The Arrhenius constants, A and E^* from the equation

$$k = A \exp. -E^*/RT \text{ cc. mole}^{-1} \text{ sec.}^{-1}$$

are given in Table III. It will be noted that the A factors are in the "normal" range for bimolecular reactions between complex molecules[13] for the units involved. This is in contrast to the results of Cadle and Schadt[14] on the corresponding reactions of ethylene and acetylene, for which quite low A factors were calculated, 1.2×10^8 and 1.9×10^6 cc. mole^{-1} sec.$^{-1}$, respectively.

TABLE III

VALUES OF A AND E^* FOR THE HYDROCARBON–OZONE REACTIONS

H.C.	A, cc. mole^{-1} sec.$^{-1}$	E^*,[a] kcal. mole^{-1}	k_{25} (calcd.), cc. mole^{-1} sec.$^{-}$
CH_4	7.2×10^{10}	14.9	0.85
C_3H_8	3.1×10^9	12.1	4.1
n-C_4H_{10}	8.2×10^8	11.1	5.9
i-C_4H_{10}	4.4×10^8	10.3	12.2
C_2H_4[a]	1.9×10^6	0	1.9×10^6
C_2H_2[a]	1.2×10^8	4.8	3.6×10^4

[a] Data of Cadle and Schadt, ref. 14.

Discussion

The reaction of ozone with paraffins proceeds with a relatively low energy of activation. Perhaps this low value should be associated with the reaction of a triplet low lying excited electronic state of the ozone molecule, normally in a $^1\Sigma$ state,[15] with hydrocarbon in the series of reactions

$$RH + O_3 \longrightarrow RO\cdot + HO_2\cdot \quad (1)$$
$$RO\cdot + RH \longrightarrow ROH + R\cdot \quad (2)$$
$$RO\cdot \longrightarrow R' = O + R''\cdot \quad (3)$$
$$R\cdot + O_2 \longrightarrow RO_2\cdot \quad (4)$$

The principal difference between the mode of reaction of normal paraffins relative to that of a branched paraffin like isobutane would then reside in the relative stability of the alkoxy radicals, RO·. In the case of isobutane, t-butoxy radical is sufficiently stable under the reaction conditions to yield, by hydrogen abstraction from RH, t-butyl alcohol. With n-butane and propane the notable absence of alcohols other than methanol is an indication that this reaction (2) is of minor importance. Acetone results from propane by the ejection of a hydrogen atom from the isopropoxy radical, from isobutane by the ejection of a methyl radical from the t-butoxy radical (reaction 3). An alternate splitting of the isopropoxy radical to acetaldehyde plus a methyl radical probably occurs with the subsequent rapid oxidation of acetaldehyde.

It is to be noted that in the temperature region investigated, 25–50°, the order of reactivity is that which would be expected on the basis of the strengths of the C–H bonds involved. Isobutane–ozone has a lower activation energy than n-butane–ozone. The ease with which the tertiary hydrogen may be withdrawn from isobutane may, in turn, account in some measure for the greater stability of the t-butoxy radical.

At low temperatures it is to be presumed that $HO_2\cdot$ and $RO_2\cdot$ are relatively inert radicals and are neutralized by recombination at the walls of the reactor. Under these conditions the over-all reaction would be second order as assumed.

PRINCETON, N. J.

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[13] A. A. Frost and R. G. Pearson, "Kinetics," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 92.

[14] R. D. Cadle and S. Schadt, THIS JOURNAL, **74**, 6002 (1952); *J. Chem. Phys.*, **21**, 163 (1953), and private communication. The infrared absorption method was employed.

[15] R. Trambarulo, S. Ghosh, C. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF CONNECTICUT]

The Kinetics of the Thermal Decomposition of Gaseous Diethyl Ketone

BY CHAS. E. WARING AND C. S. BARLOW[1]

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The kinetics of the thermal decomposition of diethyl ketone indicates that the reaction proceeds through a chain mechanism. In contrast to the thermal decomposition of acetone and methyl ethyl ketone, nitric oxide inhibits, rather than catalyzes, this reaction. Propylene also inhibits the rate of decomposition of diethyl ketone, but much more propylene than nitric oxide is required to reduce the rate to a limiting value. Analyses of the products of reaction at various time intervals have been made and these are compared with analyses made on the inhibited reactions. A reaction mechanism is proposed to account for the observed experimental facts.

Introduction

Studies of the kinetics of the thermal decomposition of acetone[2,3] and of methyl ethyl ketone[4,5] revealed interesting similarities. Both are markedly catalyzed by nitric oxide but the rates of decomposition of each are reduced to a limiting value in the presence of propylene. This latter effect has been taken as evidence that both decompositions proceed through a chain mechanism. The catalytic effect of nitric oxide, on the other hand, has been attributed to its reaction with the ketenes, present in the reaction products, to produce oxidation products.

The activation energies of acetone and methyl ethyl ketone were found to be essentially identical, namely, 68.0 and 67.2 kcal., respectively. This, together with the fact that the only saturated hydrocarbon found in the reaction product of either ketone was methane, was taken as evidence that the initial bond rupture in the decomposition of

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[1] Presented in partial fulfillment of the requirements for the Ph.D. degree at the University of Connecticut, 1951.

[2] C. A. Winkler and C. N. Hinshelwood, *Proc. Roy. Soc. (London)*, **A149**, 340 (1935).

[3] R. E. Smith and C. N. Hinshelwood, *ibid.*, **A183**, 33 (1944).

[4] C. E. Waring and W. E. Mutter, THIS JOURNAL, **70**, 4073 (1948).

[5] C. E. Waring and M. Spector, *ibid.*, **77**, 6453 (1955).

both compounds occurred at the methyl–carbonyl bond to produce methyl radicals. These, in turn, propagated the chains in each case.

The present study of the thermal decomposition of diethyl ketone has been undertaken with several ends in view. The first, of course, was to extend the knowledge of the mechanisms of ketone pyrolysis by investigating another member of this homologous series. Since the decomposition of diethyl ketone could reasonably be expected to proceed through a chain mechanism propagated by either methyl or ethyl radicals, or both, it was felt that information on this subject would further elucidate the role of free radicals in ketone decompositions. Finally, since it has been previously reported[6] that the rate of decomposition of diethyl ketone, unlike that of acetone and methyl ethyl ketone, was reduced to a limiting value by the addition of small amounts of nitric oxide, it was thought to be of some importance to examine more thoroughly the action of various inhibitors on this reaction.

Experimental

A. Apparatus.—The course of the decomposition was followed by a static manometric method using a mercury column in a 2.0 mm. capillary tube which previously had been examined and chosen for its uniformity of bore. The vapor reacted in a quartz bulb of 220-ml. capacity, surrounded by a cast bronze block which completely filled the well of an electric furnace. The reaction flask was connected to the vacuum system by a quartz-to-Pyrex graded seal. A 5-ml. bulb sealed directly into the line contained the diethyl ketone sample. By use of 2.0 mm. capillary tubing, the dead space of the reaction system was reduced to 1.5% of the total volume of the reaction flask.

To prevent the condensation of diethyl ketone in the parts of the system which projected from the furnace, all capillary tubing and taps were wound with nichrome wire and heated electrically to 80–85°. At this temperature Fisher Cellosolve 120° tap grease was found efficient with regard to consistency, vapor pressure and non-absorption of the ketone vapor.

The furnace, and hence the reaction chamber, was maintained at constant temperature to within ±0.05° by a thyratron circuit previously described.[7] A platinum–platinum, 10% rhodium thermocouple and a platinum resistance control thermometer were set in holes drilled into the bronze block close to the largest diameter of the spherical reaction bulb. Temperatures were measured with a Type K_2 potentiometer in conjunction with a sensitive optical lever galvanometer.

The pressure within the evacuated system was measured by a McLeod gage. No run was made if the pressure was greater than 10^{-5} mm.

B. Material.—The diethyl ketone was prepared by the decarboxylation of calcium propionate, a method which produces no isomeric compounds. Water, the only volatile by-product, was removed by distilling the ketone in a short, helices packed column. The material selected for use distilled within a range of 0.2° or less. The diethyl ketone so prepared was stored over anhydrous potassium carbonate to prevent internal condensation. The following table compares the observed physical constants with those of the literature

PHYSICAL CONSTANTS OF DIETHYL KETONE

	Obsd.	Lit.[8]
$n^{16.6}$D	1.3936	1.3939
B.p., °C. (corr.)	102.8	102.7
d_{24}	0.8102	0.8107

The propylene employed was Matheson Co. C.P. grade which had a purity of 99% with propane as its principal impurity. Before the propylene was injected into the reaction system, it was first bubbled through dibutyl phthalate.

Nitric oxide was prepared by the action of 50% nitric acid on copper in a Kipp generator attached to the vacuum system. Before using, the nitric oxide was passed through a Dry Ice–acetone trap to remove any water vapor or higher oxides of nitrogen.

Data and Results

1. Nature of the Decomposition.—Diethyl ketone decomposes at a conveniently measurable rate between 500.5–570° to give a total pressure increase of approximately 2.86 times that of the initial pressure down to about 75 mm. initial pressure. Below this, the ratio of the final to the initial pressure, p_f/p_i, approaches a value of approximately 4.00, as seen in Fig. 1. This increase may be ascribed to the fact that at low initial pressures, there is less tendency for condensation to take place.

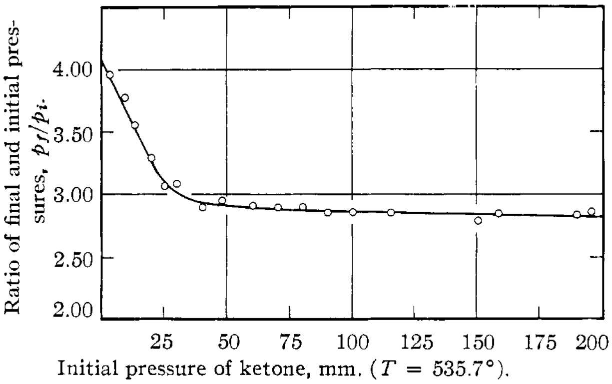

Fig. 1.

At the beginning of the decomposition the pressure increases in a characteristic exponential fashion. Instead of attaining a maximum in a reasonable length of time, however, the pressure continues to increase slowly for 12 to 14 hr., after which time no further change in pressure with time could be observed. Obviously, the processes occurring after the first 10 minutes up to 12 hr. have very little connection with the original ketone decomposition but refer to the slow decomposition of the condensation products and possibly some hydrocarbons. This same slow drift toward the end-point is also characteristic of the acetone and methyl ethyl ketone decompositions.

2. Order of Reaction.—In the decomposition of a molecule like that of diethyl ketone, complicated by secondary reactions, it is quite conceivable that a different value for the order of reaction might be obtained depending upon whether the rates are determined on the basis of a given fraction of the initial pressure or from a given fraction of the total pressure increase. Since the primary process is of greater interest, it was felt that an order based upon initial rate measurements would be more significant. Consequently, the reciprocals of various percentage increases over the initial pressure were plotted as a function of the initial pressure. Figure 2 may be taken as typical of the curves obtained. It is seen that above 75 mm. initial

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[6] C. E. Waring and C. S. Barlow, *ibid.*, **71**, 1519 (1949).

[7] S. Steingiser, G. Rosenblitt and C. E. Waring, *Rev. Sci. Inst.*, **14**, 143 (1943).

[8] "International Critical Tables," McGraw-Hill Book Co., New York, N. Y., 1933.

pressure the rates are relatively independent of initial pressure, indicating the reaction to be essentially of the first order in that range. Below the Lindemann critical pressure limit, the rate falls off rapidly and becomes almost proportional to the initial pressure, the order approaching that of second. This slow transition from first to second order characterizes the reaction as being pseudo-unimolecular.

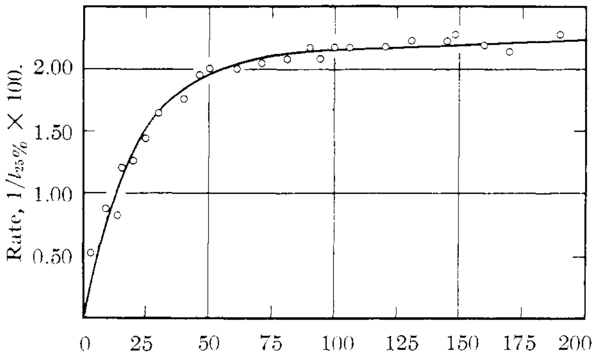

Fig. 2.—The reciprocal of 25% initial pressure increase as a function of the initial pressure at 535.7°.

Since Fig. 1 indicates that the end-points of the decomposition at various initial pressures are reliably reproducible, the determination of order based upon the final pressure increase is possible. When the half-life times were plotted as a function of initial pressures, a curve almost identical with that in Fig. 2 was obtained. Thus, by two criteria the decomposition of diethyl ketone was found to be homogeneous and predominantly of the first order.

3. Effect of Nitric Oxide.—Since the decompositions of acetone and methyl ethyl ketone are markedly catalyzed by even small amounts of nitric oxide, a careful study of its effect on diethyl ketone was undertaken. Figure 3 presents the rather unique effect of nitric oxide on the decomposition of this ketone. It is seen that for a given partial pressure of ketone, nitric oxide reduces the rate to a reproducible, limiting value and that the amount of inhibition is dependent upon the partial pressure of diethyl ketone. Unlike acetone and methyl ethyl ketone, no catalytic effect was observed even when 300 mm. of nitric oxide was added to 100 mm. of the ketone.

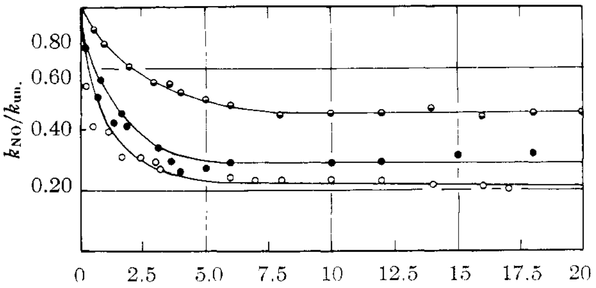

Fig. 3.—The variation of the ratio of inhibited to uninhibited rates as a function of the partial pressure of nitric oxide at 535.7° ($k = 1/t_{25\%}$): ◒, 150 mm.; ●, 100 mm.; ○, 50 mm.

The inhibiting effect of nitric oxide is good evidence that the decomposition of diethyl ketone proceeds predominantly through a chain mechanism. Since the rates are reduced to a limiting value and not to zero, it must be concluded that the reaction occurring after the chains have been removed proceeds by a rearrangement mechanism. The pressure dependency of the inhibition indicates that the inhibitor molecule reacts chiefly with the small chain carrying radical, R, rather than with the large free radical, R′, in a bimolecular reaction of the type

$$R + M \longrightarrow M' + R' + R$$

where M and M′ represent the ketone and the smaller molecule, respectively. In such a reaction the nitric oxide would be competing on equal terms with the ketone for the free radical. This, of course, would result in a pressure dependency of inhibition.

It is of interest to note that the ratio of the final to the initial pressure for the fully inhibited reaction at 100 mm. of ketone was found to be 2.86, the same as for the uninhibited decomposition. This suggests that the over-all stoichiometry is unchanged by the action of nitric oxide.

4. Effect of Propylene.—The effect of propylene on the decomposition of diethyl ketone is shown in Fig. 4. As in the case of nitric oxide, the amount of inhibition is pressure dependent, and the rates are reduced to a definite, limiting value for any given partial pressure of ketone. About ten times more propylene is required to reduce the rate to the same value as that for a given partial pressure of nitric oxide. This seems to infer that for a particular free radical, propylene may be a less efficient inhibitor than nitric oxide.

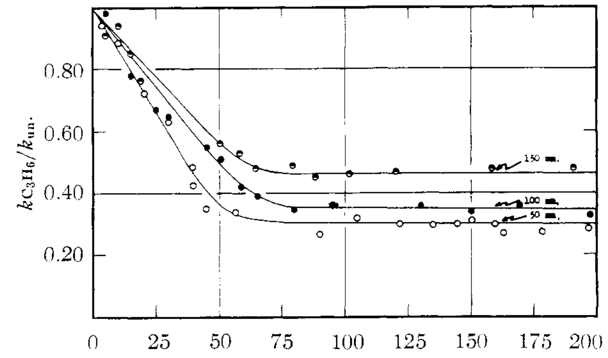

Fig. 4.—Variation of the ratio of inhibited to uninhibited rates as a function of the partial pressure of propylene at 535.7° ($k = 1/t_{25\%}$): ◓, 150 mm.; ●, 100 mm.; ○, 50 mm.

The relative effects of nitric oxide and propylene as inhibitors may be obtained by comparing the data in Figs. 3 and 4. It is evident immediately that nitric oxide and propylene do not retard the reaction to the same extent at any of the several partial pressures of ketone. The data reveal that propylene, on the average, is 15% more effective than nitric oxide as an inhibitor—a rather surprising result. In view of this, it was thought that perhaps their combined effect might be additive. However, when 10 mm. of nitric oxide and 100 mm.

of propylene, either of which in itself is sufficient to reduce the rate to a limiting value, were added to 100 mm. of ketone, the rate was the same as that when only 100 mm. of propylene were added.

The mean chain lengths at various initial pressures of diethyl ketone were computed by dividing the relative rate constants of the uninhibited reactions by those of the fully inhibited. These values are presented in Table I, together with those for acetone and methyl ethyl ketone with propylene as the inhibitor.

TABLE I

MEAN CHAIN LENGTH (k_{un}/k_{in})

Pressure (mm.)	CH_3COCH_3	$CH_3COC_2H_5$	$C_2H_5COC_2H_5$ NO	$C_2H_5COC_2H_5$ C_3H_6
50	3.2	2.8	2.7	3.7
100	3.4	2.3	2.0	2.8
150	3.4	2.2	1.3	2.0

5. **Effect of Hydrogen.**—It has been shown in a number of reactions that the rates below the Lindemann critical pressure limit can be restored to their normal values at the higher pressures by the addition of small amounts of hydrogen. In such cases the hydrogen appears to act merely by maintaining a Maxwell distribution of energy among the molecules of the reacting gas when the supply of active molecules would otherwise begin to diminish below that required to keep the rate constant at its normal value. In Table II the effect of hydrogen on the rate of decomposition of 20 mm. of diethyl ketone is presented.

TABLE II

EFFECT OF HYDROGEN ON THE RATE OF DECOMPOSITION OF DIETHYL KETONE AT 547.1°

Reaction mixture	$1/t_{25\%}$ (sec.$^{-1}$)
100 mm. ketone	0.036 (normal)
20 mm. ketone	.028
20 mm. ketone, 100 mm. H_2	.043
20 mm. ketone, 150 mm. H_2	.039
20 mm. ketone, 13 mm. NO	.009
20 mm. ketone, 100 mm. H_2, 13 mm. NO	.036

The data show that 100 mm. of hydrogen is sufficient to restore the rate of decomposition of 20 mm. of diethyl ketone to its normal value above the critical pressure limit. The addition of 150 mm. of hydrogen produced no further increase in rate. It is also of interest to note that the addition of 13 mm. of nitric oxide to the ketone–hydrogen mixture has no appreciable affect on the rate.

6. **Effect of Surface.**—In order to test the extent of homogeneity of the decomposition, the unpacked reaction flask was replaced with a bulb of the same volume but packed with uniform lengths of quartz tubing. Table III shows that an increase in the surface/volume ratio of the reaction flask produces a decrease in rate of approximately 17%.

TABLE III

EFFECT OF SURFACE/VOLUME INCREASE ON THE RATE OF DECOMPOSITION OF 100 MM. OF DIETHYL KETONE AT 547.1°

	S/V	$1/t_{25\%}$ (sec.$^{-1}$)
Unpacked bulb	1.02	0.036
Packed bulb	6.64	.030

The rates in the packed flasks were readily reproducible after a brief conditioning period.

These data may be taken as evidence that the reaction is a predominantly homogeneous one involving fairly long chains which are terminated by collision of the chain carriers at the surface.

7. **Rate Constants and Energy of Activation.**—In a complex reaction, the over-all rates have little, if any, significance since these rates are merely the summation of the various values for each individual reaction. It was felt, therefore, that by determining the initial rates of reaction, the contributions of secondary reactions to the rate constant could be eliminated to a great extent. Consequently, the energy of activation for the uninhibited decomposition of diethyl ketone was evaluated on the basis of initial rates, k_i, determined at eight different temperatures between 500.5 and 570.0°. Figure 5 presents the curve obtained by plotting the logarithms of the initial rates as a function of the reciprocals of the absolute temperatures.

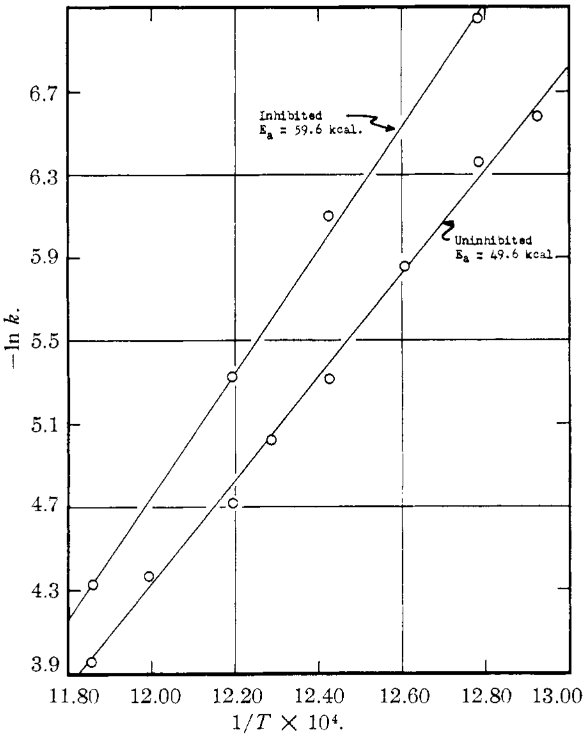

Fig. 5.—Activation energies for the uninhibited and fully inhibited nitric oxide decomposition.

From the data in Fig. 5, the energy of activation of the uninhibited reaction, calculated by the method of least squares, was found to be 49.6 kcal. The variation of the initial rate constant with temperature expressed in terms of the Arrhenius equations may be given as

$$k_i = 1.42 \times 10^{11} e^{-49,600/RT}$$

In a similar manner, the energy of activation was determined for the reaction fully inhibited by nitric oxide at four different temperatures between 508.9 and 570.0°. A plot of logarithms of the initial rate constants *versus* the reciprocals of the absolute temperatures also gave a linear relationship as shown in Fig. 5. The activation energy for the fully inhibited reaction as calculated by the method of least squares was found to be 59.6 kcal. The variation of the initial rate with temperature is given by the expression

$$k_{\mathrm{i(NO)}} = 3.68 \times 10^{13}e^{-59{,}600/RT}$$

8. Products of Reaction.—From the previous work on the pyrolysis of acetone[2] and methyl ethyl ketone,[4] it was expected that ketenes would be produced in the present reaction. Accordingly, ketenes were analyzed for at 547.1° by removing samples from the reaction system at various time intervals and shaking with water in a gas pipet. The acetic and propionic acids so formed from the ketenes were then titrated with standard sodium hydroxide using phenolphthalein as an indicator. From a knowledge of the temperature of the reaction flask and the gas pipet, the pressures in the reaction flask before and after sharing volumes with the gas pipet and the number of moles of ketene given by the titration, the total number of moles in the reaction flask at the time the sample was taken could be evaluated. Knowing the number of moles of ketenes in the reaction bulb, the temperature and total pressure, the partial pressure of ketenes in mm. may then be calculated.

Each analysis was made on a separate run at different reaction times at 200 mm. initial pressure of ketone. The partial pressures of total ketenes present in the reaction vessel at various reaction times are given in Table IV.

TABLE IV

KETENE ANALYSES FOR THE UNINHIBITED AND INHIBITED REACTIONS AT 547.1°

p_{i} = 200 mm; p_{NO} = 10 mm.

Time (sec.)	15	30	60	120	180	300	480	660
Total ketene pressure (mm.)	6.2	6.7	7.1	8.3	8.0	5.8	2.4	2.0
Ketene (mm.) inhib.	5.6	..	..	8.7	8.1	..	2.8	..

TABLE V

ANALYSES OF GASEOUS REACTION PRODUCTS FOR THE UNINHIBITED AND FULLY INHIBITED DECOMPOSITIONS OF DIETHYL KETONE AT 547.1°

	Mole % products											
Time (min.)	CO		C_2H_6		C_2H_4		CH_4		H_2		CO_2	
	un.	in.	un.	in.	un.	in.	un.	in.	un.	in.	un.	in.
0.5	36.8	33.4	30.1	32.4	28.2	29.9	3.5	3.2	0.00	0.00	1.41	1.71
1	59.6	58.3	19.1	18.0	19.1	15.3	1.7	3.0	.00	.00	0.48	1.37
2	46.1	53.2	24.9	23.8	22.0	19.7	6.5	1.4	.00	.00	.60	1.89
3	40.0	45.2	23.0	27.6	24.3	25.8	4.5	0.7	.00	.00	.42	0.82
6	32.0	32.7	28.8	36.7	30.7	29.6	7.7	0.0	.20	.00	.66	0.91
1200	42.3	48.7	23.2	17.3	6.7	6.0	25.8	26.6	.98	.57	.71	0.80

These data emphasize the fact that the ketene concentrations pass through a maximum in a manner that is characteristic of an intermediate product of reaction. From the position and magnitude of this maximum the ratio of the rates of decomposition of ketene and ketone may be estimated. Representing the over-all reaction as

$$\text{Ketone} \xrightarrow{k_1} \text{Ketene} \xrightarrow{k_2} \text{Products}$$

it can be shown that

$$k_2/k_1 = C_{\mathrm{A_0}}/C_{\mathrm{B_{max}}}\, e^{-k_1 t_{\mathrm{max}}}$$

where $C_{\mathrm{A_0}}$ = initial pressure of ketone, $C_{\mathrm{B_{max}}}$ = the pressure of ketene at the maximum, and t_{max} = the reaction time at maximum ketene concentration. k_1 and k_2 are the rates of ketone and ketene decomposition, respectively. From the experimental data, $C_{\mathrm{A_0}}$ = 200 mm., $C_{\mathrm{B_{max}}}$ = 8.3 mm., t_{max} = 120 sec. and $k_1 = 8.93 \times 10^{-3}$. Thus

$$k_2/k_1 = (200/8.3)e^{-0.00893 \times 120} = 8$$

It is of interest to note that this same value was obtained in the case of methyl ethyl ketone. The total ketene concentration is much lower, however, in the diethyl ketone decomposition.

A number of analyses for ketenes in decompositions that were fully inhibited by nitric oxide were made and the results also are given in Table IV. These results indicate that ketenes are formed in the inhibited decomposition to almost exactly the same extent as in the uninhibited reaction. It will be recalled that the catalytic effect of nitric oxide in the acetone and methyl ethyl ketone pyrolyses had been ascribed to the chemical interaction of nitric oxide with the ketenes.[4] In view of this evidence, such a hypothesis is no longer tenable.

No analyses were made on the propylene inhibited decompositions because of the difficulties in differentiating between the added propylene and that which might occur as a product of reaction.

In order to obtain an insight as to the nature of the initial processes and the subsequent reactions, samples of the reaction mixture were withdrawn from the bulb at various time intervals throughout the entire course of the decomposition at 547.1°. The undecomposed ketone and ketenes were first removed by freezing in a cold trap and the remaining gaseous mixture then analyzed in a modified Bone–Wheeler apparatus. The results of the uninhibited and nitric oxide inhibited decompositions are presented in Table V.

A comparison of the data for the uninhibited decompositions with those of the fully inhibited nitric oxide reactions shows no significant differences except in the methane concentrations. This suggests that the rearrangement mechanism, presumably operative in the fully inhibited reaction, produces the same quantity of products as the uninhibited chain reaction.

In order to show more readily what is occurring throughout the course of the reaction, the data in Tables IV and V were converted into partial pressures of products and reactants. The variations of these partial pressures with time are shown in Fig. 6.

Discussion

From the experimental data, certain marked differences between the thermal decomposition of diethyl ketone and that of acetone and methyl ethyl ketone are immediately apparent. The most outstanding difference, of course, is the effect of nitric oxide. The question naturally arises as to why nitric oxide inhibits this decomposition instead of catalyzing it as it does in the case of the other two ketones. Since ketenes are produced in all three decompositions, it is difficult to understand how nitric oxide, by reacting with ketenes, could produce inhibition in one case and catalysis in the others. The data in Table IV offer rather conclusive evidence that the formation of ketenes is unaffected by nitric oxide and that nitric oxide does not react with ketenes to any appreciable extent. Consequently, this difference cannot be attributed to the interaction of nitric oxide with ketenes.

A possible explanation for this difference may lie in the type of the free radicals propagating the chain. In the case of acetone, there can be little doubt but that the chain propagator is a methyl radical. The almost identical activation energies for methyl ethyl ketone (67.2 kcal.) and acetone (68.0 kcal.), together with the fact that the only saturated hydrocarbon in the reaction products of the former was methane, are good evidence that methyl radicals are also the chain propagators in the methyl ethyl ketone reaction. In the diethyl ketone decomposition, there exists the possibility that both methyl and ethyl radicals could be produced and that each would be effective in propagating chains. The activation energy for this reaction, however, is about 20 kcal. lower than that for the other two ketones. It is reasonable to assume that a lower activation energy would be required to break an ethyl–carbonyl bond than a carbon–carbon bond and that the energy for an ethyl–carbonyl bond where two exist in the same molecule, would be less than that for a methyl–carbonyl bond due to the influence of the additional CH_2 group. This, and the fact that the saturated hydrocarbons consisted primarily of ethane, is strong evidence that the chain propagator in the diethyl ketone decomposition must be predominantly ethyl radicals. There is experimental evidence to support the contention that nitric oxide is less efficient in removing methyl than heavier radicals. If ethyl radicals are produced in the decomposition of diethyl ketone, and methyl radicals in the other two instances, then the inhibiting effect of nitric oxide in the present reaction is readily understood.

Although this argument can reasonably account for the inhibiting effect of nitric oxide in the decomposition of diethyl ketone, it does not, of course, explain why nitric oxide catalyzes the other two decompositions. A reasonable explanation for this catalytic effect of nitric oxide on acetone and methyl ethyl ketone would be that it is the products from the interaction of $CH_3 + NO$ that are catalyzing the decomposition rather than the nitric oxide itself.

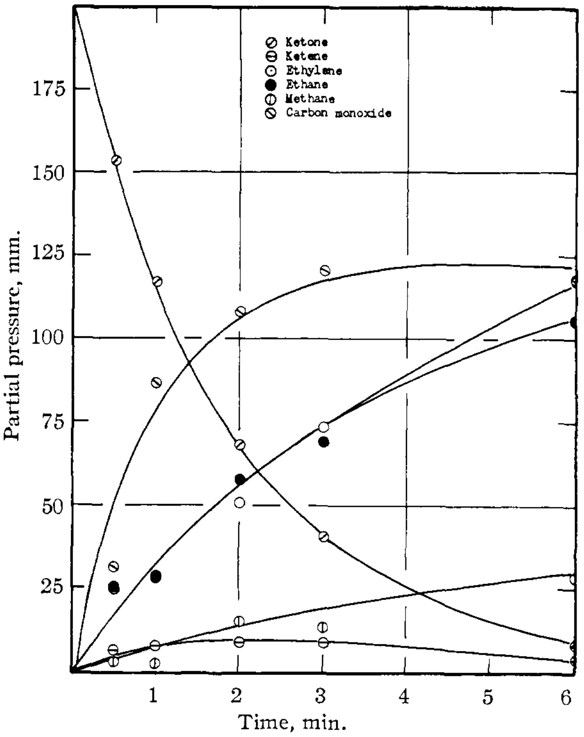

Fig. 6.—Variation of the partial pressures of reactant and products with time at 547.10°.

Support for this hypothesis is given by the data presented in Figs. 3 and 4, where it is seen that the limiting rate for the nitric oxide inhibition is about 15% less than that for propylene. This is unusual, since in all similar investigations where both nitric oxide and propylene have been employed, the amount of inhibition produced was essentially the same. This difference in the effect of the two inhibitors can be understood readily if one makes the not unreasonable assumption that some methyl radicals are also produced in the diethyl ketone decomposition. Thus, if the products from the methyl radical–nitric oxide reaction catalyze the decomposition, then the nitric oxide inhibition curves in Fig. 3 should represent a composite of two processes—inhibition due to the removal of ethyl radicals by nitric oxide and catalysis due to the products from the methyl radical–nitric oxide interaction. Due to the predominance of ethyl radicals, the catalytic effect is small (15%), but enough to prevent the limiting rate from being reduced to the value attained with propylene. Further support for this argument is found in Table V where it is seen that of the total amount of hydrocarbons formed, 10% is due to methane. Thus, there is a fair agreement between the amount of methane present and the amount of catalysis presumed to be due to the interaction of methyl radicals and nitric oxide. It also seems significant that in the presence of nitric oxide, the amount of methane diminishes rather rapidly with time and disappears after 6 minutes reaction time. The large amount of methane at 1200 minutes and the corresponding decrease in ethylene, is explained by the reaction

$$C_2H_4 \longrightarrow CH_4 + C$$

which occurs to an appreciable extent at this temperature.

The results of the inhibition studies with nitric oxide and propylene offer good evidence that approximately 60% of the decomposition of diethyl ketone proceeds through a free radical chain mechanism. The low activation energy in comparison with acetone and methyl ethyl ketone and the predominance of ethane in the reaction products are strong indications that the initial rupture of the molecule occurs at the ethyl–carbonyl bond. On this assumption and from the analytical data in Table V, the following mechanism is postulated as being the predominant chain process in this decomposition

$$C_2H_5COC_2H_5 \longrightarrow C_2H_5 + C_2H_5CO \tag{1}$$

$$C_2H_5CO \longrightarrow CH_3 + CH_2CO \tag{2a}$$

$$CH_2CO \longrightarrow {}^1/_2C_2H_4 + CO \tag{2b}$$

$$C_2H_5 + C_2H_5COC_2H_5 \longrightarrow C_2H_6 + CH_3CHCO + C_2H_5 \tag{3a}$$

$$CH_3CHCO \longrightarrow C_2H_4 + CO \tag{3b}$$

$$R + R' \longrightarrow \text{end of chain} \tag{4}$$

The experimental evidence supporting this mechanism is the following.

(1) The product analyses of the uninhibited reaction show a high concentration of ethane at the start of the reaction and this concentration remains essentially constant over the entire course. Except at the end of the reaction, the concentrations of ethylene and ethane are practically identical, indicating that ethane and ethylene must be produced in the same reaction. Steps (3a) and (3b), the recurring chain propagating steps, would account for most of the ethane and ethylene produced in the decomposition, and at the same time require them to be produced in equal quantities.

(2) The amount of methane at the start of the reaction is small. This is in keeping with the fact that step (1) and hence step (2a) occur to only a slight extent. The ratio $C_2H_6/CH_4 = 10$ in the early stages of the reaction, indicating that Step (3a) occurs ten times as often as step (2a), which is quite plausible.

(3) The increase in the methane concentration at the end of the reaction is proportional to the decrease in the ethylene concentration and may be accounted for by the reaction

$$C_2H_4 \longrightarrow CH_4 + C$$

Evidence for this reaction taking place is found in the fact that the walls of the reaction flask were coated with a shiny deposit of carbon.

(4) If all the carbon monoxide were produced by step (3b), then the concentration of carbon monoxide should equal that of ethane. It is noted from Table V that the amount of CO is always higher than that of C_2H_6, suggesting its formation by step (2b). If step (2b) is, in fact, the only source of additional carbon monoxide, then the $[C_2H_6] + [CH_4]$ should equal [CO]. This is approximately the case at 0.5 and 6.0 minutes reaction time.

(5) If, on the basis of the C_2H_6/CH_4 ratio, one assigns step (3a) a probability of 10 over that of (2a), then the calculated $p_f/p_i = 2.86$. This is the value observed experimentally above 75 mm. initial pressure.

(6) On the basis of reaction probabilities, the removal of a hydrogen alpha to the carbonyl by the ethyl radical to produce methyl ketene is strongly favored over the removal of hydrogens on the methyl groups which would result in the formation of ketene. Much more methyl ketene than ketene, therefore, should be expected in the reaction products. This is confirmed by the work of Hurd and Kocour[9] and is accounted for in the proposed mechanism.

(7) The extent of inhibition by nitric oxide and propylene was found to be dependent upon the partial pressure of ketone. This indicates that the inhibitor is competing on equal terms with the ketone for the free radical. The chain propagating process, then, must be bimolecular. Step (3a) satisfied this requirement.

With the exception of the methane concentration, the reaction products of the fully inhibited decomposition are found to be essentially the same as those from the uninhibited reaction. The residual reaction occurring at maximum inhibition could be either a molecular rearrangement or perhaps a chain of unit length. In any case, whatever mechanism is proposed should be able to account for not only the similarity in the products of reaction but also for the fact that the observed p_f/p_i ratio at the limiting rate is the same as that of the uninhibited process. On the assumption that the reaction occurring at maximum inhibition proceeds by a molecular rearrangement, the following mechanism is proposed

Reaction A:

(1) $10C_2H_5COC_2H_5 \longrightarrow 10C_2H_6 + 10CH_3CHCO$ (Primary)

(2) $\underline{10CH_3CHCO \longrightarrow 10C_2H_4 + 10CO}$ (Secondary)

$10C_2H_5COC_2H_5 \longrightarrow 10C_2H_6 + 10C_2H_4 + 10CO$

Reaction B:

(1) $C_2H_5COC_2H_5 \longrightarrow CH_4 + CH_2CO + C_2H_4$ (Primary)

(2) $\underline{CH_2CO \longrightarrow {}^1/_2C_2H_4 + CO}$ (Secondary)

$C_2H_5COC_2H_5 \longrightarrow CH_4 + {}^3/_2C_2H_4 + CO$

Reactions A and B have been weighted in accordance with the observed C_2H_6/CH_4 ratio. From the number of moles of products formed in A and B, the mole percentage of each can be calculated. If one now weights the products in A and B in accordance with their respective reaction probabilities of 10/11 and 1/11, then the contribution of each of these reactions to the total products is obtained. Table VI compares the experimental products of the fully inhibited reaction at 30 seconds reaction time with those calculated.

Table VI

	Mole, %			
	CO	C_2H_6	C_2H_4	CH_4
Exptl.	33.4	32.4	29.9	3.2
Theo.	32.9	30.3	34.2	2.6

The unusually good agreement between the experimental values for the gaseous reaction products and those obtained theoretically lends credibility to the proposed mechanism. The somewhat higher value for ethylene and the correspondingly lower one for methane results from the fact that the decomposition of ethylene to give methane was not considered.

The expected p_f/p_i ratio of reaction A would be 3.0 while that of reaction B would be 3.5. If one adjusts these ratios in accordance with their reac-

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[9] C. D. Hurd and C. Kocour, This Journal, **45**, 2167 (1923).

tion probabilities, an over-all p_f/p_i of 3.03 is obtained for the postulated rearrangement mechanism. Figure 1 indicates that experimentally, this ratio increases as the initial pressure decreases. Consequently, the slight discrepancy between the observed and the theoretical p_f/p_i ratios can readily be accounted for by the formation of complex condensation products.

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STORRS, CONNECTICUT

[CONTRIBUTION NO. 54 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

The Chemical Thermodynamic Properties of 2-Methylthiophene[1]

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Calorimetric studies of 2-methylthiophene in the temperature range 12 to 473°K. yielded the following information: values of heat capacity for the solid, the liquid [$C_{\text{satd}} = 45.85 - 0.1754\,T + 6.772 \times 10^{-4}T^2 - 6.771 \times 10^{-7}T^3$, cal. deg.$^{-1}$ mole^{-1} (213 to 344°K.)], and the vapor [$C_p^\circ = -1.745 + 9.562 \times 10^{-2}T - 4.420 \times 10^{-5}T^2$, cal. deg.$^{-1}$ mole^{-1} (375 to 473°K.)]; the heat of fusion [2263 cal. mole^{-1}] at the triple point [209.79 ± 0.05°K.]; the entropy in the liquid state at 298.16°K. [52.22 cal. deg.$^{-1}$ mole^{-1}]; the heat of vaporization [$\Delta H_v = 11651 - 3.937\,T - 1.364 \times 10^{-2}T^2$, cal. mole^{-1} (343 to 385°K.)]; the second virial coefficient in the equation of state $PV = RT(1 + B/V)$[$B = 114 - 127 \exp(900/T)$, cc. mole^{-1} (343 to 473°K.)]; and the standard heat of formation of the liquid from graphite, hydrogen and rhombic sulfur [$\Delta Hf^\circ_{298.16} = 10.86 \pm 0.21$ kcal. mole^{-1}]. Tables of thermodynamic properties for the solid and liquid states (10 to 340°K.) were computed. The calorimetrically determined properties of the vapor were used with spectroscopic and molecular structure data to evaluate the height of the barrier hindering internal rotation (900 cal. mole^{-1}) and to compute tables of the chemical thermodynamic properties at selected temperatures from 0 to 1000°K.

Thiophene derivatives constitute an important fraction of the organic sulfur compounds found in petroleum.[2] To provide the basic information for computation, by approximate statistical mechanical methods,[3] of thermodynamic data for this class of compounds, detailed studies are being made in this Laboratory of the thermodynamic properties of selected thiophene derivatives. The results of investigations of the parent compound, thiophene,[4] and of 3-methylthiophene[5] have already been published. This paper reports data for another thiophene derivative, 2-methylthiophene.

Experimental studies on 2-methylthiophene were made by the methods of low temperature calorimetry, flow calorimetry and combustion calorimetry. The results include values of the heat capacity in the solid, liquid and vapor states and the heats of fusion, vaporization and combustion. From these data were obtained values of the entropy, heat capacity and heat of formation of 2-methylthiophene in the ideal gaseous state. The calorimetric results were used with spectroscopic and molecular structure information to calculate values of the following thermodynamic functions at selected temperatures from 0 to 1000°K.: $(F^\circ - H^\circ)/T$ $(H^\circ - H^\circ)/T$, $H^\circ - H^\circ$, S°, C_p°, ΔHf°, ΔFf° and $\log_{10}Kf$.

Experimental

Physical Constants.—The 1951 International Atomic Weights[6] and the 1951 values of the fundamental physical constants[7] were used for all computations described in this paper. Measurement of temperature above 90°K. was made in terms of the International Temperature Scale of 1948,[8] and International Celsius temperatures were converted to Kelvin temperatures by adding 273.16°K. Below 90°K. the temperature scale was defined by a platinum resistance thermometer calibrated at the National Bureau of Standards in terms of the provisional scale established by Hoge and Brickwedde.[9] All electrical and mass measurements were referred to standards calibrated at the National Bureau of Standards. Energy measured in joules was converted to calories by use of the definitions, 1 cal. = 4.1840 abs. j. = 4.1833 int. j.

The Material.—The sample of 2-methylthiophene used in the low temperature and combustion studies was part of the Standard Sample of Sulfur Compound, API-USBM serial no. 21, prepared and purified by American Petroleum Institute Research Project 48A at the Laramie, Wyo., Station of the Bureau of Mines. A calorimetric study of the melting point showed that the Standard Sample contains 0.036 ± 0.01 mole % of liquid-soluble, solid-insoluble impurity. A second sample, of 99.8 mole % purity, was used in studies of the heat of vaporization and vapor heat capacity. Both samples were received in ampoules with internal break-off tips and were stored in the dark at 5°. Before use in the experiments, the samples were dried in the liquid phase with calcium hydride. They were always transferred by vacuum distillations and at no time were they in contact with gases other than dry helium.

The Heat Capacity in the Solid and Liquid States.—The low temperature thermal studies were made in an adiabatic calorimeter system similar to that described by Ruehrwein and Huffman.[10] The sample of 2-methylthiophene (0.57938 mole) was sealed in a platinum calorimeter equipped with heat-distributing gold vanes. About 30 mm. helium pres-

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(1) This investigation was part of American Petroleum Institute Research Project 48A on "The Production, Isolation and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

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