect to some variable. Moderate accuracy will suffice to determine only a small number of rate constants describing a relatively simple mechanism. Thus it is felt that a degree of accuracy such as attained in this work, even if the mechanism suggested is correct, is not sufficient to determine individual rate constants.

CLAIMS TO ORIGINAL RESEARCH.

1. The rates of formation of various products of the thermal decomposition of acetaldehyde in the presence of nitric oxide have been measured as functions of temperature and nitric oxide concentration.
2. Methyl isocyanate, an unexpected product, has been discovered in this reaction.
3. A mechanism has been suggested explaining the products and the dependence of their rates of formation on the nitric oxide concentration.
4. Approximate values for various parameters characterizing the rates of formation of some products as functions of the nitric oxide and acetaldehyde concentrations have been obtained. (These parameters are functions of various rate constants within the mechanism suggested.)
5. It has been found that gaseous mixtures of acetaldehyde and nitric oxide can undergo a slow reaction at room temperature in the dark, the products of which influence the rates of formation of various pyrolysis products; in particular, the rate of formation of nitrogen is strongly enhanced.
6. Various products of this "cold reaction" (see point 5) have been identified.
7. An attempt has been made to explain how the products of the "cold reaction" might be formed.

8. It has been proposed that pyrolyses of organic compounds possessing a double bond may differ markedly from the others in that NO adds to the double bond catalyzing fragmentation. An experiment is suggested to establish whether the formation of an oxime-like radical ($X-CR=NOH$, possible in the presence of aldehydic or olefinic hydrogen), or a displacement reaction, is the subsequent step.

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APPENDIX

Some Details of the Vapor-Phase Chromatography

Emergence Times

Average emergence times (time lags between insertion and maximum signal) of various compounds investigated on the chromatographic columns employed in the analyses are as follows:

Compound	Average emergence time (min)
H ₂	3.6 (Col. 1)
N ₂	13.6
CO ₂	9.3 (Col. 2)
N ₂ O	11.2
C ₂ H ₄	14.4
C ₂ H ₆	19.7
CH ₂ CO	20.4 (Col. 3)
H ₂ O	26
C ₃ H ₆	27.6
HCN	38
CH ₃ ONO	5.4 (Col. 4)
C ₂ H ₃ OCH ₃	6.6
CH ₃ CHO	7.6
CH ₃ NCO	13.0
C ₂ H ₅ CHO	13.4
CH ₃ COCH ₃	16.0
CH ₃ COOCH ₃	18.0
C ₂ H ₅ NCO	19.4

Compound	Average emergence time (min)
C_2H_5OH	30.2
$CH_3COOC_2H_5$	30.6
CH_3ONO_2	33.8
$(CH_3CO)_2$	56
$CH_3CH=CHCHO$	79
CH_3NO_2	137

Further Details Concerning the
Identification of Some Products

CH₃NCO

The product identified with this compound gave a mass spectrum very similar to that of CH₃NCO (ref., first supplement). An easily detectable characteristic feature in both spectra was the signal at $m/e = 27 \frac{1}{2}$ corresponding to the species $\overset{\uparrow}{\text{CH}}=\overset{\uparrow}{\text{N}}-\overset{\uparrow}{\text{C}}\equiv\overset{\uparrow}{\text{O}}$. The gas-chromatographic retention time of the unknown was identical with that of CH₃NCO.

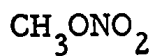
C₂H₅NCO

The unknown identified with this compound showed a largest m/e of 71 at an ionization voltage of 70 as well as of 15 V. m/e 71 is compatible with C₄H₉N (amines), C₃H₅NO, and C₂HNO₂. The first and last possibilities were excluded, the former because the unknown's gas chromatographic behavior ruled out amines, the latter because they seemed to be chemically unlikely. A comparison of the mass spectra obtained from the unknown and from ethyl isocyanate showed quite similar ratios of m/e 71 to m/e 56, which are both prominent in the range above m/e 43, below which the mass spectrum of the unknown is obscured by the presence of contaminating acetaldehyde. The gas-chromatographic retention time of the unknown was identical with that of C₂H₅NCO.

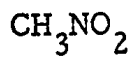
CH₃COOC₂H₃

The unknown which was identified with CH₃COOC₂H₃ showed a highest m/e 86 at 70 eV as well as at 15 eV excitation

energy, and had the same gas-chromatographic retention time. Other details of the mass spectrum were obscure because of the very small amounts of unknown that could only be sampled.



The largest m/e found in the mass spectrum of the unknown identified with CH₃ONO₂ was m/e 46. A comparison with ethanol and formic acid at high resolution showed this mass to correspond to NO₂, which is also the largest mass of the ten most prominent masses in the fragmentation pattern of CH₃ONO₂ (ref.). The gas-chromatographic retention time was equal to that of CH₃ONO₂.



The unknown identified with CH₃NO₂ was similar to it (ref.) in its mass spectrum showing a molecular ion at m/e 61 and a prominent fragment ion at m/e 46. Both gas-chromatographic retention times were the same.



The unknown identified with CH₃COOCH₃ showed a molecular ion at m/e 74. By comparison with butanol and glyoxylic acid at high resolution a mass corresponding to C₃H₆O₂ was established. Taking into account the unknown's volatility and excluding unlikely configurations (e.g. -O-O- and rings) the choice was narrowed down to ethyl formate, methyl acetate, and methoxy

acetaldehyde. Comparison of the unknown mass spectrum with that of $\text{CH}_3\text{COOCH}_3$ listed (ref.) suggested that the unknown was methyl acetate, which also showed the same gas-chromatographic behavior.

ref.: A. Cornu and R. Massot, "Compilation of Mass Spectral Data", Heyden and Son, London, 1966.

Sources of the Isocyanates used for
Testing Purposes

CH_3NCO :	K and K Laboratories
$\text{C}_2\text{H}_5\text{NCO}$:	Eastman-Kodak