[Contribution from the Departments of Chemistry of the Polytechnic Institute of Brooklyn and The University of Connecticut]

The Kinetics of the Thermal Decomposition of Gaseous Methyl Ethyl Ketone[1a]

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The kinetics of the thermal decomposition of acetone vapor has been the subject of numerous investigations. Hinshelwood and Hutchison[1d] and later Winkler and Hinshelwood,[2] established beyond doubt that the decomposition was predominantly homogeneous and of the first order. Some controversy has arisen as to whether acetone decomposes by a free radical or by a rearrangement mechanism. Although the existing experimental evidence does not permit a clear-cut decision as to which mode of decomposition predominates, there appears to be ample justification for believing that both types of mechanism occur.

The purpose of this present paper was to investigate the kinetics of the thermal decomposition of the next member of the homologous ketone series, methyl ethyl ketone, and to compare the results with those for acetone. For example, in the decomposition of acetone, the initial bond-breaking process can occur only at the methyl–carbonyl bond, regardless of whether the reaction involves a free radical or rearrangement mechanism. In methyl ethyl ketone, on the other hand, the initial bond-breaking process may occur at either the methyl–carbonyl or ethyl–carbonyl position—or at both. Hence, resulting similarities or differences in activation energies, products and mechanism would be expected, depending upon where the initial bond rupture occurred.

Experimental

A. Material.—The original material was Eastman Kodak Co. reagent grade methyl ethyl ketone, which was dried and then fractionated directly in a long column with a 10:1 reflux ratio. A middle fraction of 50 ml. distilling between 78.98 and 79.00 was selected for use. All boiling points were measured with a standard thermometer. The following table compares the observed physical constants with those of the literature:

PHYSICAL CONSTANTS OF METHYL ETHYL KETONE

	Observed	Literature[3]
B. p. (760 mm.), °C.	79.53 (cor.)	79.56°
$n^{23}\mathrm{D}$	1.3768	1.3765

The pure methyl ethyl ketone was stored over anhydrous potassium carbonate, a drying agent found by Lochte[4] to have no tendency to cause internal condensation. After the ketone had stood for three months over potassium carbonate the boiling point and refractive index were unchanged.

B. Apparatus.—The course of the decompositions 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 260-ml. quartz bulb which was connected to the system by a quartz-to-Pyrex graded seal. A 5-ml. bulb sealed directly into the line contained the methyl ethyl ketone sample. The dead space of the reaction system was reduced to 1.5% of the total volume of the reaction flask by use of 2.0-mm. capillary tubing.

To prevent the condensation of methyl ethyl ketone in the parts of the system which projected from the furnace, all capillary tubing and taps were wound with fine nichrome wire and heated electrically to 80 ± 2°. At this temperature, Fisher Cellosolve 120° tap grease was found to work very efficiently with regard to consistency, vapor pressure and non-absorption of the ketone vapor.

The remainder of the apparatus was evacuated, and the pressure was measured by a McLeod gage. No run was made if the pressure was greater than 10^{-5} mm.

The reaction flask was maintained at constant temperature to within ±0.06° by a thyratron control previously described.[5] A calibrated platinum–platinum–rhodium thermocouple was placed in contact with the reaction bulb at its largest diameter and temperatures were measured with a Type K_2 potentiometer in conjunction with a sensitive optical lever galvanometer.

Since it is known that small traces of oxygen markedly affect the rate of acetone decomposition, care was taken to eliminate this source of error in the present reaction.

Data and Results

1. Nature of the Decomposition.—The decomposition of methyl ethyl ketone was followed by measuring the rate of pressure change, supplemented by product analyses in order to disentangle complex secondary changes. At the start of the reaction the pressure increases in a characteristic exponential fashion. Instead of reaching a maximum in a reasonable length of time, however, the pressure slowly increases over a long period of time—in some cases for twenty hours. This effect is indicated in Fig. 1 where the change in pressure is plotted against time for three different initial pressures at 630.8°. Obviously, the processes going on after the first fifteen minutes up to twelve hours have no 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 decomposition.

Methyl ethyl ketone thermally decomposes at a conveniently measurable rate between 540–630° to give a total pressure increase of approximately 2.75 times that of the initial pressure. Figure 2 shows the variation of the ratio of the final to the initial pressure, p_f/p_i, with initial pressure at three different temperatures, where the final pres-

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(1d) Hinshelwood and Hutchison, *Proc. Roy. Soc.* (*London*), **A111**, 245 (1926).

[2] Winkler and Hinshelwood, *ibid.*, **A149**, 340 (1935).

[3] Felsing, Schafner and Garlock, This Journal, **56**, 2252 (1934).

[4] Lochte, *Ind Eng. Chem.*, **16**, 956 (1924).

[5] Waring and Robison, *Rev. Sci. Inst.*, **14**, 143 (1943).

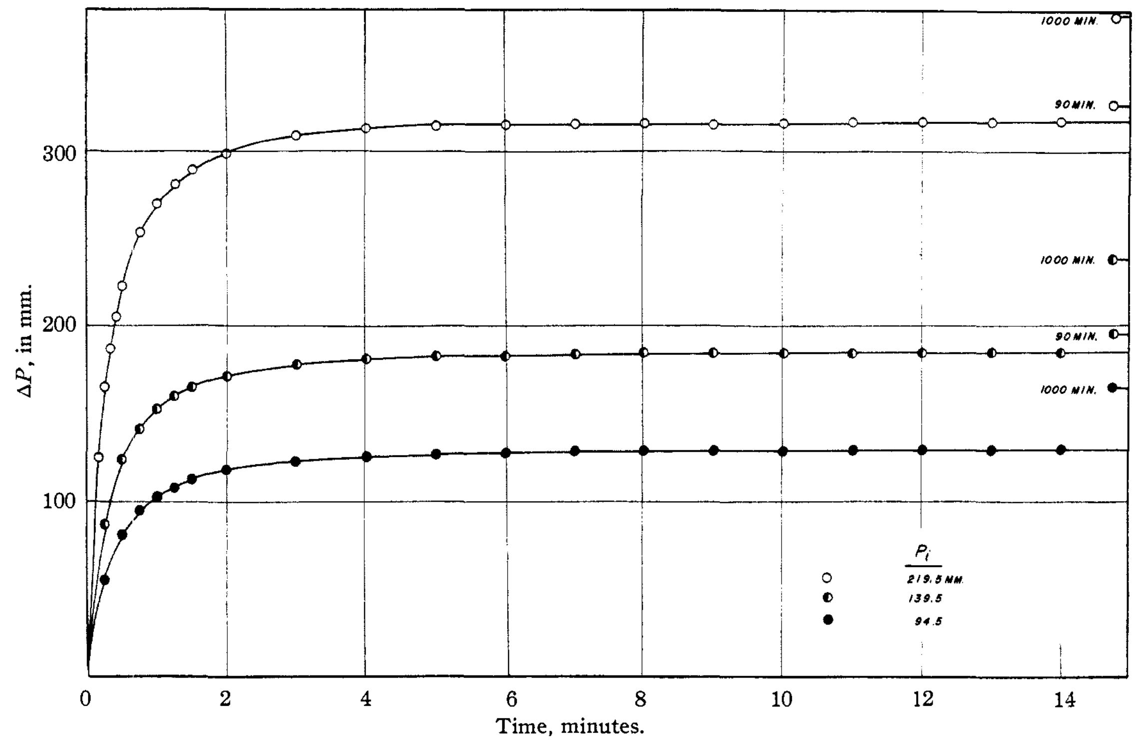

Fig. 1.—Variation of pressure with time at 630.8°: ○, run 39, 219.5 mm.; ◐, run 40, 139.5 mm.; ●, run 47, 94.5 mm.

sure is the pressure at the end of twelve hours. Above 50 mm. initial pressure the end-points ultimately reached are reasonably constant, being independent of temperature and initial pressures. At low initial pressures, the p_f/p_i ratio shows a trend toward a value a little greater than three. This may be ascribed to the fact that at low initial pressures there is less tendency for condensation to take place.

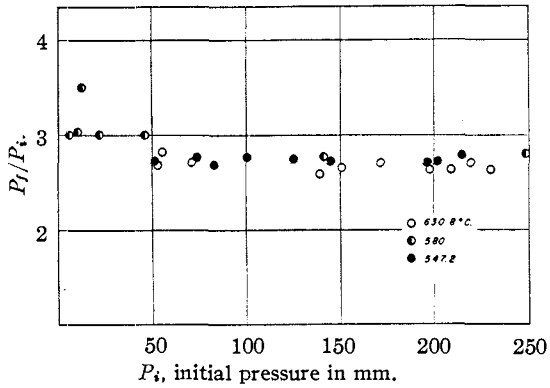

Fig. 2.—○, 630.8°; ◐, 580°; ●, 547.2°.

In a decomposition like that of methyl ethyl ketone, complicated by secondary reactions, it is quite conceivable that a different value for the order of the 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 fraction of the total pressure increase. Since the primary process is of greatest importance, more reliance should be placed upon the initial rate measurements. It will be seen, however, that the order of the reaction is the same whether determined from given fractions of the initial or final pressures.

2. **Order of Reaction.**—The decomposition of methyl ethyl ketone was found to be predominantly homogeneous and of the first order by several criteria. When the reciprocals at various percentage increases over the initial pressure are plotted as a function of the initial pressure, the rates were found to be independent of initial pressure down to 50 mm. Figure 3 may be taken as typical of the curves obtained. Above 50 mm. initial pressure the curve is parallel to the pressure axis, indicating the reaction to be of the

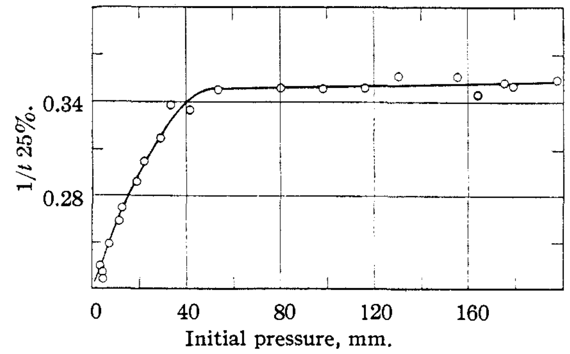

Fig. 3.—The reciprocal of 25% initial pressure increase as a function of the initial pressure at 580°.

first order in that range. Below 50 mm. the rate falls off rapidly and becomes almost proportional to initial pressure and the order approaches that of second.

Since the end-points of the decompositions at various initial pressures have been shown to be fairly reproducible, the determination of fraction-life times, based upon the final pressure increase, offers a reliable method for establishing the order of the reaction. That the decomposition of methyl ethyl ketone was of the first order is further substantiated by Fig. 4, in which the reciprocals of the half-life times are plotted against the initial pressures. Here, again, the same conclusions concerning the order may be drawn. Above 50 mm. initial pressure the decomposition is of the first order. Below this pressure the rate decreases rapidly and the order approaches that of second.

The critical pressure limit occurring at 50 mm. in the decomposition of methyl ethyl ketone is in accord with the predictions of the Lindemann theory of quasi-unimolecular reactions. A similar change in order, as determined from the half-life periods, occurs in the decomposition of acetone at 100 mm. initial pressure. This difference in the pressure at which the two compounds attain their limiting rate value depends, of course, upon how the probability of transformation of the activated molecules varies with the total energy. It is not uncommon in homologous series that the greater the number of internal degrees of freedom possessed by a molecule, the lower the initial pressure at which the rate becomes pressure dependent.

3. **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 rate values for each individual reaction. It seemed probable that methyl ethyl ketone, like acetone, would decompose through the intermediate formation of ketene. By determining the initial rate we would avoid obtaining a composite rate of decomposition for ketone and ketene. In addition, the magnitude of the activation energy determined from this rate might give a clue as to whether the reaction proceeds by a free radical or a rearrangement mechanism.

An equation for calculating the specific reaction velocity constant for the initial process was developed in the following manner.

Let p_t equal the observed over-all pressure at time, t; p_i, the initial pressure of the reactant; p, the partial pressure of the reactant at time, t; and α equal p_f^*/p_i, where p_f^* is the over-all pressure existing when all the reactant has disappeared. Then

$$p_t = p + \alpha(p_i - p) \qquad (1)$$

or

$$p = (p_t - \alpha p_i)/(1 - \alpha) \qquad (2)$$

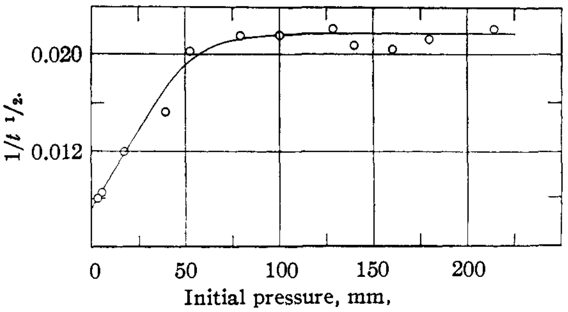

Fig. 4.—The reciprocal of half-life time as a function of the initial pressure at 580°.

The integrated form of a first order equation may be written

$$kt = \ln p_i/p \qquad (3)$$

Substituting (2) in (3)

$$kt = \frac{\ln P_i\,(1 - \alpha)}{p_t - \alpha p_i} \qquad (4)$$

Let

$$n = p_t/p_i \qquad (5)$$

where $\alpha \rightleftharpoons n \rightleftharpoons 1$ (for example, at $t_{50\%}$, $n = 1.50$)

Replacing p_t in (4) by np_i, we obtain

$$k_n = \ln\left[\left(\frac{1 - \alpha}{n - \alpha}\right)\right]\Big/t \qquad (6)$$

Thus, for the initial process, k_n is the specific rate constant when the reaction is the fraction n complete. Since k_n is a constant and α is effectively a constant and t is known, one may select two sets of values, n_1t_1 and n_2t_2, substitute them in equation (6) and evaluate k_n and α by the method of simultaneous equations. Table I gives the experimentally determined rate values for typical runs at 580° and 614°, together with the corresponding calculated values of k_n and α. The last two columns in the Table confirm our contention that k_n and α are essentially constants at a given temperature.

It will be recalled that the *ultimate* value for p_f/p_i is 2.75 rather than 2.24 or 2.12. This difference merely indicates that when p_f^*/p_i equals 2.24 or 2.12, essentially all the methyl ethyl ketone has disappeared. Hence, the subsequent pressure increases which result in a p_f/p_i value of 2.75 do not involve the initial process.

The rate values for the fractional increases over the initial pressure were determined from the pressure–time curves. The initial rate, k_i, proportional to $1/p_i dp/dt$, was also determined. In Table II are given the specific rate constants, together with the rates for various fractional increases over the initial pressure at seven different temperatures over an 84° range. The rates recorded are average values based on a number of runs in the first order range, *i. e.*, where $p_i > 50$ mm.

A plot of the logarithms of the above rate constants against the reciprocals of the absolute tem-

TABLE I

EXPERIMENTAL RATES (SEC.$^{-1}$)

	$1/t_{25\%}$	$1/t_{50\%}$	$1/t_{75\%}$	$1/t_{100\%}$
580°	0.0356	0.0155	0.00851	0.00480
614°	0.141	0.0598	0.0318	0.0168
n	1.25	1.50	1.75	2.00

CALCULATED VALUES FOR k_n AND α

	$(1/t)_1$			$(1/t)_2$		k_n		α	
n_1	580°	614°	n_2	580°	614°	580°	614°	580°	614°
1.25	0.0356	0.141	1.50	0.0155	0.598	0.00776	0.0363	2.27	2.10
1.25	.0356	.141	1.75	.00851	.0318	.00780	.0363	2.25	2.10
1.25	.0356	.141	2.00	.00480	.0168	.00803	.0352	2.23	2.13
1.50	.0155	.0598	1.75	.00851	.0318	.00813	.0363	2.22	2.10
1.50	.0155	.0598	2.00	.00480	.0168	.00809	.0348	2.23	2.13
1.75	.00851	.0318	2.00	.00480	.0168	.00770	.0342	2.26	2.14
					Av.	0.00792	0.0355	2.24	2.12

TABLE II

		Rates × 10^2 sec.$^{-1}$				
T, °C.	k_n	k_1	$1/t_{25\%}$	$1/t_{50\%}$	$1/t_{75\%}$	$1/t_{100\%}$
547.2	0.149	1.04	0.79	0.373	2.20	1.35
558.0	.223	1.50	1.06	.492	2.83	1.62
568.0	.390	2.56	1.90	.859	4.81	2.87
580.0	.844	5.02	3.56	1.55	8.51	4.80
594.7	1.61	9.89	6.96	2.98	16.3	9.02
614.0	3.62	21.30	14.10	5.98	31.8	16.8
630.8	5.61	39.80	20.90	8.72	42.9	19.6

peratures was linear in all cases, the example shown in Fig. 5 being typical.

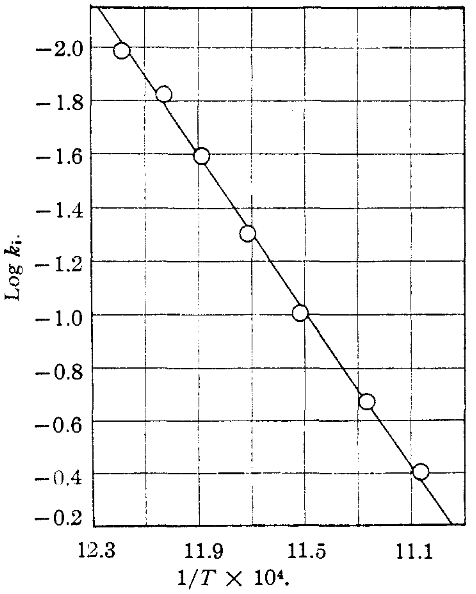

Fig. 5.

From the data in Table II, the energies of activation were calculated by the method of least squares. These values are presented in Table III.

TABLE III

Rate constants	k_n	k_1	$1/t_{25\%}$	$1/t_{50\%}$	$1/t_{75\%}$	$1/t_{100\%}$
E_a, cal.	67,200	66,400	61,850	59,000	56,300	51,900

The E_a determined from the specific velocity constants, k_n, may be taken as the most reliable, for in the calculation of k_n, the decomposition methyl ethyl ketone is isolated from the complex secondary reactions. The variation of the specific rate constant with temperature expressed in terms of the Arrhenius equation may be given as

$$k_n = 1.21 \times 10^{15} e^{-67,200/RT}$$

with a probable error of 500 cal.

It has been pointed out earlier that the activation energies calculated from rates obtained from fractional increases of the initial pressure give only an approximate cross-sectional average of the activation energies of the process from its beginning to $t_{x\%}$. The data in Table III indicate that the activation energies of the latter phases of the reaction are progressively lower than the activation energy of the initial process. If the initial products of reaction undergo no subsequent decomposition, the activation energy should, of course, be constant, regardless of when it was measured, during the course of the reaction. In complex reactions, however, each of the secondary reactions contributes proportionately to the average activation energy of the system. Consequently, such factors as the stability of the reaction products, presence of free radicals, etc., determine whether the activation energies throughout the course of the decomposition will be higher or lower than that of the initial process. Both types of reactions have been observed experimentally. In the present reaction, the decreasing E_a values indicate that products of greater instability than that of methyl ethyl ketone are decomposing and that the rates of these secondary processes must be faster than that of the initial process. That this is actually the case will be further substantiated later.

4. Analysis of Reaction Products.—From the previous work of Hurd and Kocour[6] on the pyrolysis of methyl ethyl ketone, it was expected that in the present reaction ketene and methyl ketene would be produced. Accordingly, ketenes were

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[6] Hurd and Kocour, THIS JOURNAL, **45**, 2167 (1923).

analyzed for at 580°. A sample of methyl ethyl ketone was injected into the reaction bulb in the usual fashion and an attempt was made to obtain an initial pressure of 200 mm. so that a reasonable quantity of ketene would be available for analysis. After the reaction had proceeded for a definite time interval, the gases in the reaction bulb were shared with a gas collecting pipet which was connected to the system. The pressure in the reaction bulb was measured just before and just after the volumes were shared to enable the later calculation of just what fraction of the total products in the reaction bulb had been collected in the sampling flask. The contents of the gas pipet were dissolved in water and the resulting acid solution titrated with dilute alkali using phenolphthalein as an indicator. On contact with water the ketenes reacted immediately to give acetic and propionic acids.

From a knowledge of the temperature of the reaction bulb and the gas pipet, the pressures in the reaction bulb 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 bulb at the time the sample was taken could be evaluated. Knowing the number of moles of ketene in the reaction bulb, the temperature and total pressure, one may then calculate the partial pressure in mm. of ketenes.

Each analysis was made on a separate run at different reaction times. The results were adjusted to an initial pressure of 200 mm. of ketone so that the concentrations of ketene at different times would be comparable. The partial pressures of total ketenes present in the reaction vessel at various times are given in Table IV.

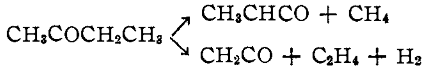
TABLE IV

KETENE ANALYSES AT 580°

P_i = 200 mm.

Time, sec.	15	30	60	120	210	300
Total ketene pressure, mm.	6.7	10.8	14.0	11.7	7.5	2.1

These results are presented graphically in Fig. 6 in the terms of relative ketene concentrations. This curve clearly emphasizes the fact that the ketene concentrations pass through a maximum in a manner characteristic of an intermediate product of reaction. This suggests that methyl ethyl ketone initially decomposes to form ketenes in accordance with the following reaction



$$CH_3COCH_2CH_3 \begin{cases} \nearrow CH_3CHCO + CH_4 \\ \searrow CH_2CO + C_2H_4 + H_2 \end{cases}$$

From the position and magnitude of this maximum the ratio of the rates of the ketone and ketene decompositions may be estimated. In the reaction

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

it can readily be shown that

$$k_2/k_1 = C_{A_0}/C_{B\text{max.}}\ e^{-k_1 t_\text{max.}}$$

where C_{A_0} is the initial pressure of methyl ethyl ketone at $t = 0$ and $C_{B\text{max.}}$ is the concentration of ketene when it has attained its maximum value and t_max is the corresponding time. From the curve in Fig. 6, $t_\text{max} = 60$ seconds, and from Table IV the corresponding value for the absolute ketene concentration, $C_{B\text{max.}}$ is found to be 14 mm. Since $C_{A_0} = 200$ mm. and at 580° $k_1 = 0.00844$, we obtain

$$k_2/k_1 = 200/14\ e^{-0.00844 \times 60} = 8$$

Thus, the decomposition of ketenes is about eight times as fast as that of the ketone. Therefore, in the decomposition of methyl ethyl ketone, the initial production of ketenes must be the rate determining process.

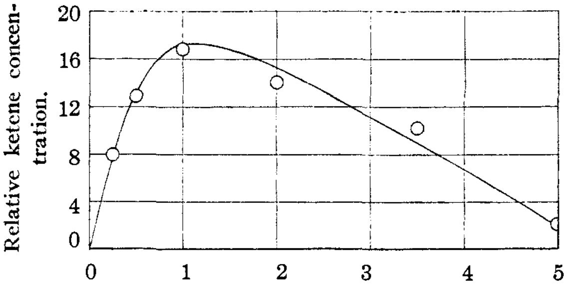


Fig. 6.

Since the analyses for ketenes indicated that the decomposition is complicated by several secondary reactions, the analyses of the final gaseous products gave little information as to the probable reaction mechanism. In order to gain a clearer insight of the initial process and the nature of the subsequent reactions, samples of the reaction mixture were withdrawn from the bulb at various stages of the decompositions at 580°. After the unchanged methyl ethyl ketone and ketenes had been dissolved out in a saturated sodium chloride solution, the remaining gaseous mixture was analyzed in a modified Bone–Wheeler apparatus. The results are presented in Table V.

TABLE V

ANALYSES OF GASEOUS REACTION PRODUCTS (T = 580°)

Products, mole %	Time, minutes					
	0.5	1	2	3	6	1200
Carbon monoxide	31.3	42.5	38.1	40.1	34.8	34.4
Higher olefins	4.08	2.00	2.20	1.75	2.90	1.76
Ethylene	26.1	15.0	18.7	11.4	16.9	1.18
Hydrogen	4.50	5.70	7.75	10.6	7.30	5.88
Hydrocarbons (CH_4)	32.6	33.5	33.4	35.1	37.7	52.7
Carbon dioxide	1.84	1.50	0.29	1.36	0.68	4.12
Carbon atom No.	1.08	1.04	1.09	1.03	1.00	1.01

In order to show more readily what is occurring throughout the course of the reaction, the data in Tables IV and V were translated into terms of partial pressures by a method similar to that employed by Waring and Horton.[7] The variations of the partial pressures of the reactant and products with reaction times are shown in Fig. 7. The partial pressure of methyl ethyl ketone is calculated from the value of *k* at 580°, and the partial pressure of each individual constituent is obtained by taking the total pressure—as given by the manometer reading—and subtracting from it the sum of the ketone and ketene pressures and apportioning the remainder according to the percentages in Table V.

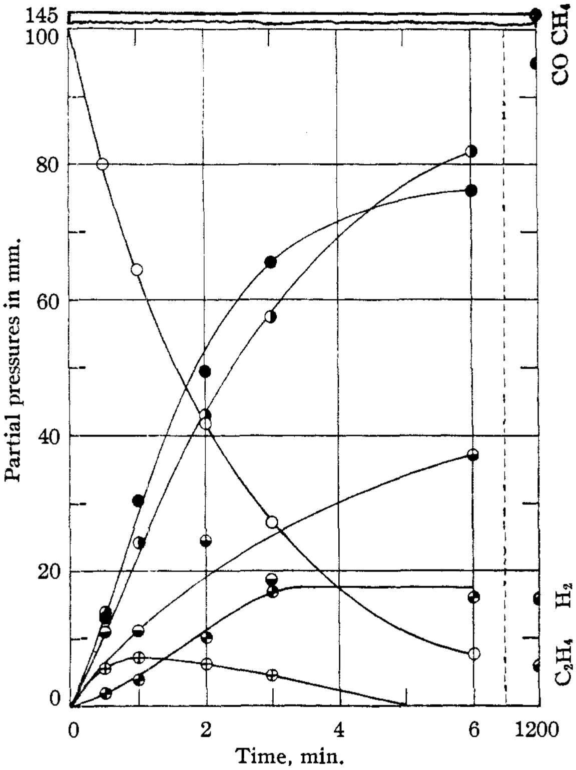


Fig. 7.—○, MeEtCO; ●, CO; ◑, CH$_4$; ◒, C$_2$H$_4$; ⧓, H$_2$; ⊕, ketene; *T* is 580°.

The analyses show that methyl ethyl ketone decomposed to give, in addition to ketenes, predominantly carbon monoxide, methane and hydrogen, together with some ethylene, higher olefins and carbon dioxide. In addition to the gaseous products, a translucent coating of graphite collected on the walls of the reaction bulb after a number of runs had gone to completion. Also, on withdrawing the decomposition products from the bulb, some condensation of a light yellow, viscous material was observed in the capillary tubing. When dissolved in alcohol, the substance showed a faint yellow fluorescence characteristic of highly unsaturated compounds.

Figure 7 also indicates that the percentage of methane steadily increases while the ethylene concentration, after attaining a maximum value, decreases in a somewhat parallel fashion. The rate of decomposition of ethylene is such that at 600°, 28% decomposes in twelve minutes.[8] This, and the fact that a deposit of carbon occurs on the walls of the reaction bulb, indicates a slow reaction of the type

$$C_2H_4 = CH_4 + C$$

The existence of other saturated hydrocarbons in the decomposition products is unlikely in view of the carbon atom value of approximately 1.0.

The presence of carbon dioxide in the products may be explained by the equilibrium reaction 2CO = CO_2 + C which goes about 24% to the right at 580°.

5. **Surface Effects.**—In order to test the homogeneity of the reaction, a number of experiments were conducted in a reaction bulb packed with uniform lengths of pyrex tubing. The surface/volume ratio of the packed bulb was 10.2 times that of the unpacked flask. The first few runs in a clean packed bulb were slightly erratic in regard to reproducibility, but after a short conditioning period in which the bulb became coated with a deposit of carbon, the results became consistent. (This same effect to a lesser extent occurred in clean, unpacked bulbs.) The increase in rate was only 3–6% greater than in an unpacked bulb. Above 600° quartz reaction bulbs were employed. Below 600°, the rates in quartz and pyrex bulbs were identical within the experimental error. From these experiments it may be

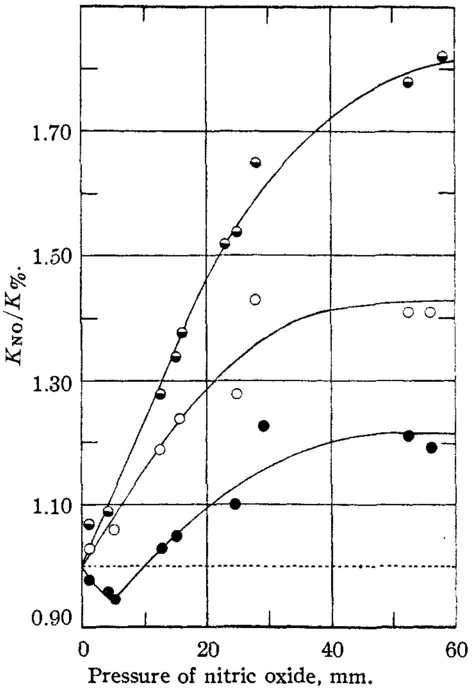


Fig. 8.—Variation of the ratio of inhibited to uninhibited rates as a function of the partial pressure of nitric oxide at 580°: ●, 25%; ○, 50%; ◒, 100% initial pressure increase.

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[7] Waring and Horton, This Journal, **67**, 540 (1945).

[8] Egloff and Parrish, *Chem. Revs.*, **19**, No. 2, Oct. (1936).

concluded that the decomposition of methyl ethyl ketone is predominantly homogeneous in character.

6. **Effect of Nitric Oxide.**—In testing for the presence of chains in the decomposition of methyl ethyl ketone, nitric oxide was employed rather than propylene since propylene undergoes considerable decomposition at 580°. The variation of the partial pressures of nitric oxide between 0.5 to 60 mm. with the ratio of the relative rates of the inhibited to the uninhibited reaction at three different percentage increases over the initial pressure are shown in Fig. 8. These curves lead to several important conclusions concerning the reaction mechanism.

From the curves it can be seen that inhibition occurs only in the initial stage of the decomposition. The ratio for 25% initial pressure increase falls off at first, attaining its minimum value at about 7 mm. partial pressure, then further addition of nitric oxide causes marked catalysis. This curve, therefore, establishes the fact that the normal decomposition of methyl ethyl ketone involves free radical chains. A large amount of inhibitor is required, however, for a relatively small amount of inhibition, hence one may infer that chain processes do not play a predominant role in the reaction mechanism. Since much more nitric oxide is required to inhibit methyl ethyl ketone than is the case with most chain reactions (*e. g.*, ethers), one concludes that the mean chain length must be extremely short. That the absolute chain length is also short is indicated by the fact that the rate is unaffected by a ten-fold surface increase.

Smith and Hinshelwood[9] draw much the same conclusions regarding the nitric oxide inhibited decomposition of acetone where the relative efficiency of nitric oxide as compared with propylene as an inhibitor is very much less than in other cases. This suggests that nitric oxide is better for attacking large radicals rather than methyl. If we assume, for the moment, that methyl radicals are formed in this reaction, then the similar behavior of methyl ethyl ketone in the presence of nitric oxide tends to lend weight to this argument.

The curves for 50 and 100% initial pressure increase, give no evidence that free radicals are present in the secondary processes of the reaction. Instead, it is in these latter stages that the catalytic effect of nitric oxide is most pronounced. This acceleration in rate may be ascribed to chemical interaction of the nitric oxide with the intermediate ketenes which are, of course, extremely reactive compounds. It seems reasonable to presume, therefore, that nitric oxide attacks the ketenes at the reactive carbonyl–carbon double bond to bring about oxidation reactions. This hypothesis is supported both by the fact that the acceleration in rate increases with increasing nitric oxide pressure, and that only the latter stages of the reaction, where ketenes are present, are appreciably affected.

Discussion

In the thermal decomposition of acetone, the initial bond rupture occurs at the methyl–carbonyl position to produce methyl radicals. The activation energy for this reaction is 68,000 cal. while that for methyl ethyl ketone is 67,200 cal. The close agreement of these values and also those of the frequency factor, is compelling argument for believing that the rupture of the corresponding methyl–carbonyl bond is responsible for the initial step in the decomposition of methyl ethyl ketone and that the mechanisms of this and the acetone decomposition must be similar in nature. This belief is further supported by the fact that the only hydrocarbon present in the reaction products was methane.

The question now arises as to whether methyl ethyl ketone decomposes predominantly through a free radical or a rearrangement mechanism. If the Rice–Herzfeld[10] chain mechanism for the decomposition of acetone is adapted to the present reaction one obtains

		E, kcal.
(1)	$CH_3CH_2COCH_3 \longrightarrow CH_3 + CH_3CH_2CO$	80
(2)	$CH_3CH_2CO \longrightarrow C_2H_5 + CO$	10
(3a)	$CH_3 + CH_3CH_2COCH_3 \longrightarrow CH_4 + CH_3CH_2COCH_2$	15
(3b)	$C_2H_5 + CH_3CH_2COCH_3 \longrightarrow C_2H_6 + CH_3CH_2COCH_2$	20
(4a)	$CH_3CH_2COCH_2 \longrightarrow C_2H_5 + CH_2CO$	48
(4b)	$CH_3CH_2COCH_2 \longrightarrow CH_3 + CH_3CHCO$	48
(5)	Radical + Radical $\longrightarrow$ end of chain	Small

$$E_0 = {}^1/_2(E_1 + E_2 + E_4 - E_3) = 62{,}500 \text{ cal.}$$

Although the over-all activation energy calculated from the energies of the individual reactions is not incompatible with the experimental value, several experimental facts make the acceptance of this mechanism as the predominant one untenable. First, the above mechanism requires methane and ethane to be produced in equivalent quantities. This would yield upon analysis of the reaction products a carbon atom number of 1.5. The experimentally determined value is 1.0. Second, the above mechanism does not account for the presence of hydrogen which was found in the gaseous products. Third, the reaction probabilities of steps (4a) and (4b), are identical (E = 48 kcal.); hence, equal amounts of ketene and methyl ketene should be produced. From the ratio of methane to hydrogen at the beginning of the reaction it can be shown that methyl ketene is produced eight times as fast as ketene. Finally, if ethyl radicals are produced to the extent of methyl, and if nitric oxide is more efficient in attacking radicals larger than methyl, then it is surprising that the magnitude of the inhibition is not greater than that found experimentally. It should be noted

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[9] Smith and Hinshelwood, *Proc. Roy. Soc.* (*London*), **A180**, 237 (1942); **A183**, 33 (1944).

[10] Rice and Herzfeld, THIS JOURNAL, **56**, 284 (1934).

that even if one chooses to disregard evidence to the contrary and assume the initial production of ethyl radicals, the result is the same.

For the reasons outlined, it is not immediately apparent how a chain mechanism, similar to that proposed by Rice and Herzfeld for acetone, can account for all the experimental facts. It might be possible to more adequately explain the data by (1) an internal rearrangement mechanism or by (2) a chain process radically different from the Rice–Herzfeld mechanism. Since the nitric oxide experiments indicate either very few chains or chains of very short length, the first possibility appears more justified. Consequently, the following rearrangement mechanism is postulated as being the most predominant process occurring

A. Primary Process

$$CH_3CH_2COCH_3 \begin{array}{ll} \nearrow CH_3CHCO + CH_4 & \quad (1) \\ \qquad\qquad\qquad\qquad \text{(slow)} & \\ \searrow CH_2CO + C_2H_4 + H_2 & \quad (2) \end{array}$$

B. Secondary Process

$$CH_3CHO \longrightarrow CO + C_2H_4 \qquad (3)$$

(fast)

$$CH_2CO \longrightarrow CO + {}^1/{}_2C_2H_4 \qquad (4)$$

C. Final Process

$$C_2H_4 \longrightarrow CH_4 + C \text{ (very slow)} \qquad (5)$$

$$2CO \rightleftharpoons CO_2 + C \quad (24\%) \qquad (6)$$

From the position and magnitude of the maximum in the ketene concentration curve it has been estimated that the rate of decomposition of ketenes is approximately eight times as fast as that of methyl ethyl ketone. The lower activation energies found in the secondary stages of the reaction may therefore be attributed to the contributions of the ketene decompositions.

At the start of the decomposition, step (1) is the only reaction producing methane and step (2) the only one yielding hydrogen. The large amount of methane at the beginning, and the relative constancy of hydrogen after its initial rise to a limiting value, indicates that these two products are produced in the initial break-up of methyl ethyl ketone. This, in turn, is *a priori* evidence that the decomposition proceeds through a rearrangement rather than a free radical mechanism. The slight decrease in hydrogen after three minutes reaction time may be attributed to its adsorption on the coated walls or to its taking part in polymerization reactions.

It has been suggested that the nearly identical activation energies of acetone and methyl ethyl ketone indicates that the latter compound also decomposes through the rupture of the methyl–carbonyl bond. Steps (1) and (2) are consistent with this premise. Further, from the ratio of methane to hydrogen at one-half minute reaction time (Table V) it can be estimated that decomposition through the methyl ketene is approximately eight times as probable as through the ketene intermediate. If the reaction took place entirely through the methyl ketene intermediate, the expected p_f/p_i ratio would be 3. If it went entirely according to step (2), the p_f/p_i ratio should be 3.5. The observed p_f/p_i ratio is 3.05 at low pressures and 2.75 at high pressures. While not too great weight should be placed on evidence of this nature, it is interesting, nevertheless, that the experimental p_f/p_i value also supports the premise that the primary process producing methyl ketene predominates. The slight discrepancy between the observed and theoretical p_f/p_i ratios can readily be accounted for by the formation of complex condensation products.

The analyses show a rather high concentration of ethylene. It comes primarily from the methyl ketene which decomposes very rapidly as soon as it is formed. The fact that the analyses reveal less ethylene than is expected as a result of steps (2), (3) and (4) is due to the slow decomposition of ethylene at 580° to form methane and free carbon as shown by step (5). It can be observed from Fig. 7 that at six minutes the carbon monoxide curve is levelling off since reactions (3) and (4) are virtually complete. The methane curve is still rising due to its formation from ethylene. After twenty hours only a few per cent. of ethylene remains and the methane concentration has increased proportionately.

Although the kinetics of the thermal decomposition of methyl ethyl ketone has not been previously studied, a number of investigations of the photochemical decomposition have been made. Norrish and Appleyard[11] and Ellis and Noyes[12] found that free methyl and ethyl radicals were formed in about equal proportion in the photochemical reaction. In addition, a mixture of ethane, propane and butane, but no methane, was found in the reaction products. This, of course, is what one would expect from a random intermixture of equal numbers of methyl and ethyl radicals. The fact that no paraffin hydrocarbon other than methane was produced in the thermal decomposition of this ketone substantiates the conclusions already drawn from the nitric oxide effects, namely, that radical chains play no appreciable part in the thermal reaction.

One further argument may be offered to support the contention that free radicals do not play an important role in the thermal decomposition of methyl ethyl ketone. The experiments conducted in packed reaction flasks do not reveal any retardation in rate. If chains of appreciable length were involved, a marked inhibition in rate should occur due to the chains being broken as the result of wall effects. If the chains are very short, of course, this effect would be negligible.

Table VI presents a comparison between the relative rates at which acetone and methyl ethyl ketone decompose at several different temperatures.

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[11] Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934).

[12] Ellis and Noyes, THIS JOURNAL, **60**, 2031 (1938); **61**, 2492 (1939).

TABLE VI

Temp., °C.	$k_{MeEtCO} \times 10^3$ sec.$^{-1}$	$k_{acetone} \times 10^3$ sec.$^{-1}$	$k_{MeEtCO}/k_{Acetone}$
550	1.73	0.709	2.44
580	7.25	3.01	2.40
600	17.5	7.50	2.33
630	28.5	65.5	2.30

$\ln k_{MeEtCO} = 34.73 - 67{,}200/RT$

$\ln k_{Acetone} = 34.33 - 68{,}000/RT$

In view of the close agreement of the terms in the rate equations, one is tempted to conclude that the same mechanism of decomposition, namely, rearrangement, is the predominant one for both reactions. Such an assumption is not altogether unwarranted when one compares other similarities. Nitric oxide inhibits both reactions to the same order of magnitude—which is not very large. Further, the values of the activation energies are higher than one normally expects for decompositions which proceed mainly by a chain mechanism. Although free radicals are undoubtedly produced in both reactions, kinetic and analytical evidence favor a rearrangement as being the predominant process.

Summary

The kinetics of the thermal decomposition of gaseous methyl ethyl ketone has been investigated between 547 and 630°. The reaction was found to be homogeneous and of the first order down to 50 mm. initial pressure. Below 50 mm. the rate falls off and the order approaches that of second.

A new method of calculating the specific velocity constants for the initial process is presented. From these rate constants at seven different temperatures the activation energy was determined and the Arrhenius equation may be given as $\ln k = 34.73 - 67{,}200/RT$.

It was found that the methyl ethyl ketone decomposition proceeded through the formation of an intermediate ketene product. Analyses were made for the ketenes and calculations revealed that the intermediate ketenes decomposed eight times as fast as the ketone. Analyses of the gaseous reaction products were made throughout the course of the decomposition.

Nitric oxide was found to produce some inhibition in the early stages of the decomposition but after the inhibition reached a maximum, further addition of nitric oxide caused marked catalysis.

The kinetic and product analysis evidence indicated that methyl ethyl ketone decomposed predominantly through a rearrangement rather than a free radical mechanism, and a decomposition mechanism is proposed that is in keeping with the experimental facts.

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[13] Original manuscript received May 9, 1946.

[CONTRIBUTION FROM THE LABORATORY OF INORGANIC CHEMISTRY OF THE TECHNICAL UNIVERSITY, DELFT, HOLLAND]

On Critical Phenomena of Saturated Solutions in Binary Systems

BY G. A. M. DIEPEN AND F. E. C. SCHEFFER

Introduction

The purpose of this investigation was to find out some binary systems which might be adapted for exact measurement of the solubility of solids in supercritical gases.

The fact that slightly volatile solids can be dissolved in supercritical gases has been ascertained by several workers. The examination of Smits,[1] supplemented later by Smits and Treub[2] concerning the system ether–anthraquinone explained this phenomenon by means of the phase rule.

When we consider the most simple systems formed by a volatile substance, A, and a slightly volatile substance, B, having its melting point above the critical temperature of A, *i. e.*, those systems in which no chemical compounds nor mixed crystals are formed and in which no immiscibility in the liquid phase occurs, we conclude that they can be divided into two main groups:

1. Systems in which the three-phase line S_B-L-G (S_B = solid B, L = liquid, G = gas) runs without interruption from low temperatures to the triple-point of B. The critical line runs without interruption from the critical point of A to the critical point of B.[3] In such a system saturated solutions cannot show critical phenomena; only unsaturated solutions have a critical point, L = G.

If at a temperature lying above the critical temperature of A, one starts with a sufficient quantity of solid B, and compresses gas upon it, he finds that a homogeneous gas phase can only be reached after the system has passed through a liquid state. For, at the three-phase pressure, a saturated solution is formed along with solid B and gas. With further decrease in the volume, the pressure remains constant until all solid B has disappeared; at that instant the system enters the area of unsaturated solution plus gas phase.

With further increase of pressure the critical point of the unsaturated solution is finally attained, provided at least that the volume and the

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[1] Smits, *Verslag Akad. Wetenschappen Amsterdam*, **12**, 335 (1905); *Z. physik. Chem.*, **51**, 193 (1905); *ibid.*, **52**, 587 (1905).

[2] Smits and Treub, *Verslag Akad. Wetenschappen Amsterdam*, **20**, 142 (1911); *ibid.*, **20**, 148 (1911).

[3] For the *p–t* projection of such a system see Bakhuis-Roozeboom, "Die heterogene Gleichgewichte," Vol. II, 1, p. 372.