

The added electrolyte can also be thought of as influencing the system by "screening" the repulsive electrostatic interactions among the heteropolyanions. This reduces the ordering effect of these interactions which in turn results in greater scattering and correspondingly higher apparent molecular weights. One would then expect, in the limit of "swamping" electrolyte, to obtain the formula molecular weight.

Doty and Steiner<sup>16</sup> have given a quantitative treatment for solutions of macro-ions in the presence of additional electrolyte using this point of view. In their theory, the quantity  $(HcM_2/\tau - 1)$  can only take on positive values, corresponding to apparent molecular weights either less than or equal to the formula molecular weight. Our results show that this quantity takes on negative values with high concentrations of added electrolyte, where the apparent molecular weight is greater than the formula molecular weight, showing that this theory

(16) P. Doty and R. F. Steiner, *J. Chem. Phys.*, **20**, 85 (1952).

cannot represent the behavior of the phosphotungstic acids under these conditions.

For the practical problem of determining the molecular weight of compounds like the phosphotungstic acids, it is not enough merely to add a quantity of *swamping electrolyte*. From Fig. 4, it can be seen that the apparent molecular weight increases with added salt to an upper limit appreciably greater than that corresponding to the molecular formula. Therefore, the light scattering data should be obtained at more than one salt concentration. This will lead to an upper limit for the molecular weight. Since, for heteropoly compounds, the empirical formula weights are usually known, the light scattering measurements in combination with other techniques may serve to establish the molecular species. For example, with 12-PTA the upper limit of 3800 is only consistent with monomeric molecules, since the empirical formula weight is 2916.

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## The Thermal Decomposition of Ketene<sup>1</sup>

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The thermal decomposition of ketene has been studied in a static system at 396–563° with most of the work in the region 498–550° at pressures near 100 mm. In addition to carbon monoxide, ethylene and methane reported in the earlier work as major products, carbon dioxide and allene (under some conditions) were found in large amounts. Methane appears to be produced mainly in secondary reactions. The percentages of ketene determined by analysis had no simple relationship to the pressure change. Data from experiments with initial pressures of 44–329 mm. at 520° indicated that the rate of formation of carbon dioxide has a second-order dependence on the initial pressure. Likewise the order of ketene disappearance with respect to the initial pressure at 520 and 550° is almost two. The process for formation of carbon monoxide appears to be complex. Addition of allene and its products increased the rate of carbon monoxide formation.

In view of the importance of ketene in the thermal decompositions of acetone,<sup>2</sup> acetic acid,<sup>3</sup> acetic anhydride,<sup>4</sup> cyclobutanone,<sup>5</sup> methyl acetate<sup>6</sup> and ethyl acetate<sup>6</sup> and its lesser occurrence in other thermal reactions, it seemed important to investigate further the behavior of ketene alone. Since the ketene formed in the pyrolyses of acetone,<sup>2</sup> biacetyl<sup>7</sup> and methyl ethyl ketone<sup>8</sup> has been found to undergo subsequent reactions during the course of the decomposition, additional information concerning ketene would be of interest in the consideration of the products and mechanisms of these other decompositions.

From experiments with ketene in a flow system at 1150° Muller and Peytral<sup>9</sup> reported the following major products: CO, 66%; C<sub>2</sub>H<sub>4</sub>, 20%; CH<sub>4</sub>, 8%.

However, in a static system at 540° Williamson<sup>10</sup> found that methane was considerably more important than ethylene. In contrast to the earlier work<sup>9,10</sup> carbon dioxide was observed by Akeroyd<sup>11</sup> to be another major product at 570°. Allene was postulated, but not detected experimentally.<sup>11</sup> From pressure measurements Williamson<sup>10</sup> concluded that the order of the ketene decomposition in the initial stages is approximately 1.5. He reported an abnormal retardation of the reaction after 5–6% pressure increase. It was assumed that this pressure increase corresponded to 10–12% reaction. One of the purposes of the present study was to obtain analyses for the unreacted ketene as well as the products, during the reaction in a static system.

### Experimental

**Materials and Apparatus.**—For the first half of the experiments in this research ketene from the pyrolysis of acetone in a "ketene lamp"<sup>12</sup> was used after fractionation in a low temperature Podbielniak column (90 cm., Heli-Grid packing). The boiling point for samples distilled at 75 cm. pressure was –50 to –51°. <sup>13</sup> By reaction with water

(1) Abstracted from the Ph.D. thesis of W. B. Guenther, University of Rochester, 1954. This work was supported by a grant from the Celanese Corporation of America.

(2) F. O. Rice and R. E. Vollrath, *Proc. Natl. Acad. Sci. U. S. A.*, **15**, 702 (1929).

(3) C. H. Bamford and M. J. S. Dewar, *J. Chem. Soc.*, 2877 (1949).

(4) E. Peytral, *Compt. rend.*, **193**, 1199 (1931).

(5) M. N. Das, F. Kern, T. D. Coyle and W. D. Walters, *THIS JOURNAL*, **76**, 6271 (1954).

(6) K. K. Georgieff, *Can. J. Chem.*, **30**, 332 (1952).

(7) W. D. Walters, *THIS JOURNAL*, **62**, 880 (1940).

(8) C. E. Waring and W. E. Mutter, *ibid.*, **70**, 4073 (1948).

(9) J. A. Muller and E. Peytral, *Compt. rend.*, **196**, 279 (1933).

(10) A. T. Williamson, *THIS JOURNAL*, **56**, 2216 (1934). For later work see ref. 28.

(11) E. I. Akeroyd, Ph.D. Thesis, Cambridge University, 1936.

(12) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

(13) H. R. Johnson and M. W. P. Strandberg, *J. Chem. Phys.*, **20**, 687 (1952).

and titration with standard base solution this material was found to be at least 98.4–99.0% pure. The infrared spectrum of the ketene corresponded to the spectrum in the literature<sup>14</sup> and revealed no impurities. For the later experiments ketene was prepared by the pyrolysis of acetic anhydride vapor<sup>15</sup> flowing through a quartz tube at 500–520° at 5–10 mm. pressure. Acetic acid and anhydride were removed by passage through traps at –20° and –78° and the ketene was caught in a third trap at –196°. After degassing and trap-to-trap distillation, with the liquid kept below –50°, this ketene analyzed 99.4–99.9% for several preparations. The ketene was stored as a solid at –196° to prevent polymerization.

One sample of allene (99.9% pure) was obtained from Professor F. O. Rice of Catholic University. The allene used for most of the experiments was prepared by Professor M. Szwarc of the New York State College of Forestry and was fractionated in this Laboratory in the Podbielniak column. The middle fraction boiling at about –35° was used. The infrared spectrum of each sample was essentially the same and corresponded to those in previous reports.<sup>16</sup> It gave no test for methylacetylene.

Methylacetylene was obtained from Farchan Research Laboratories, Cleveland. The methylene cyclobutane came from Reaction Products Inc., Painesville, Ohio, and was purified by fractionation by Mr. Eugene Johnson in this Laboratory. The acetic anhydride was J. T. Baker analyzed reagent grade material. The biacetyl from concurrent work<sup>17</sup> was used for two experiments. The diketene used in some exploratory experiments was made by dimerization of ketene in acetone solution; it was purified by fractional distillation before use.

Gases obtained from the Ohio Chemical and Surgical Equipment Company and degassed before use were: ethylene 99.5%, propylene 99.5%, and carbon dioxide 99.9%. Carbon monoxide (>95%) came from the Matheson Company.

The apparatus for the pyrolyses was similar to that previously described.<sup>18</sup> The decompositions were performed in a cylindrical Pyrex bulb of 440-ml. volume with a thermocouple well at its center. The temperature was measured with a standardized platinum–platinum, 13% rhodium thermocouple connected to a Leeds and Northrup Type K-2 potentiometer. In the present work in order to deactivate the surface of the reaction vessel successive charges of ketene were allowed to decompose in the vessel until the rate of ketene disappearance decreased to a constant rate. After use the reaction bulb was found to have a dark-brown to black film on the inner surface. Experiments were also carried out in a bulb packed with thin-walled Pyrex tubes which increased the surface to volume ratio thirty-fold and in a reaction vessel with the inner walls coated with potassium chloride.

**Analyses.**—For the titration of the unreacted ketene, the gaseous reaction mixture was expanded into a tube containing degassed water at –196°. After 12 hr. at room temperature with occasional shaking the solution of acetic acid formed was boiled gently to remove carbon dioxide and titrated with standard sodium hydroxide solution. To check this method, the ketene in the gaseous reaction mixture sometimes was allowed to react with a standard anhydrous solution of ethanolamine in dioxane. After one hour, with frequent shaking, this solution was diluted with water and titrated with standard acid. Agreement between the two methods was within the experimental error expected.

For the quantitative analyses of the gaseous products the undecomposed ketene was removed by reaction with aniline or acetic acid. In a number of the experiments mass spectrometric analyses<sup>19</sup> were performed on the portion of the

reaction mixture volatile at –78°. In many of the experiments the reaction products (free from ketene) were analyzed for carbon monoxide and carbon dioxide. The gases volatile at –196° were removed and the carbon monoxide was absorbed in Burrell "COsorbent." The gases volatile at –78° were next withdrawn and the carbon dioxide usually was absorbed in 40% KOH solution.

**Products.**—The gaseous products of the reaction in the temperature range 498–563° are indicated by the mass spectrometric analyses shown in Table I. The results in the last two columns of Table I are in relatively good agreement with the analyses of Akeroyd<sup>11</sup> for the decomposition at 570° (*viz.*, 49–53% CO, 22–25% CO<sub>2</sub>, 8–10% C<sub>2</sub>H<sub>4</sub>, 15–17% CH<sub>4</sub> and 0.3–0.9% H<sub>2</sub>). Mass spectrometric analyses of the products from a 104 mm. experiment at 396° indicated that at about 400° CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> probably are the most important gaseous products, the percentage of CO<sub>2</sub> being two and a half times that of C<sub>2</sub>H<sub>4</sub> after 70 min. of reaction.

TABLE I  
KETENE DECOMPOSITION PRODUCTS VOLATILE AT –78°  
(MOLE %)<sup>a</sup>

Temp.	498	519°	519 <sup>ob</sup>	548°	563°
P <sub>0</sub> , mm.	100	114	102	47	105
Reaction time, min.	5	20	20 <sup>b</sup>	75	40
CO	19.1	41.7	40.4	48	48
CO <sub>2</sub>	52.5	30.8	32.1	22	20
C <sub>2</sub> H <sub>4</sub>	4.8	9.8	9.8	10	10
CH <sub>4</sub>	0.7	7.0	6.3	14	15
C <sub>3</sub> H <sub>4</sub>	20.1	2.7	4.3	0.6	0.3
H <sub>2</sub>		1.9	1.7	1.8	3.3
C <sub>3</sub> H <sub>6</sub>	0.2	1.6	1.3	2.0	2.3
C <sub>4</sub> H <sub>8</sub>	(0.05)	1.2	1.1	0.4	0.3
C <sub>4</sub> H <sub>6</sub>	1.0	0.4	0.8	0.3	0.2
C <sub>2</sub> H <sub>2</sub>	1.2	0.6	1.0	...	...
Res. <sup>c</sup>	0.4	2.3	1.2	0.9	1.0

<sup>a</sup> The amount of decomposition in the experiments at 519°, where about 75% of the ketene has decomposed, is considerably greater than that in the experiment at 498°. For the experiments at 548 and 563° probably at least 95% of the ketene has decomposed. <sup>b</sup> Denotes packed reaction vessel with a 30-fold increase in surface to volume ratio. <sup>c</sup> Rest of the volatile products.

That allene (C<sub>3</sub>H<sub>4</sub>) was formed in an experiment with 118 mm. of ketene at 443° (reaction time, 30 min.) was shown by means of infrared absorption measurements on the products volatile at –78° after removal of ketene. Likewise the infrared absorption band of allene near 830–840 cm.<sup>-1</sup> with its characteristic series of maxima and minima<sup>16</sup> was evident in the reaction mixture from a 10 min. experiment with 105 mm. ketene at 518°. The infrared data indicated that any absorption due to methylacetylene<sup>14</sup> in the products is small compared to that due to allene. From the infrared results no appreciable amount of allene appeared to remain after 75 min. of reaction of 130 mm. of ketene at 546°. It is known that allene will yield a precipitate with a mercuric chloride solution. Although this is not a specific test for allene, a negative test would indicate the absence of allene. From 82 mm. ketene after reaction for 10 min. at 389° a heavy white precipitate formed in the presence of a mercuric chloride solution and from a packed bulb experiment at 452° (131 mm. ketene, 30 min.) a small precipitate was obtained.

Some of the mass spectrometric analyses indicated that the following products might be present to the extent of about 1%: C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>CO. However, no formaldehyde was detected when Lebbin's resorcinol test<sup>20</sup> was used on water solutions of the products at 520° (133 mm. ketene, reaction time, 19 min.) and at 548° (59 mm. ketene, 4 min.).

To look for diketene in the products the reaction mixture formed from 100 mm. ketene after 10 min. at 519° was removed quickly and passed through traps at –50 and –78°. Water was added to react with any condensed diketene and

(20) J. F. Walker, "Formaldehyde," Reinhold Publ. Corp., New York, N. Y., 1944, p. 246.

(14) Infrared Spectral Data, American Petroleum Institute Project 44, Carnegie Institute of Technology, Pittsburgh, Pennsylvania, Curve 699, ketene. Curve 45, methylacetylene.

(15) C. J. Fisher, A. F. MacLean and A. W. Schnizer, *J. Org. Chem.*, **18**, 1055 (1953).

(16) R. C. Lord and P. Venkateswarlu, *J. Chem. Phys.*, **20**, 1237 (1952).

(17) W. B. Guenther, C. A. Whiteman and W. D. Walters, *THIS JOURNAL*, **77**, 2191 (1955).

(18) D. W. Vanas and W. D. Walters, *ibid.*, **70**, 4035 (1948).

(19) The analyses were performed by R. C. Wilkerson of the Celanese Corporation of America and by the Consolidated Engineering Corporation.

allowed to stand at least 14 hours. Upon titration with base no evidence for the presence of diketene was obtained. Although the reaction is not a fast, simple process,<sup>21</sup> it was found by tests with diketene itself that under the experimental conditions diketene would have caused the neutralization of some of the base. From a 107 mm. experiment at 401° in which 24% of the ketene had reacted the number of meq. of base required for titration corresponded to about 0.05 of the ketene disappearing. If diketene were the substance yielding the acid, it is possible that one out of every five to ten molecules which had disappeared would be present as diketene.<sup>22</sup>

As observed in earlier work, a dark material of low volatility condensed in the cooler portions of the tubing near the reaction vessel. More seemed to be formed at low than at high temperatures.

### Results

**At 550°.**—Figure 1 shows the data for the disappearance of ketene, the pressure rise and the formation of carbon monoxide and carbon dioxide with an

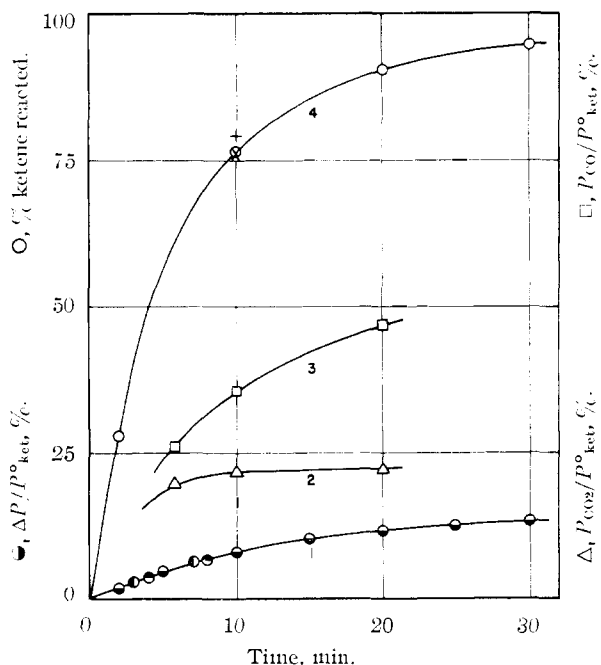


Fig. 1.—Decomposition of 100 mm. ketene ( $\pm 10$  mm.) at  $550 \pm 1^\circ$ . Curve 1, pressure increase;  $\bullet$ , unpacked bulb;  $\circ$ , packed bulb;  $\ominus$ , KCl-coated bulb. Curve 2,  $\text{CO}_2$  formed. Curve 3, CO formed. Curve 4, % ketene reacted:  $\circ$ , unpacked bulb;  $\times$ , packed bulb;  $+$ , KCl-coated bulb.

initial pressure of 100 mm. ketene at  $550^\circ$ . From the results it is apparent that more than 75% of the ketene has reacted in the first ten minutes, but very little pressure change has occurred in this time. The long slow pressure rise after 8–10 minutes, previously reported<sup>10</sup> as accounting for the major portion of the over-all pressure increase, takes place after most of the ketene has disappeared. In a 143 mm. experiment at  $550.5^\circ$  similar to the one cited by Williamson,<sup>10</sup> it was found by analysis that 84% of the ketene had disappeared in 10 min.

(21) A. B. Boese, Jr., *Ind. Eng. Chem.*, **32**, 16 (1940).

(22) With pure diketene at  $300\text{--}348^\circ$  in the packed bulb the pressure rises to a maximum and then falls. After 7 min. at  $348^\circ$  or 14 min. at  $300^\circ$  no non-condensable gases were observed, but an acidic substance, perhaps ketene (not carbon dioxide or diketene), was present.

As seen in Fig. 1, the pressure increases and the amounts of ketene disappearing in the packed and KCl-coated vessels agree with the values obtained in comparable experiments in the unpacked reaction vessel. The surfaces of the packed and KCl-coated vessels had been deactivated by a series of experiments at  $520^\circ$  which will be discussed in the next section.

**At  $520^\circ$ .**—Figure 2 gives the results of experiments with 100 mm. ketene at  $520^\circ$ . Inspection of curve 2 in Fig. 2 (also in Fig. 1) reveals that the

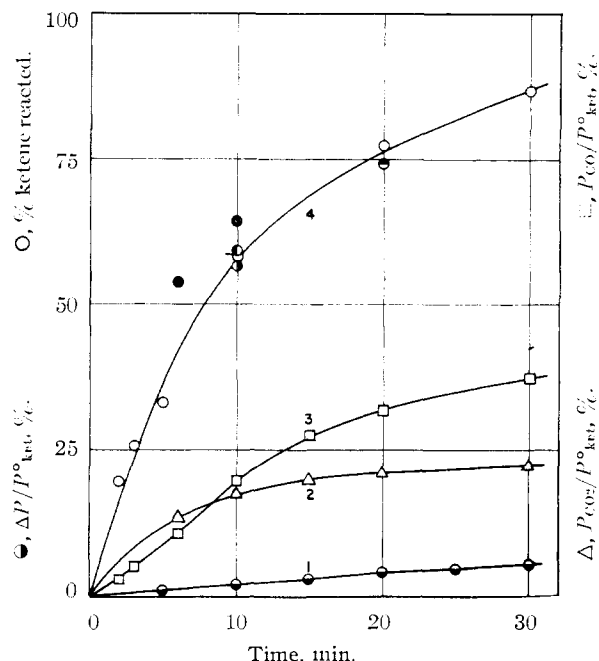


Fig. 2.—Decomposition of 100 mm. ketene ( $\pm 7$  mm.) at  $520 \pm 1^\circ$ . Curve 1, pressure increase. Curve 2,  $\text{CO}_2$  formed. Curve 3, CO formed. Curve 4, % ketene reacted:  $\circ$ , titrated with base solution;  $\bullet$ , ethanolamine method;  $\ominus$ , 48 mm. propylene added;  $\bullet$ , 99 mm.  $\text{N}_2$  added; — horizontal line indicates experiment with 3 mm.  $\text{NO}$  coincides with points shown;  $\bullet$ , allene and its products added, the point at 6 min. represents 42 mm. allene introduced 3.2 min. before ketene and the point at 10 min. represented 19 mm. allene introduced 4 min. before ketene.

rate of formation of carbon dioxide is very slow in the later stages of the reaction where the ketene pressure is low. This behavior could be explained mainly on the basis that carbon dioxide is formed by a higher order process (probably second order). The rate of formation of carbon monoxide (curve 3, Fig. 2) appears to increase during the first ten minutes of the decomposition and after 75% of the ketene has disappeared, much more of the oxygen from the ketene molecules that react seems to appear in the form of carbon monoxide rather than carbon dioxide. To find out whether there is an appreciable conversion of carbon dioxide into carbon monoxide (or *vice versa*) during the decomposition of ketene, the experiments shown in Table II were performed with added carbon dioxide or carbon monoxide. The analyzed values for CO and  $\text{CO}_2$  in the products (corrected for the amount added) are compared with the values taken from curves 2

and 3 in Figs. 1 and 2 for pure ketene alone. In view of the large amount of added gas, the experimental error in the analyses, and slight differences in the conditions, the closeness of the values in the presence and absence of added gas indicates that no rapid interconversion takes place under the conditions for Figs. 1 and 2.

TABLE II  
DECOMPOSITION OF KETENE IN THE PRESENCE OF ADDED GASES

$P_{\text{ket}}^0$ , mm.	Add. subst.	$P_{\text{A.S.}}$ , mm.	Products formed			
			$P_{\text{CO}}/P_{\text{ket}}^0$ , %		$P_{\text{CO}_2}/P_{\text{ket}}^0$ , %	
			Anal.	From curve 3	Anal.	From curve 2
112 <sup>a</sup>	CO <sub>2</sub>	40	33.6	32	21	21
112 <sup>b</sup>	CO <sub>2</sub>	41	30	28	21	20
101 <sup>c</sup>	CO	36	27	25	18	19

<sup>a</sup> 20 min. at 520°. <sup>b</sup> 6.5 min. at 550°. <sup>c</sup> 5.5 min. at 550°.

As a further test that the reaction  $2\text{CO} \rightarrow \text{CO}_2 + \text{C}$  might be of significance in this study<sup>8</sup> carbon monoxide (154 mm.) was allowed to remain in the reaction vessel for 26 min. at 519°, but analyses showed that not more than a few tenths of a per cent. of carbon dioxide could have been formed. Similarly to check whether carbon dioxide could form carbon monoxide by reaction with carbon-containing compounds on the walls of the bulb, carbon dioxide (109 mm.) was kept in the reaction vessel 45 min. at 550°, but any carbon monoxide formed was negligible (less than 0.01%).

In the analysis of carbon monoxide the volume of the remaining non-condensable gas (chiefly methane) was measured. At 520° for 100 mm. ketene the residual non-condensable fraction amounted to only one-eighth that of carbon monoxide during the first 3–6 min. of reaction but increased to about one-fourth after 30 min. A plot of the quantity of this residual portion against time gave the appearance of a process with an induction period.

The data for the percentage of ketene which has reacted after 10 min. for various initial pressures at 520 and 550° are shown as curves 1 and 2 in Fig. 3. The increase in the percentage of reaction for higher initial pressures indicates that the over-all order for the disappearance of ketene is greater than one. At 520° the pressure for the 300 mm. experiments did not follow curve 1, Fig. 2, but decreased slightly before it started to rise.

The influence of the surface was studied at 520° in the packed and KCl-coated vessels. When the surface was not thoroughly deactivated, the ketene disappeared at a faster rate than in the normal unpacked bulb and with 100 mm. ketene a small pressure decrease occurred at the start of the reaction. The surface was poisoned by allowing a number of samples of ketene (or acetone) to decompose in the vessel. With an adequately deactivated surface the pressure change after 10 min. was positive. For four experiments showing such behavior the percentage of ketene disappearing averaged 58% in the packed vessel and 57% in the KCl-coated vessel compared with 58–59% reaction in 10 min. with the usual bulb.

**At 499°.**—As observed in earlier work,<sup>11</sup> the pressure change within the first 20 min. for experiments near 100 mm. was found to be slight. However,

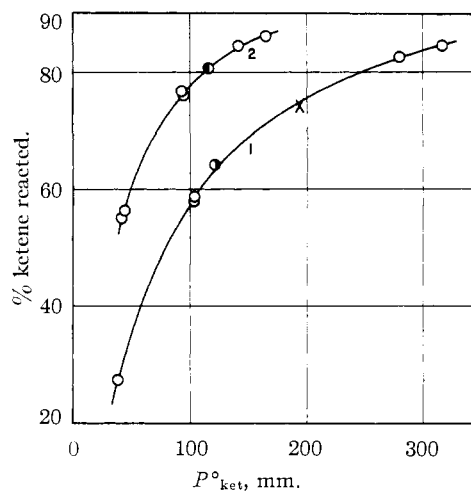


Fig. 3.—Percentage of ketene disappearing after 10 min. for different initial pressures at 520 ± 1.5° (curve 1) and at 549.5° (curve 2). O, unpacked bulb; X, packed bulb; ●, 49 mm. propylene added; ○, 57 mm. CO added.

carbon dioxide and carbon monoxide are being formed during this time as shown by the data in Fig. 4. Carbon dioxide is more important than carbon monoxide near the beginning of the reaction and the curves are similar in shape to the early portions of the curves at 520°.

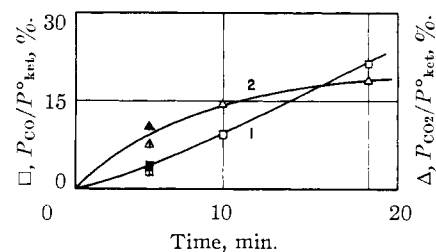


Fig. 4.—Decomposition of 100 mm. ketene at 499°. Curve 1, CO formed. Curve 2, CO<sub>2</sub> formed. ■, ▲, mass spectrometric analyses of CO and CO<sub>2</sub>, respectively. □, △, values from an 83 mm. experiment.

**At 450° and Below.**—Ketene at initial pressures of 60–250 mm. underwent a pressure decrease at 450°. The maximum rate of pressure fall occurred some minutes after the start of the reaction and depended on the initial pressure raised to a power higher than one, probably about two. In two preliminary experiments near 150 mm. the pressure fell to a minimum value (about three-fourths of the initial pressure) after 70–80 min. and then rose very slowly. A mass spectrometric analysis for an experiment at 447° (157 mm., 31 min.) showed that carbon dioxide, carbon monoxide and allene are the main gaseous products, the carbon monoxide amounting to ~0.4 of the carbon dioxide. Titration of a reaction mixture (102 mm., 446°) indicated at least 40% ketene disappearance after 20 min. when the pressure had decreased 10%. If any other acid-forming substance is present in the mixture, the % loss of ketene will be higher. From gas analyses it appears that carbon dioxide and carbon monoxide account for the major portion of the oxygen atoms from the ketene molecules disappearing in 20 min. at 450°. In a single experiment

in the packed bulb (131 mm., 452°) the pressure decreased several-fold faster than in the unpacked bulb and reached a lower value. Allene at pressures of 32 and 114 mm. was found to undergo a pressure decrease in the packed bulb at 450°, but at neither pressure did the rate of pressure fall equal that for 131 mm. ketene.

For 100 mm. experiments near 400° the rate of pressure decrease in the packed vessel was approximately fourfold greater than the maximum rate in the unpacked bulb, indicating that a portion of the reaction at 400°, as well as 450°, in the unpacked bulb is heterogeneous. Although further poisoning might have lessened the heterogeneity, no extensive studies were undertaken in this lower temperature range. With 100 mm. initial pressure in the packed bulb at 399° the pressure leveled off at about half its initial value after 100 min., but the process is probably not a simple one since some non-condensable gas was formed in both the packed and unpacked bulbs.

**Effect of Added Substances.**—Various substances were added to ketene to ascertain whether the decomposition would be affected. Results from some of the experiments at 520 and 550° in the presence of nitrogen, carbon monoxide, propylene or nitric oxide have been given in Figs. 2 and 3 and indicate that under the conditions used there is not a large effect upon the rate of ketene disappearance. The data in Table II and the first three experiments in Table III showed that the addition of carbon monoxide, carbon dioxide, ethylene or propylene did not greatly alter the rate of formation of carbon monoxide or carbon dioxide. However, since two experiments shown in Fig. 2 indicated that allene plus its pyrolytic products increases the rate of ketene disappearance, an investigation of its effect upon the formation of carbon monoxide and carbon dioxide was undertaken. The data given in Table III show that allene with its products markedly increases the rate of carbon monoxide

TABLE III  
EFFECT OF ADDED SUBSTANCES UPON THE FORMATION OF  
CARBON MONOXIDE AND CARBON DIOXIDE IN THE  
DECOMPOSITION OF KETENE

$P_{\text{ket.}}$ , mm.	Add subst.	$P_{\text{A.S.}}$ , mm.	$P_{\text{CO}}/P_{\text{ket.}}$ , %	$P_{\text{CO}_2}/P_{\text{ket.}}$ , %
Temp. 530 ± 1°; reaction time, 6 min.				
104	.....	0	10.7	13.6
95	C <sub>2</sub> H <sub>4</sub>	50 <sup>a</sup>	10.5	11.4
105	CH <sub>2</sub> CH=CH <sub>2</sub>	47 <sup>a</sup>	12.6	13.8
91	CH <sub>2</sub> =C=CH <sub>2</sub>	29 <sup>b</sup>	29	11
102	CH <sub>2</sub> =C=CH <sub>2</sub>	45 <sup>c</sup>	27	11
97	CH <sub>2</sub> =C=CH <sub>2</sub>	49 <sup>d</sup>	27	11
105	CH <sub>2</sub> =C=CH <sub>2</sub>	22 <sup>e</sup>	24	..
101	CH <sub>2</sub> =C <sub>4</sub> H <sub>6</sub> <sup>f</sup>	49 <sup>b</sup>	33	12
106	CH <sub>3</sub> C≡CH	45 <sup>g</sup>	24	14

<sup>a</sup> Introduced shortly before ketene. <sup>b</sup> Gaseous mixture of ketene and added substance introduced into bulb. <sup>c</sup> Introduced 4 min. before ketene.<sup>23</sup> <sup>d</sup> Introduced 4 min. before ketene. Pressure was 31 mm. when ketene was added. <sup>e</sup> Introduced 5 min. before ketene. Pressure was 17 mm. when ketene was added. <sup>f</sup> Methylene cyclobutane. <sup>g</sup> Introduced 4.5 min. before ketene. Pressure was 43 mm. at the time ketene was added.

<sup>23</sup> Pressure had decreased to 30 mm. at the time ketene was added.

production. The small decrease in carbon dioxide can probably be explained by a lower average pressure of ketene over the time of reaction as a result of a more rapid disappearance of ketene to form carbon monoxide. The increase in the formation of carbon monoxide in the presence of methylene cyclobutane may be due chiefly to the presence of allene since methylene cyclobutane yields allene and ethylene upon decomposition in the neighborhood of 450°. <sup>24</sup> Moreover, at least some of the methylacetylene will have isomerized into allene.<sup>25</sup>

In two exploratory experiments biacetyl was added to ketene at 548 and 449° (5 and 15%, respectively) to see whether free radicals from the biacetyl decomposition might affect the reaction. From the pressure-time curve at 548° and from the analyses of carbon monoxide and carbon dioxide at 449°, no evidence was obtained that a long chain reaction<sup>26</sup> to form these oxides had been promoted. There seemed to be some increase in carbon monoxide (from the ketene) and perhaps carbon dioxide, but this effect may not have been due to free radicals. Likewise, mixing 12 mm. of acetone, which is decomposing, with 99 mm. of ketene at 550° produced no appreciable effect on the amounts of oxides formed from the ketene. In these experiments corrections were applied for the decompositions of the added substances.

### Discussion

In view of the observed products the processes occurring in the decomposition of ketene in a static system at 520 and 550° can be divided into one type producing carbon dioxide<sup>27</sup> and another type producing carbon monoxide. The formation of carbon dioxide seems to have a maximum rate at the start, but the curve for 520° (and 499°) indicates that the formation of carbon monoxide is a complex process the rate of which accelerates for some time after the start of the reaction. Examination of the data shows that the quantity (CO+2 CO<sub>2</sub>) is quite close to the amount of ketene that disappears, averaging about 95% of the ketene reacted at 520° and about 102–103% at 550° where the data are fewer. The value is probably slightly less than 100% since Akeroyd<sup>11</sup> found a small quantity of oxygen in the polymeric liquid products.

To find the order of the reaction giving carbon dioxide, experiments were performed at 520° with ketene pressures of 329 mm. (3.5 min. reaction) and 44 mm. (20 min. reaction) in addition to these at 100 mm. From the analyses for carbon dioxide and carbon monoxide the ketene pressure at the time of removal could be computed and second-order rate constants for the formation of carbon dioxide calculated. Over this sevenfold pressure range the constants did not vary more than ±7%, indicating a second order for the process yielding carbon dioxide. It was of interest to get an estimate of the

(24) Unpublished results of Eugene Johnson in this Laboratory.

(25) R. N. Meinert and C. D. Hurd, *THIS JOURNAL*, **52**, 4540 (1930).

(26) That ketene with its products may have an inhibiting effect on free radical chain reactions was indicated by the following: addition of 22 mm. ketene to 191 mm. dimethyl ether at 525° reduced the observed pressure increase in 5 min. from 39% to 20–21%.

(27) The carbon dioxide found in the pyrolyses of several ketones probably arises from ketene. See J. R. McNesby, T. W. Davis and A. S. Gordon, *THIS JOURNAL*, **76**, 823 (1954); F. O. Rice and W. D. Walters, *J. Chem. Phys.*, **7**, 1015 (1939); and ref. 8.

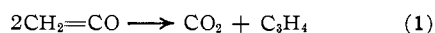
order of the over-all ketene disappearance by analyzing for the ketene reacting at different initial pressures. For pressures between 39 and 316 mm. at 520° the second-order rate constants showed less variation than those with an order of 1 or 1.5. The approximately second-order behavior is also indicated by the results in Table IV. For a second-order reaction the time for a given fraction of reaction is inversely proportional to the initial concentration. On this basis it is possible to calculate for each experiment the time needed to achieve the same % reaction if the initial pressure were 100 mm. (column 4). Then, from curve 4 in Fig. 2 (or Fig. 1) the time actually required to reach this fraction of reaction for a pressure of 100 mm. can be read off (column 5).

TABLE IV  
DECOMPOSITION OF KETENE AT DIFFERENT INITIAL PRESSURES

$P_{\text{ket.}}$ mm.	% react.	Time, min.	Time for 100 mm. to reach same % react.	
			Calcd. as second order	Taken from curve 4
Temp. 520°				
309	69	5	15.5	15
316	85	10	31.6	28
279	83	10	27.9	26
71	13	2	1.4	1.6
42	54	20	8.4	8.9
39	27	10	3.9	3.6
Temp. 550°				
165	86	10	16.5	15.3
45	56	10	4.5	5.0
42	55	10	4.2	4.8

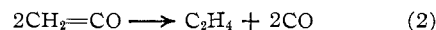
The general agreement of the values in columns 4 and 5 indicates that the order for the over-all disappearance of ketene is almost two (probably slightly less). The order depends on both the carbon dioxide and carbon monoxide reactions. If the order of ketene disappearance were calculated from data at increasing times with a constant initial pressure, it would be more affected by the complexity of the carbon monoxide processes. On account of the shapes of the carbon monoxide curves in Figs. 2 and 4, any calculated order for carbon monoxide formation would depend upon the extents of the decomposition in the experiments used and the order obtained from experiments of the present type might not be very significant. The activation energy for carbon dioxide production was calculated from the second order constants at 499, 520 and 550°. A plot of  $\log(k/T^{1/2})$  against  $1/T$  gave a value of  $E$  in the neighborhood of 35 kcal./mole.

For the formation of carbon dioxide the following reaction would seem to be in accord with the analyses and the kinetics



The allene would disappear in subsequent reactions. Allene at pressures near 750 mm. had been found to form polymers rapidly at 400–600° with gaseous products also forming at 500–600°.<sup>25</sup> In the present work a pressure-decreasing reaction was observed for 55 mm. allene at 450° and for 12–49 mm. at 520° (see footnotes, Table III).

Some carbon monoxide may be formed by the over-all process



but as the reaction progresses, one or more of the products accelerates the formation of carbon monoxide by a process which can be written in a general way (mechanism not specified)



where P is allene or some other product. That products other than allene are probably effective is indicated by the formation of carbon monoxide in the later stages of the reaction where the allene pressure is small.

In this study the various analytical results have shown that there is a deficiency of carbon and hydrogen in the products volatile at  $-78^\circ$ . The polymeric liquid, in which Akeroyd<sup>11</sup> found almost equal numbers of carbon and hydrogen atoms, may account for the deficiency. The production of methane appears to be due to secondary reactions since it builds up only after much of the ketene has decomposed. That the reaction  $\text{C}_2\text{H}_4 \rightarrow \text{CH}_4 + \text{C}$  is not of importance in this work was evidenced by the fact that the addition of 50 mm. of  $\text{C}_2\text{H}_4$  to 95 mm. of ketene at 520° gave after 6 min. only a 0.3 mm. increase in the residual non-condensables ( $\text{CH}_4 + \text{H}_2$ ).

The results at 450° and below indicated that under the conditions used there are several processes occurring in the reaction mixture. The importance of diketene in the reaction, particularly at the lower temperatures has not been determined, but an activated complex similar to the 3-butenic- $\beta$ -lactone structure for diketene would seem likely for reaction 1. As a result of the complexity of the ketene reaction, it seems advisable to postpone further consideration of the mechanism until additional data are available.<sup>28</sup>

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(28) When this manuscript was being prepared, a paper by J. R. Young on this same subject was listed in the *J. Chem. Soc.*, as accepted for publication, but the results of the research were not seen until the article appeared in *J. Chem. Soc.*, 2909 (1958).