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The Kinetics of the Thermal Decomposition of Gaseous Methyl *n*-Propyl Ketone

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The thermal decomposition of methyl *n*-propyl ketone has been found to be first order within the pressure range of 10–200 mm. and between 500–570°. The rate of decomposition is inhibited in the presence of propylene, indicating that the reaction proceeds through a chain mechanism. Nitric oxide catalyzes the reaction in a manner similar to that of acetone and methyl ethyl ketone but in contrast to diethyl ketone. The activation energies of the normal and inhibited processes have been determined and analyses on both the uninhibited and inhibited reactions have been made at various time intervals throughout the course of the decomposition. A reaction mechanism is proposed to account for the observed experimental data. The results of this investigation are compared with those on the previous homologs.

Introduction

The kinetic investigations of the thermal decomposition of acetone,[2,3] methyl ethyl,[4,5] and diethyl[6,7] ketone revealed certain interesting similarities and differences. The rates of all three are reduced to a definite limiting value in the presence of propylene, indicating that the decomposition proceeded predominantly through a chain mechanism. In all three cases, the amount of inhibition was dependent upon the partial pressure of ketone, suggesting that the chain propagating step was bimolecular.

When nitric oxide was employed as an inhibitor, marked catalysis occurred in the rates of decomposition of acetone and methyl ethyl ketone. In sharp contrast, the diethyl ketone rates were reduced to a reproducible, limiting value and no catalysis was observed even when 300 mm. of NO was added to 100 mm. of ketone.

In the acetone and methyl ethyl ketone decompositions, the experimental evidence left little doubt but that the chains in both cases were propagated almost exclusively by methyl radicals. The experimental evidence was equally conclusive, on the other hand, that the chain process in diethyl ketone was propagated predominantly by ethyl radicals, although methyl radicals also were produced to an extent of a few per cent.

Since there existed the possibility that methyl *n*-propyl ketone could decompose through a chain mechanism propagated by methyl, ethyl or propyl radicals—or by any combination of them—it was thought worthwhile to investigate the mechanism of this reaction and to compare the results obtained with those of the previously investigated members of this homologous series. It was also felt that a study of the effects of various inhibitors on the decomposition of this compound might further serve to elucidate the role of free radicals in the reactions of ketones.

Experimental

A. **Apparatus.**—The rates of decomposition were measured in a static manometric system using a mercury column in a 2.0 mm. capillary tube which had been examined and chosen for its uniformity of bore. The reaction flask was a spherical Pyrex bulb of about 150-ml. capacity. This fitted closely inside a cast bronze block which completely filled the well of an electric furnace. A platinum–90% platinum 10% rhodium thermocouple and platinum resistance thermometer were set close to the reaction flask at its largest diameter in holes drilled into the bronze block. The temperature of the furnace was maintained constant to within ±0.05° by a thyratron circuit previously described.[8] Temperatures were measured with a Type K_2 potentiometer in conjunction with a sensitive optical lever galvanometer.

The methyl *n*-propyl ketone sample was stored in a 5-ml. bulb sealed directly into the vacuum line through a vacuum stopcock. By use of 2 mm. capillary tubing the dead space of the reaction system was reduced to 2% of the total volume of the reaction flask. All parts of the glass system which projected from the furnace were wrapped with nichrome wire and heated electrically to prevent condensation of the ketone vapor. Fisher Cellosolve 120° tap grease was found to be the most suitable lubricant from the standpoint of consistency, vapor pressure and non-absorption of the ketone vapor. The remainder of the system was that commonly employed for obtaining high vacuum. The pressure of the system was determined by means of a calibrated McLeod gage and no run was made if the pressure were greater than 10^{-5} mm.

B. **Material**—Eastman Kodak methyl *n*-propyl ketone was fractionated in a four-foot, helices-packed column having an efficiency of 25–30 theoretical plates. The main fraction which distilled within 0.2° of the corrected literature boiling point of 101.7° was collected. The refractive index of this fraction did not, however, agree within the third decimal of the literature value, nor did it change after careful refractionation. This seemed to indicate that some impurity of nearly the same boiling point was present and hence distillation methods had to be abandoned.

The fractionated methyl *n*-propyl ketone was transformed into its bisulfite addition product by shaking with an excess of a saturated solution of sodium bisulfite at room temperature. The suspension of the addition product was cooled to 0°, the crystalline material filtered, washed with ether, and dried on a porous plate. The ketone was recovered by steam distillation, washed with sodium bicarbonate and distilled water, dried over anhydrous potassium carbonate and refractionated. The fraction boiling within 0.1° of the literature value of 101.7° was collected and stored over anhydrous potassium carbonate in a dark bottle and kept refrigerated. The refractive index of this fraction was 1.3898 as compared to the literature value of 1.3895.

Since impurities conceivably could be responsible for the observed catalytic effects of nitric oxide, great care was taken to prepare the nitric oxide in as pure a state as possible. Accordingly, nitric oxide was prepared by the method of Johnston and Giauque,[9] which consists in adding 50% H_2SO_4 to 4 *M* KNO_2 in 1 *M* KI. This preparation is claimed to yield a product of 99% purity.

The nitric oxide so produced was passed through H_2SO_4 and then through concentrated KOH, and finally through a solid CO_2–acetone trap before being collected and stored.

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(1) The data presented were submitted in partial fulfillment of the requirements of the Ph.D. degree at the University of Connecticut, June, 1953.

(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).

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

(7) C. E. Waring and C. S. Barlow, *ibid.*, **78**, 2048 (1956).

(8) S. Steingiser, G. Rosenblit and C. E. Waring, *Rev. Sci. Inst.*, **14**, 143 (1943).

(9) H. L. Johnston and W. F. Giauque, THIS JOURNAL, **51**, 1394 (1929).

The resultant product was colorless and remained so during the course of the investigations.

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

The hydrogen employed was also Matheson Co. c.p. grade and used without further purification.

Data and Results

1. **Nature of the Decomposition.**—Methyl *n*-propyl ketone decomposes at a conveniently measurable rate between 500–570° to give a ratio of the final to the initial pressure, p_f/p_i, of 3.11 in the pressure range of 100–200 mm. At pressures below 100 mm., the p_f/p_i ratio increases and approaches a limiting value of 3.60. This effect suggests that condensation reactions are occurring in the secondary processes of the decomposition.

2. **Order of Reaction.**—Since the primary process was considered to be the most important, the order of reaction was therefore determined from initial rate measurements. Figure 1 indicates that the decomposition is of the first order down to about 20 mm. initial pressure.

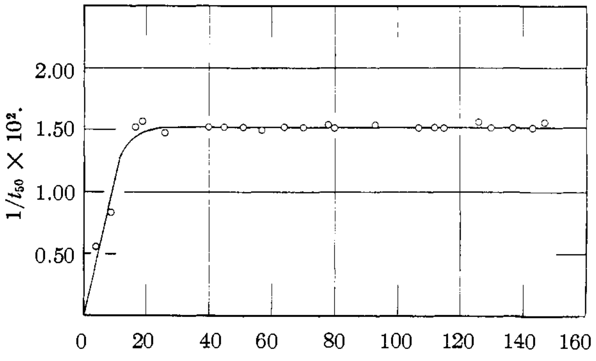

Fig. 1.—The reciprocal of 50% initial pressure increase as a function of the initial pressure at 550°.

3. **Effects of Propylene.**—The effect of propylene on the thermal decomposition of methyl *n*-propyl ketone was studied at three different initial pressures of ketone at 550° and the results are presented in Fig. 2. It was found that propylene underwent no appreciable decomposition at this temperature over a period of 15 minutes reaction time. Since this was greater than the time for a 100% increase over the initial pressure, no correction was necessary.

4. **Absolute and Mean Chain Lengths.**—The value for the absolute length of chains occurring in the decomposition of methyl *n*-propyl ketone may be evaluated in the following manner. It is generally accepted that the limiting rate represents the condition where all, or practically all, of the chains have been eliminated. The residual reaction is then assumed to be a rearrangement process, or a chain of unit length. In inhibited reactions, the usual assumption is that each molecule of inhibitor can, by colliding with a free radical, remove it and thereby successfully terminate a chain. If the absolute length of a chain is 1000 units, and if enough inhibitor is added so that each hundredth molecule in the system is a chain terminator, the chain length will be reduced, on the average, to 100 units, or to one-tenth its original value. In like manner, if each tenth molecule is an inhibitor, the chain length would be reduced to 10 units, or to one-hundredth of its original value. On the basis of these assumptions it is apparent that the chain length in an inhibited reaction is approximately equal to the reciprocal of the mole fraction of inhibitor.

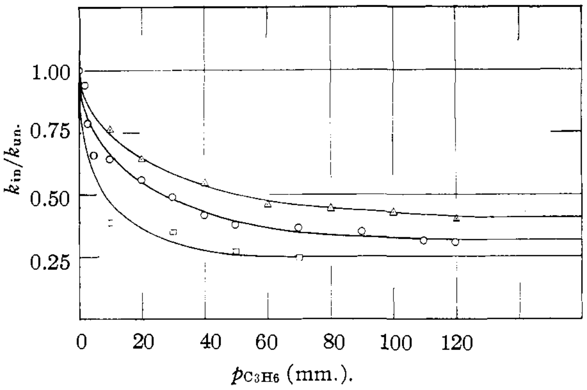

Fig. 2.—Variation of the ratio of inhibited to uninhibited rates as a function of the partial pressure of propylene at 550°: □, 50 mm. ketone; ○, 100 mm. ketone; △, 150 mm. ketone.

At the limiting value, the ratio of the rates of the inhibited to the uninhibited reactions gives information as to the fraction of the rate due to chains and to rearrangement. For example, it is seen in Fig. 2 that at 50 mm. ketone pressure, $k_{in}/k_{un} = 0.25$ at the limiting rate. Hence, approximately 75% of the normal rate is due to chain processes and 25% to rearrangement. If only enough propylene is added to reduce the chain mechanism to one-tenth its original value, then the rate of reaction under these conditions would be a composite of 25% due to the molecular mechanism and $0.1 \times 75\% = 7.5\%$, due to the chain processes. This would give 32.5% of the uninhibited rate as the result of these two contributions. By graphical interpolation, in Fig. 2, the amount of propylene required to reduce the rate to 32.5% of its normal value is found to be 38 mm. Since the partial pressure of ketone at the start of the reaction is 50 mm., the approximate mole fraction of propylene is 38/50 + 38, or 0.43. The average length of the chains when the chain mechanism is suppressed to one-tenth of its normal value is then

$$\text{Chain length} = 1/N_{pr} = \frac{1}{0.43} = 2.3 \text{ units}$$

Thus, when the rate of the chain reaction has been reduced to one-tenth of its original value, the absolute chain lengths have also been reduced from their original length to one-tenth this value, 2.3, by propylene inhibition. The approximate value, then, for the absolute chain length would be ten times 2.3, or 23 units. By this method the absolute chain lengths were calculated for all the ketones investigated to date. The mean chain lengths were also evaluated by dividing the relative rate constants of the uninhibited reaction by those of the fully inhibited. Finally, the per cent. of free radicals formed in the decomposition of the various ketones has been calculated from the expression

$$R\% = \frac{\text{mean chain length} - 1}{\text{absolute chain length}} \times 100 = (k_{un}/k_{in} - 1)/A \times 100$$

where A is the absolute chain length. Table I presents all these data.

TABLE I

VALUES FOR THE ABSOLUTE AND MEAN CHAIN LENGTHS AND THE PER CENT. OF FREE RADICALS IN THE DECOMPOSITIONS OF VARIOUS KETONES AT 550°

Ketone	Absolute chain length 50 mm.	Absolute chain length 100 mm.	Mean chain length 50 mm.	Mean chain length 100 mm.	Free radicals formed (%) 50 mm.	Free radicals formed (%) 100 mm.
CH_3COCH_3	20–25	20–25	3.3	3.3	5	10
$CH_3COC_2H_5$	20–25	20–25	3.2	2.7	10	10
$C_2H_5COC_2H_5$	20–25	25–30	3.6	2.9	10	10
$CH_3COC_3H_7$	20–25	25–30	4.1	3.2	15	10

It should be mentioned that as a check, the approximate values for the absolute chain lengths were calculated at several different fractions of the normal chain rate. In all cases, a value between 20–25 was obtained.

5. Effect of Nitric Oxide.—A careful investigation of the effect of nitric oxide on methyl *n*-propyl ketone was undertaken at 50, 100 and 150 mm. initial pressures of ketone. It is immediately apparent from Fig. 3 that nitric oxide strongly catalyzes this decomposition even at low partial pressures of the inhibitor. The same results were obtained with 50 and 150 mm. of ketone.

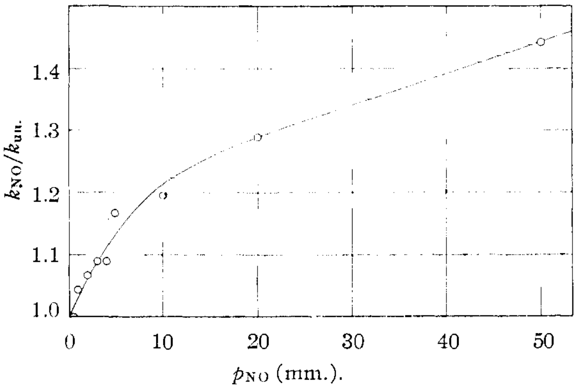

Fig. 3.—Variation of the ratio of catalyzed to uninhibited rates as a function of the partial pressure of NO for 100 mm. ketone at 550°.

It was thought to be of interest to determine the effect of the addition of nitric oxide on this decomposition when sufficient propylene had been added to reduce the rate to the limiting value. Figure 4 shows the results obtained when the ratio of the nitric oxide catalyzed, fully-inhibited propylene rates to the uninhibited rate are plotted as a function of the partial pressure of NO. For comparison purposes, the corresponding propylene inhibition curve is also included.

It is seen that nitric oxide produces catalysis even in the fully inhibited propylene decomposition. If one subtracts the percentage increases in rate due to the addition of NO from the corresponding percentage decreases in rate due to the addition of comparable amounts of propylene, it is found that propylene is, on the average, 16% more effective as an inhibitor than nitric oxide is as a catalyst. In the decomposition of diethyl ketone, nitric oxide was also observed to be 16% less effective than propylene as an inhibitor. Preliminary investigations of this behavior seem to indicate that NO reacts chemically with olefins to about this extent at 550°.

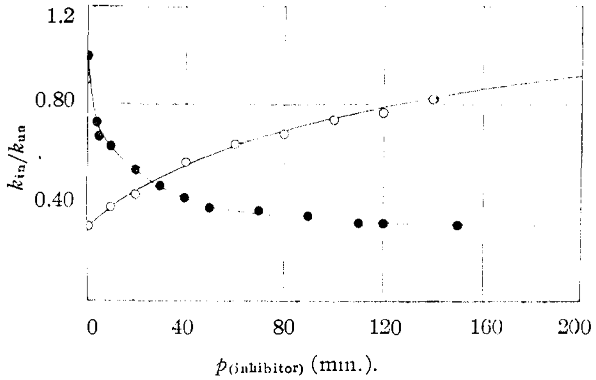

Fig. 4.—Comparison of the ratio of inhibited to uninhibited rates as a function of the partial pressures of propylene and of propylene + nitric oxide for 100 mm. of ketone at 550°; ● $p_{C_3H_6}$; ○, 100 mm. C_3H_6 + p_{NO}.

6. Effect of Surface and of Hydrogen.—A tenfold increase of the surface-to-volume ratio had no appreciable effect on the rate of decomposition. Likewise, the addition of hydrogen produced no change in rate.

7. Energy of Activation.—In Fig. 5 the logarithms of the reciprocals of the times for a 25% increase over the initial pressure are plotted as function of the reciprocals of the absolute temperature for the uninhibited reaction and that fully inhibited by propylene. The activation energies were calculated by the method of least squares and the variation of the relative rate constants with temperature for the uninhibited reaction in terms of the Arrhenius equation is

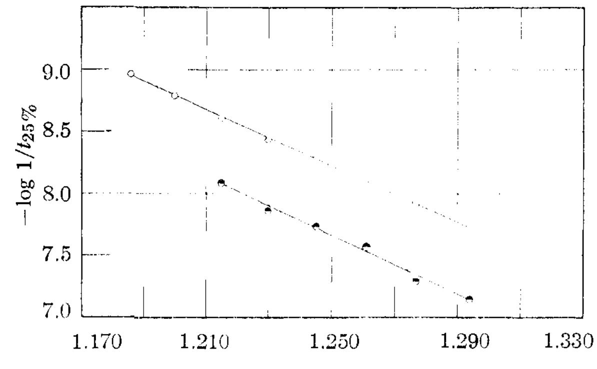

Fig. 5.—Activation energies for the uninhibited (○, E_a = 51.750 kcal.) and propylene inhibited (◓, E_a = 56.200 kcal.) decompositions of methyl *n*-propyl ketone.

$$k(1/t_{25\%}) \quad 7.81 \times 10^{11}e^{-51,750/RT}$$

TABLE II

ANALYSES OF GASEOUS REACTION PRODUCTS FOR THE UNINHIBITED, NITRIC OXIDE CATALYZED, AND PROPYLENE INHIBITED DECOMPOSITIONS OF METHYL *n*-PROPYL KETONE AT 550°

Ketones, p = 150 mm.; NO, p = 10 mm.; C_3H_6, p = 120 mm.

Mole % products

Time	CO			CH_4			C_2H_4			C_3H_6			Total olefins			H_2			CO_2		
(min.)	Un	NO	C_3H_6	Un	NO	C_3H_6	Un	NO	C_3H_6	Un	NO	C_3H_6	Un	NO	C_3H_6	Un	NO	C_3H_6	Un	NO	C_3H_6
0.5	21.1			47.5			13.6			14.6			28.2			1.8			1.4		
1	22.3	22.1	12.6	47.0	51.3	53.7	15.6	7.8		11.5	13.7		27.1	21.5	28.0	1.9	2.0	0.0	1.6	3.2	5.5
2	24.4	25.2	15.3	46.2	46.4	51.6	14.7	13.1		12.0	10.4		26.7	23.5	27.1	1.6	2.2	0.0	1.2	2.7	6.0
3	24.9	28.0	18.3	45.9	45.5	49.7	13.5	11.8		11.5	10.8		25.0	22.6	26.7	1.8	1.8	2.6	2.3	1.8	2.6
4	26.9		21.4	45.0		48.2	13.9			11.0			24.9		25.0	1.7		2.7	2.0		2.7
5	26.5		22.0	46.1		51.1	12.6			11.3			23.9		24.4	1.7		0.6	1.9		1.9
10	28.3	28.0	22.0	46.5	47.9	47.0	14.9	12.9		6.6	6.0		21.5	18.9	19.5	2.2	2.6	3.7	1.6	2.6	3.3
15	27.1			50.3			16.6			2.3			18.9			2.1			1.7		
30	29.7			50.4			12.0			3.7			15.7			2.9			1.4		
60	29.5			55.2			7.1			3.3			10.4			3.1			1.8		
360	30.0			59.8			4.3			0.8			5.1			4.3			0.8		
540	33.1			60.5			1.4			0.4			1.8			3.9			0.4		
720	31.9			60.0			2.7			0.9			3.6			3.1			1.3		
1440	30.5	31.9		62.3	60.5		1.5	0.8		1.0	1.7		2.5	2.5		4.3	4.2		0.5	0.8	
2880	28.3			65.5			0.8			0.0			0.8			5.0			0.6		

For the propylene inhibited decomposition one obtains

$$k(1/t_{25\%}) = 1.07 \times 10^{13}e^{-56,200/RT}$$

The specific rate constants, k_n, were also calculated at eight different temperatures between 500 and 570° by a method previously described.[4] The variation of these constants with temperature may be expressed by

$$k_n = 1.85 \times 10^{12}e^{-52,350/RT}$$

Thus, the agreement between the activation energies calculated by two independent methods is seen to be quite close.

8. **Products of Reaction.**—To obtain an insight as to the initial process and the subsequent reactions, samples of the reaction products were withdrawn from the reaction vessel at various time intervals throughout the entire course of the decomposition at 550°. Prior to the analysis of the gaseous products, the unreacted ketone and ketenes were first removed in a cold trap. The remaining gaseous products were then analyzed for in a modified Bone–Wheeler apparatus.

The reaction products from the nitric oxide catalyzed and the propylene inhibited decomposition also were analyzed for at 550°. In the propylene inhibited runs, it was assumed that the amount of propylene added could be subtracted directly from the total olefins since it had been established that propylene itself underwent no appreciable decomposition over the first 15 minutes at this temperature. All these data are presented in Table II.

A comparison of the data for the uninhibited decompositions with those of the nitric oxide catalyzed reactions show them to be practically identical in almost every case. In the propylene inhibited decompositions the only significant differences are in the carbon monoxide, and, perhaps the methane concentrations. These data indicate further that the catalytic reaction, and the reaction occurring after the chains presumably have been removed by propylene, produce the same quantity of products as the uninhibited chain process.

It was thought worthwhile to determine if there was any change in the ratio of the gaseous products at different temperatures. Analyses made at 530° and 540° on the uninhibited reaction were found to be comparable to those at 550° at corresponding pressure increases.

Ketenes were analyzed for in both the uninhibited, catalyzed and inhibited decompositions at 550° by a method previously described.[4,7] The results of these analyses are shown in Fig. 6. It is immediately evident that neither nitric oxide nor propylene have an appreciable effect upon the amount of ketenes formed in the decomposition of methyl *n*-propyl ketone. This confirms the work of previous investigators[7] who found the same amount of ketenes were produced in the uninhibited and nitric oxide inhibited decompositions of diethyl ketone. It now seems reasonably sure that the catalytic effect of nitric oxide on certain ketones is not due to chemical interaction of the nitric oxide with the ketenes.

The data in Fig. 6 indicate that the ketene concentrations pass through a maximum in a manner characteristic of an intermediate reaction product. From the time and position of the maximum, the ratio of the rates of decomposition of ketene and ketone, k_2/k_1, were calculated in the usual fashion.[4,7] The ratio k_2/k_1 was found to be 8, approximately, just as in the case of methyl ethyl and diethyl ketones.

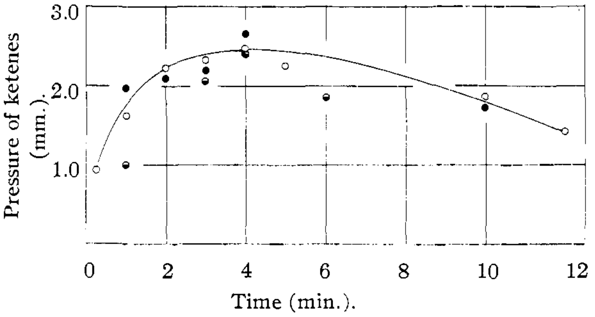

Fig. 6.—Variation of ketene concentrations with time for 100 mm. of ketone at 550°: ○, uninhibited; ●, NO catalyzed; ◒, propylene inhibited.

Discussion

The results of the inhibition studies with propylene indicate that approximately 70% of the decomposition of methyl *n*-propyl ketone occurs by a free radical chain mechanism. Since methane is the only saturated hydrocarbon found in the reaction products, the evidence is rather conclusive that the initial rupture of molecule takes place at the methyl–carbonyl bond. Methyl *n*-propyl ketone possesses ten hydrogens which the methyl radical so formed may remove. There are, however, four different kinds of carbon–hydrogen bonds in this molecule and each has a different reaction probability.[10] The most probable reaction of the methyl radical is with the secondary hydrogens alpha to the carbonyl. Considering only this most probable reaction for the moment, the following mechanism can be written for the predominant chain process in the decomposition of methyl *n*-propyl ketone

$$CH_3COCH_2CH_2CH_3 \longrightarrow CH_3 + COCH_2CH_2CH_3 \quad (1)$$

$$COCH_2CH_2CH_3 \longrightarrow CO + C_2H_4 + CH_3 \quad (2)$$

$$CH_3 + CH_3COCH_2CH_2CH_3 \longrightarrow CH_4 + CH_3COCHCH_2CH_3 \quad (3)$$

$$CH_3COCHCH_2CH_3 \longrightarrow CH_3CH_2CHCO + CH_3 \quad (4)$$

$$CH_3CH_2CHCO \longrightarrow C_3H_6 + CO \quad (5)$$

On the assumption that the chains are short and that all methyl radicals eventually end up as methane, the over-all reaction becomes

$$2CH_3COCH_2CH_2CH_3 \longrightarrow 3CH_4 + 2CO + C_2H_4 + C_3H_6 \quad (6)$$

From the number of moles of product the calculated mole percentages of gaseous products are: 43% CH_4, 28.4% CO, 14.3% C_2H_4, and 14.3% C_3H_6. These values compare not unfavorably with those in Table II.

If the other three possibilities for the removal of hydrogen by the methyl radical are considered and the products from these four reactions are weighted in accordance with their reaction probabilities, it can be shown that this over-all percentage of products does not differ appreciably from the values obtained from equation 6.

The proposed mechanism requires that the ratios of CO/C_nH_{2n} and C_2H_4/C_3H_6 be equal to unity. Table II shows this to be the case during the early stages of the decomposition. Experimentally, the ratios of CH_4/CO and CH_4/C_nH_{2n} have a value of about 2 as compared to the theoretical value of 1.5. At ten minutes reaction time, however, the experimental value is 1.64.

From the available experimental data on the thermal decomposition of ketones it is now possible to draw some general conclusions. Acetone, methyl ethyl, diethyl, and methyl *n*-propyl ketones all decompose predominantly through a free radical mechanism. The products of reaction are essentially similar in each case, both as to species and concentration. Where differences in species do exist they are those that would be normally anticipated from the molecular structure, *e.g.*, the predominance of ethane in diethyl ketone and propylene in methyl *n*-propyl ketone.

The evidence for chain processes occurring in these decompositions is the fact that the rates in each case are reduced to a limiting value by the addition of propylene. Since the amount of inhibition is dependent upon the partial pressure of ketone in all cases, it is evident that the inhibitor molecule reacts chiefly with the small chain carrying radical, R, in a bimolecular reaction of the general type

$$R + M = M^1 + R^1 + R$$

where M and M^1 are the ketone and saturated hydrocarbon, respectively, and R^1 is a free radical larger than methyl or ethyl. In the case of acetone, methyl ethyl, and methyl *n*-propyl ketone, the only saturated hydrocarbon found in reaction products was methane. This, together with other experimental facts, indicates beyond doubt that the chain processes in each of these reactions is propagated by methyl radicals. On the other hand, the large predominance of ethane in the diethyl ketone decomposition leads to the conclusion that ethyl radicals propagate the chain in this reaction.

The most unusual difference in the decomposition of these compounds is their behavior in the presence of nitric oxide. It is immediately evident from the experimental data that nitric oxide strongly catalyzes all reactions in which methyl radicals are present but produces inhibition when larger free radicals are involved. Not so apparent perhaps, is the reason for this peculiar effect. The data in Fig. 6 and similar results on diethyl ketone[7] have quite well eliminated the possibility that this effect can be due to an interaction of nitric oxide with ketenes. There are, however, three possible explanations that can be offered to account for this striking difference in behavior.

1. It has been suggested previously[7] that the catalytic effect of nitric oxide in the presence of methyl radicals may be due not to the nitric oxide itself, but rather to the products resulting from the interactions of methyl radicals with nitric oxide. Extending this hypothesis, it seems plausible to presume that the products from such an interaction might be specific in catalyzing the decomposition of only those compounds that contain a methyl carbonyl group. Support for this is found in the decomposition of aldehydes where it is found that acetaldehyde[11,12] is markedly catalyzed by nitric oxide, whereas the decomposition of the higher aldehydes[12,13] involving radicals larger than methyl, are inhibited. In order for this hypothesis to be completely tenable, of course, it would be necessary to show that the products from the interaction of nitric oxide with the higher radicals differ in some significant manner.

It should be mentioned here that there may be some question as to whether nitric oxide does, in fact, actually inhibit any chain reaction which is propagated solely by methyl radicals. A review of the literature on the nitric oxide inhibited decompositions of saturated hydrocarbons, ethers and aldehydes leaves this point in doubt. The only compounds in these groups which unquestionably decompose to produce only methyl radicals are methane, dimethyl ether and acetaldehyde. Of these, the ether[14] is the only example in which the

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(10) F. O. Rice, THIS JOURNAL, **56**, 488 (1934).

(11) L. A. K. Staveley and C. N. Hinshelwood, *Nature*, **173**, 29 (1936); *J. Chem. Soc.*, **812** (1936).

(12) J. R. E. Smith and C. N. Hinshelwood, *Proc. Roy. Soc.* (*London*), **A180**, 237 (1942).

(13) J. R. E. Smith and C. N. Hinshelwood, *ibid.*, **A175**, 131 (1940).

(14) L. A. K. Staveley and C. N. Hinshelwood, *ibid.*, **A159**, 192 (1937).

evidence for inhibition by nitric oxide appears unambiguous.

2. Another not unreasonable explanation would be that the catalytic effect of nitric oxide may be only an indirect one. In the decomposition of ketones appreciable quantities of unsaturated hydrocarbons are produced. It has been amply demonstrated that these compounds can inhibit free radical chain reactions. The normal, "uninhibited" decomposition of these ketones, then, may simply represent the rate of a reaction which is already partially inhibited by these olefinic product molecules. Nitric oxide molecules, in the presence of methyl radicals, may react preferentially with the olefinic inhibitor and thereby enable the chains to increase to their normal length, with a resulting increase in the rate. While many experimental examples can be offered to support this hypothesis, it is difficult to reconcile this view with the fact that nitric oxide inhibits the diethyl ketone decomposition in the presence of olefins, but also catalyzes the decomposition of acetaldehyde where no olefins occur as products.

3. The catalytic effect of nitric oxide can also be accounted for in yet another way. Certain reactions of aldehydes and ketones in solution occur only when there is a methyl group attached to the carbonyl, *e.g.*, the haloform reactions. It is logical to assume that the peculiar effect of this particular linkage would be also operative, to some extent at least, in the gas phase. The catalyzed reaction, therefore, may involve a complex chemical reaction of nitric oxide at the methyl–carbonyl linkage, rather than with the methyl radicals themselves. The fact that nitric oxide produces catalysis even in the fully inhibited decomposition tends to support this view. Support for this hypothesis is also found in the decompositions of aldehydes and ketones where it is noted that nitric oxide catalyses only those compounds having a methyl–carbonyl bond. Finally, the work of Gantz and Walters[15] on the iodine catalyzed decomposition of ketones reveals that iodine behaves in a manner remarkably similar to that of nitric oxide. It was found that iodine strongly catalyzes the decomposition of acetone and methyl ethyl ketone. Significantly, however, iodine produces only a slight catalysis in the case of diethyl ketone. They interpret their results as indicating that the catalyzed reaction is a complex one involving the chemical reaction of iodine atoms. It seems reasonable, therefore, that the mechanism of the nitric oxide and iodine catalyzed reactions are closely analogous.

Unfortunately, the available experimental data do not enable one to arrive at an unequivocal decision as to which explanation is correct. Each has a certain amount of experimental evidence for support. In the final analysis, experiment alone will decide. Investigations are now being conducted in this laboratory in an effort to obtain unambiguous answers to some of the questions raised and these results will be reported shortly.

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[15] G. M. Gantz and W. D. Walters, THIS JOURNAL, **63**, 3412 (1941).

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[CONTRIBUTION FROM THE INSTITUTE OF GENERAL AND INORGANIC CHEMISTRY AND CENTER OF NUCLEAR CHEMISTRY, UNIVERSITY OF PADOVA]

Kinetics of Displacement Reactions at the Sulfur Atom. I. Isotopic Exchange between Sulfite and Alkylthiosulfates

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The kinetics of the isotopic displacement of sulfite from some alkyl thiosulfates have been studied. The reaction is first order with respect to both reagents and it may be classified as an S_N2 reaction. The exchange exhibits a strong *p*H dependence which is interpreted as being due to the formation of bisulfite ions. Electrolytes catalyze the exchange. The effect of the addition of NaCl has been studied in the range of ionic strength 0.03 to 0.17. The Brønsted equation is not followed. It has been pointed out that the catalysis is particularly strong when multicharged positive ions are present. The temperature dependence of rate has been determined for the following compounds: ethyl, benzyl, allyl, carboxymethyl thiosulfates and ethane dithiosulfate. Entropies and heats of activation have been evaluated. The free energies of activation for the thiosulfate, trithionate and alkyl thiosulfate exchanges are compared and the possible structure of the activated complex is discussed.

Introduction

In the last fifteen years very important progress has been made in the chemistry of sulfur. Particularly significant are the advances in the field of polythio compounds. Here the achievements are mainly due to the work and conceptions of Olav Foss.[1] As a result of his study a new picture covering the entire field has been drawn. The main features of this picture are: (i) in the polythionic compounds the sulfur atoms are in an unbranched chain; (ii) many of the typical reactions of polythionic compounds (with sulfite, thiosulfate, cyanide, etc.) are nucleophilic substitutions at the sulfur atom and can be interpreted in terms of the base strengths of the displacing and displaced groups. The fundamental soundness of these

[1] O. Foss, *Det. Kgl. Norske Videnskabers. Skrifter*, 1945, Nr. 2 (1947); *Acta Chem. Scand.*, **3**, 1385 (1949); **4**, 866 (1950).