594. *The Thermal Decomposition of Keten.*

By J. R. Young.

Keten has been pyrolysed in silica at *ca.* 100 mm. and 510—590°, reaction being followed by direct analysis of products. Disappearance of keten followed a second-order law. Consideration of the curves of formation of products and, in particular, the $CO_2 : CO$ ratio leads to the tentative conclusion that the first stages of the reaction mechanism are:

$$\begin{aligned} 2CH_2{:}CO &\longrightarrow CH_2{:}C{:}CH_2 + CO_2 \\ CH_2{:}C{:}CH_2 &\longrightarrow C_2H_2 + {:}CH_2 \\ {:}CH_2 + CH_2{:}CO &\longrightarrow \cdot CH_3 + \cdot CH{:}CO \end{aligned}$$

which are followed by the attack of the methyl radical and probably of the $CH\vdots$ radical (from breakdown of $\cdot CH{:}CO$) on keten. The chain length of the later stages increases with temperature, and the chain process may overwhelm the bimolecular breakdown at high temperatures.

THREE previous investigations of the thermal decomposition of keten have given contradictory results. Williamson [1] concluded that in the temperature range 500—550° it was a unimolecular decomposition complicated by a simultaneous dimerisation which accounted for an initial fall in pressure at low temperatures. His final analysis of products (CO ~66%, CH_4 30%, C_2H_4 3·0%) disagreed with that found by Muller and Peytral [2] at 1120° (CO 66%, CH_4 10%, C_2H_4 22%). The larger ratio of ethylene to methane found by Muller and Peytral might be due to a change of mechanism at the higher temperature. However, the third study, by Akeroyd,[3] yielded results which conflict with the earlier work: a typical analysis of Akeroyd's products at 570° was CO 52%, CO_2 23%, CH_4 16%, and C_2H_4 9%, where the appearance of carbon dioxide is a new feature. Akeroyd

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[1] Williamson, *J. Amer. Chem. Soc.*, 1930, **54**, 2216.

[2] Muller and Peytral, *Compt. rend.*, 1933, **196**, 379.

[3] Akeroyd, Ph.D. Thesis, Cambridge, 1936.

interpreted his results in terms of a unimolecular breakdown (1) supplemented by a bimolecular reaction (2):

$$CH_2{:}CO \longrightarrow \cdot CH_2\cdot + CO \quad . \quad . \quad . \quad (1)$$

$$2CH_2{:}CO \longrightarrow CH_2{:}C{:}CH_2 + CO_2 \quad . \quad . \quad . \quad (2)$$

Apart from the detail of the second stage this mechanism is kinetically compatible with Williamson's results, and both Akeroyd and Williamson proposed a kinetic order of 3/2 in keten.

In the present investigation pyrolyses have been carried out in a static system at temperatures in the range 510—570°, with initial pressures up to 300 mm. The kinetic results were obtained from periodic direct analyses of products and thus avoid errors which can be shown to arise from simply following pressure. Gas analyses were made by gas chromatography, which was also applied to the purification of the keten used.

EXPERIMENTAL

Preparation of Keten.—Acetone was refluxed over an electrically heated filament in a " keten lamp ".[4] The gases produced were cooled in three stages, a condensate at 20° was returned to the boiling-flask, a second (at −80°), which was a concentrated solution of keten in acetone, was rejected, and a third (at −195°) was worked up for keten. The amount of this condensate was relatively small but it contained very little acetone, which assisted subsequent purification. This was carried out by trap-to-trap distillation at successively −185°, −145°, −80°, and −80°. The keten remained in the residue in all stages except the third where it was separated from residual acetone. In the final stage the vapour was frequently chromatographically analysed until pure.

The yield (*ca.* 4% overall) on the final stage of this operation is largely determined by the difficulty of freeing the residual keten from propene and acetylene, which although initially present in small amounts become concentrated into the penultimate distillate. The keten finally prepared was consistently 98·5% pure and was stored under liquid nitrogen, the contaminants being propene *ca.* 1·2% and acetylene 0·3%; a higher purity would require column distillation. The vapour analyses made during the final operation showed that small amounts of material containing up to 20% of these impurities could be collected as intermediate fractions.

Kinetic Measurements.—The apparatus used for injection and removal of the sample or for following the pressure is shown in Fig. 1. The furnace was constructed from heat-resistant stainless-steel pipe of 3½" bore and ½" wall, with flanged ends. This was electrically heated and had a zone of uniform temperature sufficiently large to contain the silica reaction bulb (capacity 114 ml.). When this was run from a constant-voltage source the temperature stability was within ±0·25° for short periods and the day-to-day variation was not much greater.

At the commencement of each experiment the whole apparatus was evacuated to *ca.* 10^{-5} mm. for ½ hr. With the reaction bulb shut off at the three-way tap T_1, keten was admitted from A to the measuring bulb B which was also connected to the mercury manometer. Tap T_2 was then closed, trapping a sample at room temperature in the calibrated volume (137·5 ml.) between taps T_2 and T_6. Tap T_5 was next closed and the connecting tubes pumped free from keten before reversal of tap T_1 to connect the reaction bulb C with the manometer. Taps T_6 and T_2 were then opened and the sample was rapidly pushed by the rising mercury, through the sintered seal D, into the reaction bulb C. The pressure change was followed either manually or with an automatic device.[5] Samples were taken by admitting the reaction mixture to a Ward–Leroy still[6] E, cooled to −195°, *via* taps T_1 and T_4, etc., causing virtually instantaneous condensation of all products other than methane and carbon monoxide. The still was used in the normal way to fractionate the products and, in general, three fractions were removed, *viz.*, at −195° hydrogen, carbon monoxide, and methane (F_1), at −150° ethylene and ethane (F_2), and at −80° carbon dioxide, keten, propene and traces of C_4 hydrocarbons (F_3). Each fraction was transferred *via* a Töpler pump to the gas burette attached to the chromatography-column

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[4] Hurd, *Org. Synth.*, Col. Vol. I, 1932, p. 324.

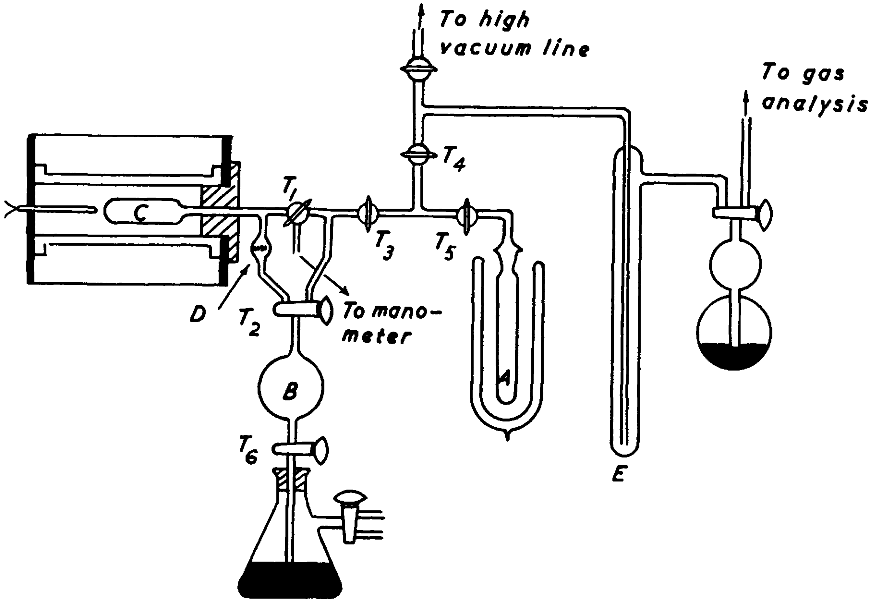
[5] Young, *Chem. and Ind.*, in the press.

[6] Leroy, *Canad. J. Res.*, 1950, **28**, *B*, 492.

inlet. After measurement of its volume, the sample was injected directly into the carrier gas stream and conducted through the appropriate column.

Chromatographic Analysis.—Three columns were used for the complete analysis: column 1, containing 14 g. of active charcoal at 70°, was used for fraction F_1, giving carbon monoxide and methane directly and hydrogen by difference (however, when nitrogen was used as carrier gas all three gases were determined); column 2 containing 11·6 g. of active charcoal at 160° was used for fractions F_2 and F_3, but recorded carbon dioxide only when used for fraction F_3; column 3 containing 10 g. of dinonyl phthalate on 24 g. of Celite 505 separated fraction F_3 and recorded all components. In most cases fraction F_3 was analysed on column 2, giving carbon dioxide directly and keten by difference; occasional analysis of samples on column 3 gave a quantitative measure of keten and allene. A detector of thermal-conductivity type similar to that described by Brooke, Murray, and Williams[7] was used: when thermally insulated this was stable and free from drift; at a chart speed of 1″ per min., with 1″ on the recorder scale = 1 mv and 150 mA bridge current, sensitivities between 12·0 and 4·7 cm.^{2}/ml. at N.T.P. were obtained, depending on the standard operating conditions. Plots of peak area against sample volume plots were linear and the analytical accuracy was $\pm\sim$1·5% when estimated from the spread of the calibration plots.

Fig. 1.



A typical set of results is given in the table. The reproducibility of such analyses was good and variation on individual products rarely exceeded ±5% of the amount present.

Reaction conditions: 570°, P_0 = 150 mm. (7·84 ml. of keten at N.T.P.);
5 min. reaction time.

Volume of fractions: F_1 4·75, F_2 0·74, F_3 1·89 ml. (N.T.P.).

	H_2	CO	CH_4	C_2H_4	C_2H_6	CO_2	$CH_2{:}CO$
Peak areas (cm.^{2}) ...	—	42·8	11·2	2·4	1·0	6·1	—
ml. (N.T.P.)	0·23	3·56	0·96	0·49	1·21	1·26	0·63
Mean of 4 runs	0·29	3·54	0·91	0·47	0·26	1·23	0·68

H_2 and $CH_2{:}CO$ are by difference.

The Ward–Leroy still gave clean separation of the products as long as the total charge was small. The maximum permissible charge was not determined but was probably about 25 ml.

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[7] Brooke, Murray, and Williams, in Desty's "Chromatography," Butterworth, London, 1957, p. 333.

(N.T.P.) of mixture. If larger samples were used, particularly if these contained a high proportion of involatile material, fraction F_3 invariably contained traces of C_2 hydrocarbons indicating incomplete separation.

Identification of Allene.—The final fraction from the still, F_3, normally contained carbon dioxide and keten with several minor peaks following that of keten. The emergence times of these additional products from column 3 (standard conditions) are given below under the headings A—F. Compound A occurred in greatest quantity and passed through a maximum during the early stages of reaction. Some of this compound was separated from a number of analyses: its infrared spectrum identified it as allene. The peaks B—F were not identified but from their emergence times it is probable that they are C_4—C_8 hydrocarbons.

TABLE 1. *Product analyses for keten pyrolysis at 511°, expressed as moles % on initial reactant.*

Reaction time (min.)	H_2 (diff.)	CO	CH_4	C_2H_4	C_2H_6	CO_2	Allene	Keten (diff.)
			At $P_0 = 280 \pm 2$ *mm.*					
¼	—	—	—	—	—	—	2·3	—
½	—	—	—	—	—	—	4·1	—
¾	—	—	—	—	—	—	5·4	—
1	0·2	8·0	0·5	1·1	—	8·0	5·6	69·8
1½	—	—	—	—	—	—	5·7	—
2	1·1	14·6	1·2	2·1	0·2	12·8	5·1	55·7
4	—	—	—	—	—	—	2·5	—
5	2·0	31·4	4·5	3·9	0·4	17·5	—	30·1
6	—	—	—	—	—	—	1·4	—
15	2·8	42·1	8·6	4·4	0·9	19·7	—	14·9
			At $P_0 = 140 \pm 1$ *mm.*					
¼	—	0·4	—	—	—	—	1·5	—
½	—	1·1	—	—	—	—	2·7	—
1	—	3·1	0·4	1·0	0·3	5·0	4·9	80·3
2	0·1	7·1	0·6	1·1	0·1	7·6	6·7	73·0
4	—	14·7	1·5	2·1	0·3	12·7	4·3	58·7
6	—	—	—	—	—	—	2·1	—
7	1·7	26·2	3·2	3·4	1·1	16·7	1·0	41·1
12	2·1	38·7	7·3	3·7	0·9	17·9	—	26·5
25	2·6	47·0	9·6	5·2	1·0	26·2	—	17·5
			At $P_0 = 70 \pm 1$ *mm.*					
7	—	24·6	3·0	3·7	0·7	12·8	—	55·1
15	—	30·2	4·9	4·7	0·6	14·1	—	40·0
25	—	43·2	8·2	5·6	0·9	15·4	—	28·2

Compound	$C_2H_4 + C_2H_6$	C_2H_2	C_3H_6	$CH_2{:}CO$	A	B	C	D	E	F
Elution time (sec.)	54	110	138	174	241	300	350	550	1100	1650

Since pure allene was not prepared it was estimated by assuming that its area sensitivity was the same as that found for propene. The curves for production of allene are shown in Fig. 6.

Results.—The pyrolysis was studied at five temperatures between 570° and 510°. At each, pressure–time curves were plotted and analytical kinetic runs were carried out for various initial pressures between 70 and 300 mm. In a few instances the pressure–time curves showed an initial fall which decreased through successive runs. In order to detect any variation in product ratio accompanying this effect, 3—5 analytical runs were made for each set of conditions, always first with a " burnt-out " reaction bulb. No significant differences were found between successive analyses and in the following the mean results are reported. Table 1 exemplifies the results at a single temperature.

The results obtained at 140 mm. and 511° are plotted in Figs. 2 and 3. The general features revealed in these figures were reproduced under all other conditions of pressure and temperature. We remark: (i) The keten decomposed is equal (within experimental error) to ($2CO_2$ + CO). (ii) The initial rate of formation of carbon dioxide is similar to that of allene formation and greater than that of carbon monoxide formation, though the latter inequality is reversed after *ca.* 35% decomposition. (iii) Formation rates for ethylene and methane show similar behaviour to those for carbon dioxide and carbon monoxide respectively. (iv) Ethane and hydrogen are relatively unimportant products, and allene behaves as an unstable intermediate product. (v) The progress of the decomposition of keten is adequately described by a second-order rate equation.

Plots of time against the reciprocal of the keten pressure show a slope which is independent of the initial pressure within the range studied. Fig. 3 shows such plots for the data of Table 1 and also for the experiments at 570°. The second-order rate constants so obtained have been used throughout for characterising the reaction and the results are given in Table 2.

FIG. 2. *Product–time curves for pyrolysis of keten at* 511° *and* 140 *mm.*

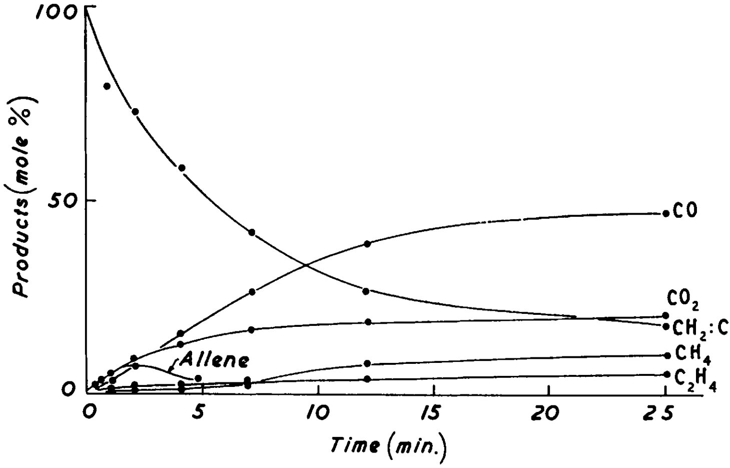


FIG. 3. *Second-order plots for decomposition of keten.*

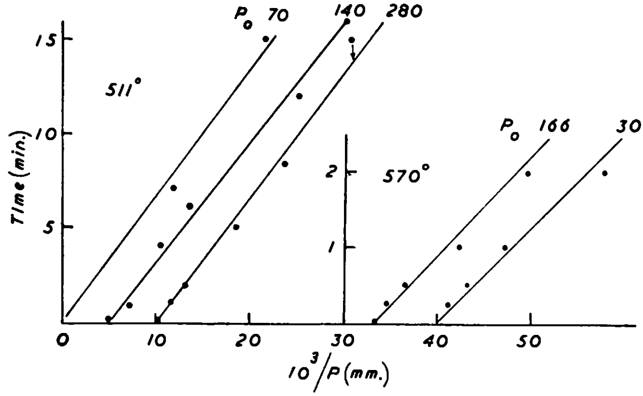


TABLE 2. *Second-order velocity constants* (*mole*$^{-1}$ *l. sec.*$^{-1}$) *for thermal decomposition of keten.*

	P_0 (mm.)						P_0 (mm.)		
Temp.	70	105	140	280	Mean k_c	Temp.	140	280	Mean k_c
511°	1·08	—	1·24	1·24	1·19	550°	3·13	—	3·13
522	—	1·72	1·70	—	1·71	554	—	3·64	3·64
535	2·28	—	2·07	—	2·17	570	6·0	6·9	6·4

The mean values for k_c give the Arrhenius plot shown in Fig. 4, from which the mean apparent activation energy is evaluated as 35·8 kcal. mole^{-1} and the rate constants are given by:

$$\ln k_c \text{ (mole}^{-1}\text{ l. sec.}^{-1}) = 23{\cdot}13 - 35{\cdot}8/\boldsymbol{R}T$$

However, the plot is not perfectly linear and there is a suggestion that the activation energy is increasing throughout the temperature range studied; thus the three upper temperature points indicate E_a *ca.* 50 kcal. mole^{-1}.

Pressure–Time Curves and Material Balances.—Typical examples of the pressure–time curves are shown in Fig. 5. The ratio of the final to the initial pressure is approximately 1·15 in the temperature range 560—570° for initial pressures of about 200 mm. There is some indication that it may rise towards 1·25 at 600°. The exact variation was not investigated

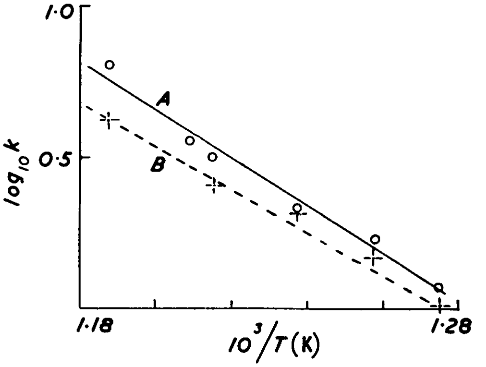


Fig. 4. *Arrhenius plots for* (*A*) *decomposition of keten and* (*B*) *formation of carbon dioxide.*

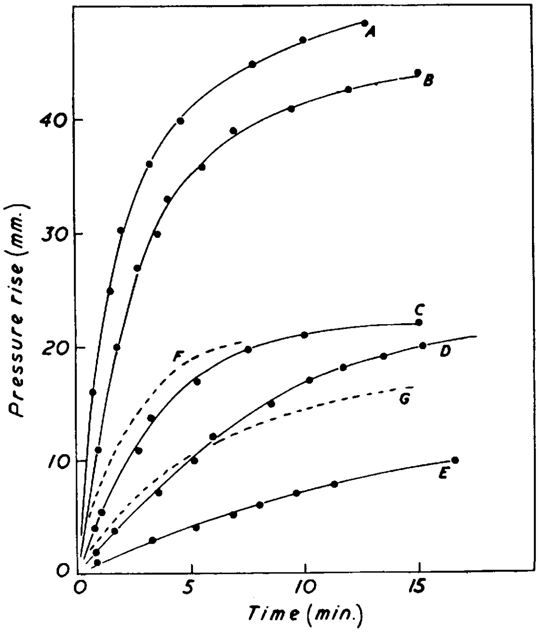


Fig. 5. *Rise in pressure during pyrolysis of keten.*

A, 568° *and* 300 *mm.*
B, 552° *and* 284 *mm.*
C, 552° *and* 150 *mm.*
D, 525° *and* 218 *mm.*
E, 510° *and* 135 *mm.*
F, 552° *and* 140 *mm.*
G, 510° *and* 135 *mm.*

For the significance of the broken curves see text.

since the slow breakdown of tars that accumulated in the neck of the bulb tended to produce slightly variable values under fixed conditions.

In early experiments, an initial pressure drop was observed. This fall could be as much as 4% of the initial pressure and diminished with successive runs, as reported by other workers.[1, 2] The behaviour was consistent with the presence of a volatile polymerisable impurity which decreased in concentration as successive samples were removed from a sample stock. In support of this explanation it was found that the effect could be produced by deliberate addition of acetylene to the keten storage bulb. If successive samples were allowed to evaporate from the liquid mixture the pressure drop gradually diminished. As has already been mentioned, acetylene occurs in keten prepared by a keten lamp, and this material is concentrated in the keten fraction as purification proceeds.

Williamson[1] attributed the pressure drop to initial dimerisation of keten. Against this we have never observed its occurrence with keten of established purity. Moreover, we have performed several flow pyrolyses of keten without detecting its dimer in the products although the contact times were chosen to fall within the early diminished pressure region. This is in agreement with the observations by Rice and Roberts[8] that diketen is completely and quantitatively dissociated at ~500° in contact times of 0·04 sec.

An anomaly concerning the pressure–time curves is that the observed pressure at a given reaction time is always greater than the pressure calculated from the product analysis for that time. This is illustrated by the following comparison, giving the numbers of molecules in the system as determined by the two procedures for reaction at 550°:

	Reaction temp.	Initial pressure	Reaction time (min.) and no. of moles in system						
			0	$\frac{1}{4}$	$\frac{1}{2}$	1	2	$3\frac{1}{2}$	5
From pressure ...	552°	284	100	101	102	104	105	111	112
By analysis	550°	280	100	97·0	95·4	93·1	95·0	96·4	98·9
Decomposition (%)			0	15	28	50	71	80	87

The discrepancy arises because compounds of high molecular weight are formed along with the products reported. An "average" formula for the material unaccounted for may be obtained by equating the molecular deficit to the deficit in the material balance. Thus for the case above we obtain the following results for 550° and 280 mm.:

Decomp.	Element recovery (% on keten decompd.)			Mols.	Average formula as lost material	
(%)	C	H	O	lost	C_x	H_y
15	59	60	101	4·0	3·1	3·0
28	64	69	92	6·6	3·1	2·6
50	57	49	100	10·9	4·0	4·7
71	55	45	100	10·0	6·4	7·8
80	50	39	98	14·6	5·5	6·7
87	52	40	99	13·1	6·4	8·0

Remembering that these figures are approximate, and combining all experimental errors additively, we may generalise the results and conclude: (i) oxygen recovery is complete; (ii) carbon recovery decreases from 60% to 50% during the reaction; (iii) hydrogen recovery decreases from 60% to 40% during the reaction; (iv) the "average" composition of the unanalysed products is substantially constant at C_nH_n, where n increases with reaction time. These features were evident at all temperatures.

The "average" formulæ indicate the kind of product which may occur. The chromatographic analyses revealed traces of acetylene in the early and increasing amounts of C_4 hydrocarbons in the late stages. In addition, tars and free carbon are formed. It is therefore evident that the unanalysed products have a wide range of molecular weight and probably of constitution also. The carbon : hydrogen ratios in these compounds are probably less than unity owing to the formation of free carbon.

For these reasons the observed pressure–time curves tend to give incomplete information concerning the actual decomposition of keten. This is revealed in Fig. 5 where the broken curves show the amounts of keten decomposed (obtained by analysis). In drawing these curves the scales were adjusted so that the final pressure ($= 1·17 \times P_0$) is equal to total decomposition.

Decomposition in the Presence of Added Gases.—In order to investigate certain aspects of the reaction mechanism various runs were made with mixtures of keten with hydrogen, carbon monoxide, carbon dioxide, and propene severally.

Keten–hydrogen mixtures. A mixture of equal parts of keten and hydrogen was heated at 535° and 280 mm. total pressure. The product analyses are compared in Table 3 with those for the reaction of pure keten at 140 mm. and the same temperature. The obvious effects of hydrogen are: (i) a slight increase in the rate of disappearance of keten; (ii) general enhancement of methane formation; and (iii) enhancement of carbon monoxide formation which is more marked in the first part of the reaction. The decreasing recovery of hydrogen is certain evidence that hydrogen is removed in some important reaction. High accuracy is not claimed for these values owing to the large quantity of hydrogen which had to be estimated.

[8] Rice and Roberts, *J. Amer. Chem. Soc.*, 1943, **65**, 1677.

Keten–carbon monoxide mixtures. Equal parts of keten and carbon monoxide were heated at 535° and 280 mm. total pressure. The analyses for the mixtures were comparable with those for the pure reactant and there is no effect attributable to carbon monoxide.

[Similar results were obtained with carbon dioxide (10%) and with propene (10%). In the case of propene correction had to be made for the slow simultaneous decomposition of this compound, which lowered the accuracy of analysis.]

TABLE 3. *Products from pyrolysis of* 1 : 1 *keten–hydrogen mixture at* 535° *and* 280 *mm.*

Reaction time (min.)	H_2 Recovery (%)	CO	CH_4	C_2H_4	C_2H_6	CO_2	Keten	
1	100	11·2	3·2	1·2	0·3	7·7	67	
	—	7·6	0·8	1·1	0·4	7·1	72	H_2 absent
2	100	24·2	7·6	3·0	0·1	9·9	49	
	—	16·0	2·2	2·0	0·3	11·7	61	H_2 absent
4	98	38·2	14·9	1·8	0·6	11·7	28	
	—	30·2	4·3	3·7	0·1	13·2	45	H_2 absent
7	92	44·5	20·1	3·4	1·4	11·9	16	
	—	39·2	7·5	6·0	0·3	14·8	29	H_2 absent
12	80	55·7	24·9	3·8	1·3	10·9	12	
	—	50·8	10·6	5·3	1·3	17·2	16	H_2 absent

A more delicate test of the effect of propene was carried out at 510°, in which the amounts of carbon monoxide alone were measured during the early stages of the reaction. The results in Table 4 reveal no marked effect although the propene concentration was raised to 33%.

TABLE 4. *Comparative carbon monoxide analyses for the pyrolysis of pure keten and* 2 : 1 *keten–propene mixture at* 510° *and* 140 *mm.*

Reaction time (min.)	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{4}$	$1\frac{1}{2}$	
Moles of CO per 100 moles	0·4	1·1	1·7	2·1	3·5	4·3	C_3H_6 absent
	0·4	1·2	—	3·4	—	5·5	33% C_3H_6

The significance of these results will be discussed in the following section.

DISCUSSION

Since the material balances show no loss of oxygen, carbon monoxide and dioxide together account for all the keten decomposed at a given instant. On the other hand, when we have allowed for methane, ethane, ethylene, and propene, the losses of carbon and hydrogen are still so high (40—50%) that we know relatively little of the hydrocarbon products of the decomposition. In these circumstances the main course which the reaction takes has to be argued from the form of the carbon monoxide and dioxide production curves and the secondary products have to be used as supporting evidence.

The formation of carbon dioxide alone gives curves with slopes at zero time approximately proportional to P_0^2, as shown by the following table:

Temp.	P_0 (mm.) of keten	$[d(CO_2)/dt]_{t=0}$ (mm. min.$^{-1}$)	P_0^2 (relative)	Rate (relative)
511°	70	8·75	1	1
511	140	8·4	4	4·8
511	273	19·2	15	11
522	105	5·7	1	1
522	142	11·1	1·8	1·9
535	70	4·2	1	1
535	199	16	4·2	3·8
550	144	29	1	1
550	290	69	4	2·4
570	166	58	1	1
570	300	135	3·2	2·3

Additional evidence of second-order dependence is provided by the fact that the slopes of the carbon dioxide curves fall to half their initial value at about 30% decomposition.

Since the early portions of the allene curves closely follow those for carbon dioxide, there is a strong probability that both these substances are products of the same bimolecular reaction, *viz.*, equation 2 (p. 2910). We are here in agreement with Akeroyd though his evidence for this step was less direct.

The initial rates of carbon dioxide formation have been reduced to a common P_0 (70 mm.) at each temperature by assuming a second-order equation and finally taking the mean rate. The resulting relative rates are:

Temp.	511°	522°	535°	550°	541°
Relative $[d(CO_2)/dt]_{t=0}$	1	1·5	2·2	3·2	5·2

The Arrhenius plot (Fig. 4) of these values is reasonably linear and gives an apparent activation energy of 37 kcal. mole^{-1}. We therefore regard the experimental activation energy from keten disappearance as reflecting the change in rate of reaction (2).

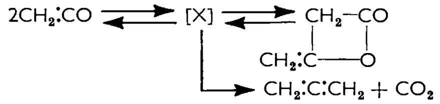
Photolysis studies of keten provide some support for reaction (2). Kistiakowsky and Marshall [9] demonstrated the presence of allene in low-temperature photolysis and conclusively proved that it did not result from reactions involving ethylene. At the same time they showed that the reactions (3) occurred:

$$\left.\begin{array}{l} {:}CH_2 + CO \longrightarrow CH_2{:}CO^* \\ CH_2{:}CO^* + M \longrightarrow CH_2{:}CO + M \end{array}\right\} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \qquad (3)$$

More recently Chanmugam and Burton,[10] investigating temperature effects on the photolysis, found that carbon dioxide, whose production was negligible at room temperature, became an increasingly important product at higher temperatures until at 412° their analysis was CO 53·07, CH_4 2·42, C_2H_4 16·06, C_2H_6 0·09, CO_2 13·45, C_2H_2 0·69, Tars 8·3%.

Whilst no connection between the formation of carbon dioxide and allene was suggested in either of the above papers, it seems consistent with the facts to suggest they are related by reaction (2), probably involving excited keten molecules at the lower temperatures.

The suggestion of reaction (2) together with the failure to observe diketen as a trace product does not exclude the possibility that diketen, or a transition complex based on it, occurs as an intermediate. Moreover, the accumulating evidence [11] in favour of the β-lactone structure of the dimer, helps to bring the present results into line with the pyrolyses of various β-lactones (to olefin and carbon dioxide) reported by Staudinger.[12] The objection to this scheme is the quantitative yield of keten observed by Rice and Roberts on pyrolysis of diketen. It would be possible by arbitrary adjustment of the relative magnitudes of the rate constants to explain all the observations in terms of the detailed mechanism for reaction (2) shown below:



However, this scheme cannot be reconciled with the activation energies or the polarisation characteristics of the reactions involved. Thus the exothermic dimerisation proceeds slowly, if at all, in the gas phase at normal temperature, although a surface reaction occurs on the glass walls. This behaviour is paralleled in solution where the rate of dimerisation increases with polarity of the solvent and shows acid–base catalysis; for the uncatalysed reaction in acetone Rice and Greenburg [13] found an activation energy of 11 kcal. mole^{-1}.

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[9] Kistiakowsky and Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 88.

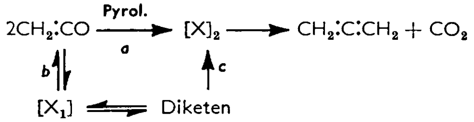
[10] Chanmugam and Burton, *ibid.*, 1956, **78**, 509.

[11] Bader, Gutowsky, Williams, and Yankevick, *J. Amer. Chem. Soc.*, 1956, **78**, 2385.

[12] Staudinger, *Annalen*, 1907, **356**, 63; Staudinger and Kon, *ibid.*, 1911, **381**, 38.

[13] Rice and Greenburg, *J. Amer. Chem. Soc.*, 1934, **56**, 2132.

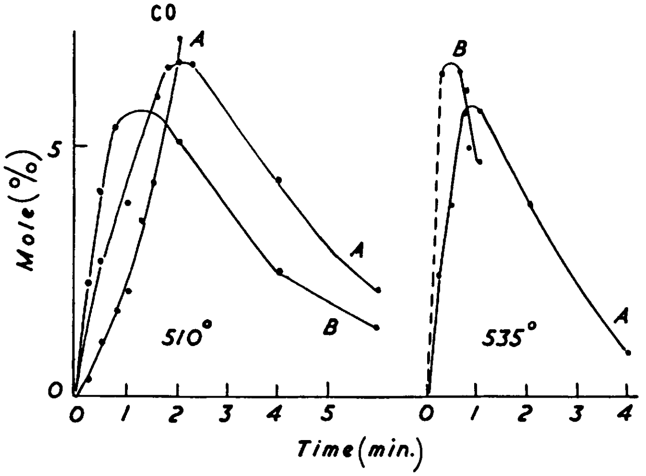
Thus the dimerisation probably involves a polarised transition state which can be reached in a suitable environment with a much lower activation energy than that required for reaction (2), namely, *ca.* 37 kcal. mole^{-1}. It is, therefore, suggested that the transition state involved in dimer-formation undergoes stabilising interactions with the solvent which distinguish it from that concerned in the pyrolysis. On the basis of this argument it is suggested that the relation of pyrolysis to dimerisation may be expressed by the following scheme:



a, $E_a \sim 37$; *b*, $E_a \sim 11$; *c*, $E_a \sim 37$ kcal. mole^{-1}.

The formation of carbon monoxide presents a more complex problem. There is a short induction period which, whilst scarcely discernible in the product trace of Fig. 2, appears in all other cases and has been confirmed by careful measurements at low conversions (Fig. 6). The latter results have been reported in Table 4 where it is also shown that propene has no marked effect on the form of this induction. An explanation in terms of delayed attainment of the reaction temperature is unlikely as experiments with an inert gas (carbon dioxide) showed that the final temperature is reached in a few seconds. Moreover, formation of methane shows a similar but longer induction period, the maximum rate being reached in *ca.* 7 min. at 511°.

FIG. 6. *Formation of allene and early formation of carbon monoxide.*



A, 140 *mm.* *B*, 280 *mm.*

We wish first to decide whether the mechanism for carbon monoxide is independent of that for carbon dioxide formation, *i.e.*, whether we are dealing with simultaneous or consecutive reactions. Evidence against simultaneity can be deduced from consideration of CO_2 : CO ratios at various stages of decomposition. An estimate of the kinetic order of the carbon monoxide rate was obtained by ignoring the early induction period and drawing approximate tangents at zero time. This revealed that the initial rate is proportional to $P_0^{1\cdot5}$, as shown by the following figures.

Temp.	511°	511°	511°	535°	535°	570°	570°
P_0 (mm.) of keten	70	140	280	70	140	166	300
$[d(CO)/dt]_{t=0}$ (mm. min.$^{-1}$)	3	6	25	4	12	75	135
Relative rate	1	2	8	1	3	1	2
Relative $P_0^{1\cdot5}$	1	2·8	8·0	1	2·8	1	2·5

Let us assume for the moment that the exponent of P_0 is in fact unity; as will be seen, this leads to a simple result from which the effect of substituting other powers, including 3/2, can be deduced.

The detailed mechanism of carbon monoxide formation is irrelevant to our purpose provided it does not lead also to the formation of carbon dioxide. Since $d(CO + 2CO_2)/dt = -d(CH_2{:}CO)/dt$, straightforward integration of the rate equations for simultaneous first-order (carbon monoxide) and second-order (carbon dioxide) reactions gives the expressions:

$$P_{CO} = \frac{1}{\alpha} \ln \frac{A\alpha \exp(-k_1 t) - 1}{A\alpha - 1}$$

$$P_{CH_2:CO} = \frac{A \exp(-k_1 t)}{1 - A\alpha \exp(k_1 t)}$$

$$2P_{CO_2} = P_0 - (P_{CO} + P_{CH_2:CO})$$

where k_1 = first-order rate constant for CO formation, k_2 = second-order rate constant for CO_2 formation, $\alpha = k_2/k_1$ (mm.$^{-1}$), and $A = P_0/(1 + \alpha P_0)$ (mm.).

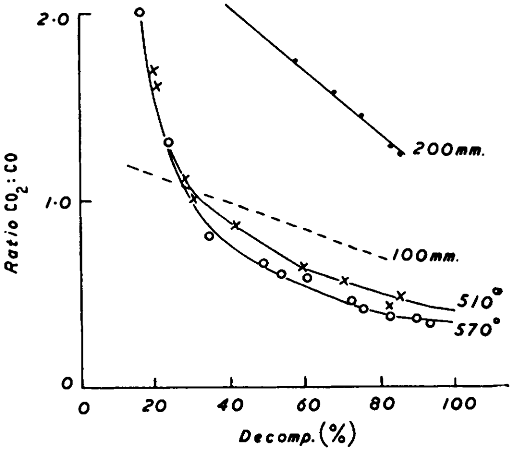


FIG. 7. CO_2 : CO *ratio as a function of decomposition.*

Curves: mixed initial pressures, × *at* 510° *and* ○ *at* 570°.

Straight lines: theoretical curves for $\alpha = 0{\cdot}025$ *and* $P_0 = 100$ (– – –) *and* 200 *mm.* (——).

Trial calculations showed that these equations gave curves broadly similar to the experimental ones for $0{\cdot}01 < \alpha < 0{\cdot}05$; by choosing $\alpha = 0{\cdot}025$, values of the CO_2 : CO ratio were obtained from the theoretical curves for various degrees of decomposition of keten.

In Fig. 7 we have plotted the calculated ratio curves for $P_0 = 100$ and 200 mm. and $\alpha = 0{\cdot}025$, together with the experimental ratio curves for 511° and 570°. It is apparent that there is a greater overall change in the experimental ratio than is shown by the theoretical plots. But even more striking is the effect of altering the initial pressure which, as might be expected, changes the theoretical curve but has no effect upon the experimental ratio.

We can reasonably infer what the effect of other choices of the order of simultaneous carbon monoxide formation on these curves would be. With formation of carbon monoxide also of the second order, *i.e.*, with the rates of formation of carbon monoxide and dioxide equally dependent on P_0, the CO_2 : CO ratio would be constant and independent of both the extent of decomposition and the pressure; as the assumed order of the carbon monoxide reaction decreased from two we would observe increasing dependence of the ratio on both initial pressure and on extent of reaction. It appears then that the experimental curves cannot be reconciled with a mechanism for carbon monoxide formation which is independent of that for carbon dioxide formation and is of constant order with respect to keten over an appreciable range of decomposition.

Additional evidence against independence of these mechanisms can be deduced from the strikingly low temperature dependence of the $CO_2 : CO$ ratio, as revealed in Fig. 7.

It follows, if the arguments are correct, that the mechanisms for formation of carbon dioxide and monoxide are linked in some way. Broadly, there are two possibilities to consider: (*a*) carbon dioxide is formed by reaction (2), and subsequent attack on keten by products derived from this reaction leads to the formation of carbon monoxide; and (*b*) carbon monoxide and dioxide both arise from long-lived activated keten molecules, which either decompose unimolecularly to carbon monoxide and a methylene radical, or react with another keten molecule to give carbon dioxide and allene.

The second proposal was originally made by Akeroyd; we would have to assume also, in order to explain the induction period now observed in carbon monoxide formation, that the methylene radicals initiate further breakdown of keten to carbon monoxide. It is, however, difficult to see how, on this basis, the $CO_2 : CO$ ratio could be independent of P_0 since higher values of P_0 would still initially favour production of carbon dioxide at the expense of monoxide.

The first possibility is suggested both by the induction period in carbon monoxide formation and by the observation that the end of this induction period appears to coincide with the maximum in the curve of allene concentration. Accordingly one might suggest that allene initiates a chain decomposition of keten by splitting, to give acetylene and a methylene radical:

$$CH_2{:}C{:}CH_2 \longrightarrow C_2H_2 + {:}CH_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

The calculated heat of this reaction, if one assumes that methylene is in its lowest state (see Laidler and Casey [14]), is 77 kcal. mole^{-1}, which is not very different from that for reaction (1) (71 kcal. mole^{-1}). Reaction (4) is not in conflict with the little known properties of allene, since Fichter and Spiegelberg [15] reported its breakdown to methane, ethane, and acetylene above 500°.

The continuation of carbon monoxide formation by attack of methylene radicals on keten is a speculation but a slightly expanding chain is required to maintain the rate of carbon monoxide formation. We tentatively suggest that the propagating stages may be:

$$\begin{aligned} {:}CH_2 + CH_2{:}CO &\longrightarrow {\cdot}CH_3 + {\cdot}CH{:}CO \\ {\cdot}CH{:}CO &\longrightarrow {\vdots}CH + CO \\ {\cdot}CH_3 + CH_2{:}CO &\longrightarrow CH_4 + {\cdot}CH{:}CO \\ {\vdots}CH + CH_2{:}CO &\longrightarrow {:}CH_2 + {\cdot}CH{:}CO \end{aligned}$$

Termination by combination of methylene radicals to ethylene could then be more important in the early stages (accounting for the initial rise in ethylene concentration), whilst later other processes involving the new radicals predominate. The high material loss (giving tars and higher hydrocarbons) exemplifies the complexity of the situation. The effects of hydrogen addition (*i.e.*, increasing rate and enhancing methane production) could result from modification of the propagation stages by reactions such as:

$$\begin{aligned} H_2 + {\cdot}CH_3 &\longrightarrow CH_4 + H{\cdot} \\ H{\cdot} + CH_2{:}CO &\longrightarrow {\cdot}CH_3 + CO \end{aligned}$$

The existence of such a mechanism is favoured by observations by Chanmugam and Burton [10] and Knox, Norrish, and Porter,[16] who found that the quantum yield of keten photolysis increased with temperature. It is also relevant that whilst the former workers found appreciable carbon dioxide and little acetylene at 412°, the latter achieved instantaneous temperatures of between 500° and 800° in high-intensity flash photolysis, finding no carbon dioxide but appreciable amounts of acetylene.

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[14] Laidler and Casey, *J. Chem. Phys.*, 1949, **17**, 1087.

[15] Fichter and Spiegelberg, *Helv. Chim. Acta*, 1929, **12**, 1161.

[16] Knox, Norrish, and Porter, *J.*, 1952, 1477.

Thus there seems to be strong evidence that the chain mechanism of breakdown of keten never leads to carbon dioxide and is favoured by increasing temperature. On the arbitrary assumption that every allene molecule formed provides a methylene radical for chain propagation, and using the limiting CO_2 : CO ratios of 0·4 at 510° and 0·34 at 570°, we estimate the chain length to be 2·5 at 510° and 3·0 at 570°. These values compare with quantum yields of 2 at 412° [10] and 6 at 700—900°.[15] The comparison is reasonable even though our estimates are probably lower than the actual lengths of the chains. This temperature effect suggests that at least one of the propagation stages has a sensible activation energy but nothing more can be said on the basis of this tentative mechanism.

In future work it will be important to establish the nature of chain initiation and a decision between the two possibilities presented might be made by study of the decomposition of allene and its effect on the breakdown of keten supported by low-pressure pyrolyses of keten.

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