270. *The Photochemical Decomposition of Keten by Means of Light of Very High Intensity.*

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The photochemical decomposition of keten has been studied by using a flash-discharge lamp with a useful output of 10^{23} quanta/second and an effective duration of 1·5 milliseconds.

At low intensities, or in the presence of a large excess of inert gas, the products are mainly carbon monoxide and ethylene as found under normal photolysis conditions. As the intensity is increased, or the inert-gas pressure decreased, hydrogen and acetylene are formed in increasing amounts until eventually they, with some carbon, become the major products and the quantum yield of keten decomposition increases to a value of over 6. This change is shown to be caused by the adiabatic nature of the photolysis, the short times involved and high radical concentration resulting in a very high temperature followed by rapid quenching of the reaction. By analysis of the products under different conditions of intensity, pressure, and dilution, it is possible to follow the course of the complex reactions taking place, and the results show fairly clearly that carbon formation takes place by successive dehydrogenation of C_2 hydrocarbons, followed by polymerisation to graphite. Higher hydrocarbons and polymers are almost absent from the products of the high-intensity decomposition and in excess of methane the first hydrocarbon formed is ethane.

Attempts to obtain the absorption spectrum of methylene are discussed in relation to this work.

In a preliminary note we have described the effects of very high intensity radiation on several well-known photochemical reactions (Norrish and Porter, *Nature*, 1949, **164**, 658). It is essential that these effects should be understood if full advantage is to be taken of the high radical and atom concentrations which are obtained by use of the flash discharge and which make possible the study of free-radical reactions by direct methods such as absorption spectroscopy (Porter, *Proc. Roy. Soc.*, 1950, *A*, **200**, 284; *Discuss. Faraday Soc.*, 1950, **9**, 60). A detailed analysis of the products of photolysis of keten, by aid of the flash discharge, has therefore been undertaken with the primary object of testing the hypotheses originally put forward to explain the effects of high-intensity radiation. Keten was chosen because of our interest in two special aspects of this sytem : first, the methylene radical which has so far eluded all attempts at detection by absorption spectroscopy and, secondly, the mechanism of carbon formation in the homogeneous gas phase. The latter is of great importance but is not suitable for study in photochemical reactions at normal intensities.

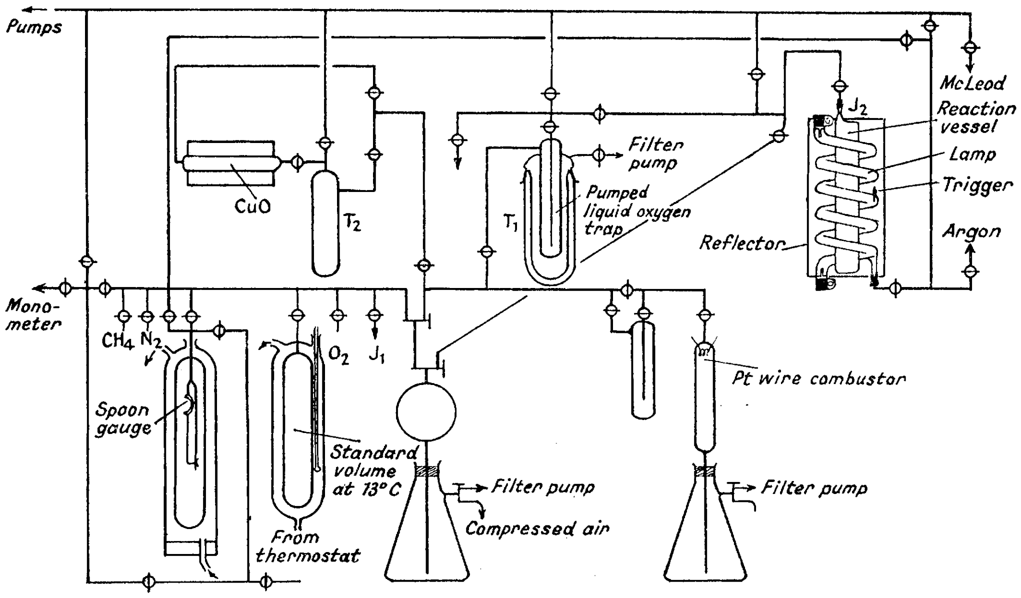
Experimental

Keten, prepared by pyrolysis of acetone (Hurd and Tallyn, *J. Amer. Chem. Soc.*, 1925, **47**, 1427), was purified by three distillations between traps at −111°, −139°, and −196°, a small fraction being collected in the middle trap. It was stored under liquid nitrogen, where it could be kept indefinitely without changing composition. Analysis, by combusion in excess of oxygen and by absorption on potassium hydroxide, indicated a purity of 98%. Nitrogen was prepared by decomposition of sodium azide, using Justi's procedure (*Ann. Physik*, 1931, **10**, 983), which gives an extremely pure product. Methane, from a cylinder, was condensed in a trap surrounded by liquid oxygen pumped down to a pressure of 10 cm. Hg where its temperature was about −198°. Most of the condensate was pumped away, and half the residue was expanded into a bulb by allowing the trap to warm. Combustion showed a purity of greater than 99% of methane. Oxygen was prepared electrolytically, dried ($CaCl_2$), passed over platinised asbestos heated to 350°, and finally again dried (P_2O_5).

The apparatus used in these experiments, consisting of the flash lamp and reaction vessel with associated gas-handling and gas-analysis equipment, is shown in Fig. 1. The flash lamp is similar in construction to that described by Porter (*loc. cit.*) except that here the metre tube is coiled around a quartz reaction vessel of 125-c.c. capacity, the whole being surrounded by a reflector coated with magnesium oxide. The tube was evacuated to 10^{-6} mm. Hg and refilled with argon to a pressure of 10 cm. Hg before each flash, and the energy from a 480 μF bank of condensers, charged to 4000 v, was used in all these experiments. A single flash has a duration of 1·5 milliseconds, during which more than 10^{20} quanta are dissipated between 2000 and 5000 Å, as determined by uranyl oxalate actinometry.

The pressures of reactant and product gases were always measured in the thermostated standard volume at a temperature of 13° by means of a spoon gauge. After the flash, the gaseous products were pumped into trap T_1, surrounded by liquid oxygen at a temperature of about $-198°$. The non-condensable gases, consisting of hydrogen, carbon monoxide, methane, and nitrogen if present, were transferred to the standard volume for pressure measurement, and then to the tube containing copper oxide at 300°. There, hydrogen and carbon monoxide were oxidised, and the resulting water and carbon dioxide condensed out in trap T_2 by liquid air, the methane and any nitrogen being returned to the standard volume for pressure measurement. Combustion in excess of oxygen showed this residue to be in fact methane (besides any nitrogen). The liquid air around trap T_2 was replaced by a dry ice–acetone mixture, and the carbon dioxide drawn off and measured. Hydrogen was calculated by difference. Trap T_1 was then allowed to warm to room temperature, and the condensables were transferred from it into the standard volume and their pressure read. Excess of keten was removed by absorption on a succession of potassium hydroxide beads and the gases were then condensed into an evacuated bulb attached to the apparatus at joint J_1 and removed to the capillary burette shown in Fig. 2.

FIG. 1. *General arrangement of photolysis and analysis apparatus.*



The residual gases were now analysed for acetylene by absorption on cuprous chloride and for ethylene and propylene together by fuming sulphuric acid, by the usual microtechnique (Farkas and Melville, " Experimental Methods in Gas Reactions," Macmillan, 1939, p. 183). The small amount of remaining gas was assumed to be ethane, since combustion analysis of the condensable mixture had shown that C_2 compounds were present almost exclusively. In the runs made in the presence of methane this residue was relatively large and a combustion analysis was made to verify that it was ethane.

In order to analyse any carbon deposited and polymer formed, a measured amount of excess of oxygen was admitted to the reaction vessel and the full heat of a Bunsen burner was played on the walls of the vessel. This was found to oxidise the deposit completely to carbon dioxide and water. By the usual separations with liquid nitrogen and with dry ice–acetone, the oxygen used and carbon dioxide produced were determined.

The analyses of the carbon deposits from individual runs, showing that slightly more oxygen was consumed than appeared in the carbon dioxide produced, led to the belief that the deposit might consist of some hydrogen-containing polymer in addition to the elementary carbon. This was confirmed by tests for water, which were positive though not, of course, suitable for quantitative estimation. The figures given for hydrogen in the solid products are calculated from the oxygen deficiency.

Combustion analyses were carried out in the usual way, a 5-fold excess of oxygen being used. Sample and oxygen pressures were measured in the standard volume, and the gas transferred to the combustion vessel where complete combustion was obtained by heating the platinum wire to redness. The gases were then removed, first *via* a liquid-air trap, and then *via* a carbon dioxide–acetone trap, and the oxygen and carbon dioxide pressures measured in the standard volume. Tests with known mixtures showed these methods of analysis to be reliable.

In view of the appreciable amount of carbon dioxide found among the products of the thermal decomposition of keten by Akeroyd (Thesis, Cambridge Univ., 1936), a test was made for this gas in our experiments. The keten was removed by an amount of water which was too small to dissolve a significant volume of carbon dioxide, and this was then determined by absorption in potassium hydroxide.

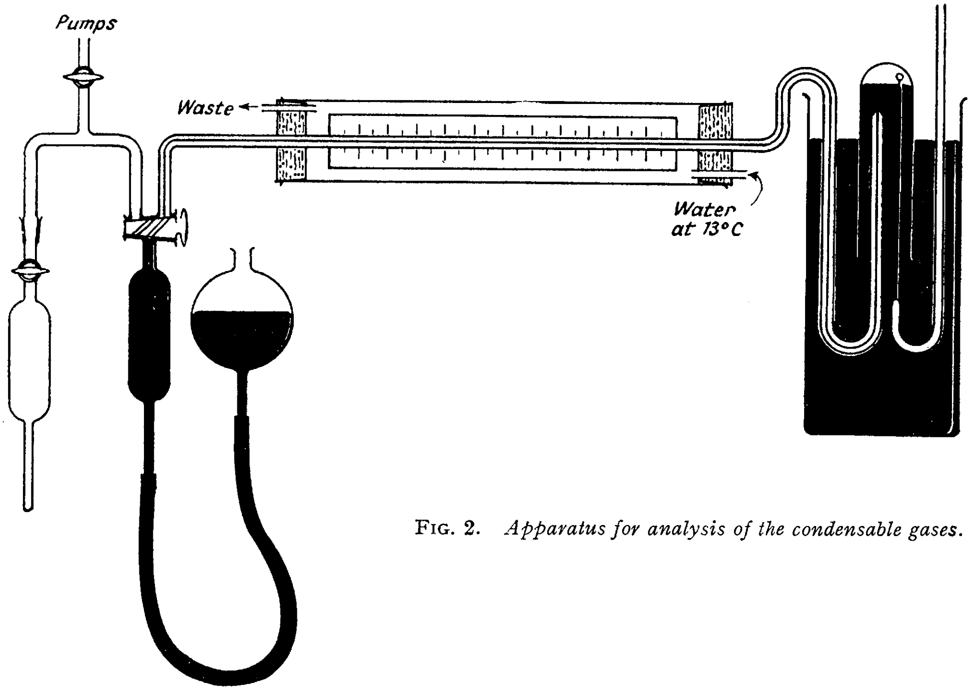


FIG. 2. *Apparatus for analysis of the condensable gases.*

RESULTS

Analysis of the gaseous products revealed the presence of methane and, at high decompositions, relatively large amounts of hydrogen. Combustion of the condensable gases showed that they consisted of C_2 hydrocarbons almost exclusively. The gaseous products were also investigated by infra-red and ultra-violet spectroscopy. Infra-red analysis indicated large amounts of acetylene in the hydrocarbon products from high-decomposition runs, as well as ethylene, but only a very small trace of propylene and no absorption by other molecules. Ultra-violet investigations showed that aromatic hydrocarbons were entirely absent, the products being investigated in a 1-m. absorption path under conditions such that less than 1% of benzene, toluene, etc., would have been easily detected. Analysis proved the absence of carbon dioxide, and combustion of the solid products showed that a small amount of hydrogen was present in addition to carbon.

Complete analyses of the products for CO, CH_4, H_2, C_2H_6, C_2H_4, C_2H_2, carbon, and hydrogen in the solid were now carried out under a variety of conditions. The reproducibility of the analyses was satisfactory, but the percentage decomposition under identical conditions showed variations which were sometimes greater than analytical errors. In particular, there was a definite trend with time, the decomposition decreasing with the age of the lamp. It was thought that this might be caused by poisoning of the gas filling and, in an attempt to improve the reproducibility, the lamp was freshly filled with gas before each run. It is now known, in the light of detailed investigations on the properties of these lamps (Christie and Porter, in course of publication), that better reproducibility is obtained by using the same gas filling, the decrease in output of the lamp being caused by reduced transparency of the quartz, mainly by deposition of the material of the electrodes. Very good reproducibility of output is obtained

TABLE 1. *Low light intensity.*

Run	51	41	30	31	32	36	38	43	45	35	34	46
P (CH_2:CO)	10·0	29·5	59·1	60·3	59·8	90·2	90·3	90·5	180·3	60·0	60·0	60·0
P (N_2)	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	0·0	29·9	60·6	297·2
Decompn., %	39·6	64·4	61·8	58·4	58·6	24·0	24·6	27·2	6·0	41·1	27·6	7·5
Pressures of gaseous products :												
P (CO)	4·0	19·0	36·5	35·2	35·0	21·6	22·2	24·7	10·7	24·7	16·6	4·5
P (H_2)	0·9	7·9	19·1	13·3	16·3	3·6	2·3	2·8	0·0	3·8	0·9	—
P (CH_4)	0·0	1·3	2·4	3·8	2·8	2·1	3·0	3·0	0·0	2·1	0·0	0·0
P (C_2H_2)	0·45	7·2	10·4	5·6	6·2	1·5	6·4	2·1	0·1	2·4	1·1	0·2
P (C_2H_4)	0·70			2·4	2·0	4·1		4·9	3·7	4·0	4·1	1·5
P (C_2H_6)	0·17			0·5	0·7	0·9		0·6	0·3	1·3	1·3	0·4
Solid :												
P (C_2)	*	small	large	large	5·5	1·6	1·1	1·5	*	1·4	0·4	*
P (H_2)	—	—	—	—	0·8	0·4	0·0	0·0	—	0·8	0·2	—
Balances :												
C_2	3·3	—	—	—	33·3	20·0	19·0	23·0	9·5	22·5	15·2	4·4
H_2	3·3	—	—	—	34·3	20·6	—	22·5	7·4	21·8	14·3	4·4
Gaseous products, %												
CO	63·6	53·7	53·1	57·9	54·9	63·2	65·5	64·8	72·2	63·3	67·7	61·5
H_2	15·2	22·3	27·8	21·8	26·7	11·5	6·8	7·4	0·0	11·6	5·4	—
CH_4	0·0	3·7	4·1	6·3	4·3	6·0	8·9	7·9	0·0	5·3	0·0	0·0
C_2H_2	7·3	20·3	15·1	9·2	9·8	4·4	18·9	5·4	0·8	6·3	4·6	2·6
C_2H_4	11·2			4·0	3·2	12·1		12·9	24·8	10·1	16·9	20·5
C_2H_6	2·7			0·9	1·1	2·7		1·5	2·3	3·4	5·4	5·1

* Invisible.

TABLE 2. *High light intensity.*

Run	52	53	54	58	56	59	57	55
P (CH_2:CO)	60·2	60·6	10·0	10·0	10·4	10·0	10·2	10·5
P (N_2)	0	0	0	0	20·5	19·6	83·4	320·3
Decompn., %	90·7	91·0	94·3	90·6	92·7	92·5	88·9	82·1
Pressure of gaseous products :								
P (CO)	54·6	55·1	9·4	9·0	9·6	9·2	9·0	8·7
P (H_2)	35·5	37·3	5·3	5·1	4·5	5·1	2·4	0·2
P (CH_4)	0·6	0·2	0·2	0·0	0·0	0·0	0·4	0·4
P (C_2H_2)	13·9	13·7	3·6	3·4	4·7	4·0	1·9	1·1
P (C_2H_4)	0·2	0·4	0·04	0·08	0·2	0·2	0·9	1·8
P (C_2H_6)	0·6	0·4	0·15	0·15	0·4	0·3	0·4	0·6
Solid :								
P (C_2)	large	9·2	small	0·5	small	0·5	invisible	invisible
P (H_2)	—	1·4	—	0·0	—	0·0	—	—
Balances :								
C_2	—	51·4	8·6	8·6	10·1	9·1	7·9	8·1
H_2	—	54·8	9·8	9·1	10·8	10·4	8·1	7·5
Gaseous products, % :								
CO	51·8	51·0	50·5	51·0	49·5	49·4	60·0	67·6
H_2	33·7	35·8	28·3	28·7	23·3	27·2	16·3	1·5
CH_4	0·6	0·2	1·0	0·0	0·0	0·0	2·5	2·9
C_2H_2	13·2	12·3	19·2	19·1	24·3	21·2	12·5	8·8
C_2H_4	0·2	0·3	0·2	0·4	1·0	0·8	6·3	14·7
C_2H_6	0·6	0·3	0·8	0·8	1·9	1·3	2·5	4·4

if the energy per flash is slightly reduced, to about 3000 joules per flash, and the same gas filling is used throughout. The variation in decomposition between similar runs is not more than a few units %, however, which is not serious for the present purpose. The data in Table 1 are obtained with a lamp whose intensity had been considerably reduced. In Table 2 the same lamp was used after being cleansed with hydrofluoric acid, resulting in a higher intensity.

TABLE 3. *Effect of added methane at constant total pressure.*

Run	46	50	49
P ($CH_2{:}CO$)	60·0	60·8	60·2
P (CH_4)	0	120·3	300·4
P (N_2)	297·2	180·9	0
Decompn., %	7·5	7·4	10·6
Products :			
P (CO)	4·5	4·5	6·4
P (H_2)	0·8	0·0	0·0
P (CH_4)	0·0	115·2	292·7
P (C_2H_2)	0·2	0·13	0·1
P (C_2H_4)	1·5	1·43	2·1
P (C_2H_6)	0·4	1·45	4·4

The details of the analysis of the products of decomposition are given in Tables 1 and 2 for the low- and high-intensity lamps respectively, and in each case the effect of keten pressure and of the addition of nitrogen are studied. In Table 3 the effect of added methane is given, the total pressure $P(CH_4 + N_2)$ being constant. The balances C_2 and H_2 are the sum of carbon and hydrogen in the products, and are to be compared with the pressure of carbon monoxide produced representing the keten decomposed. Keten polymer, formed as solid, was negligible, as shown in the combustion analyses and also by the agreement found between keten removed and carbon monoxide produced. The balances show that no other major products were present.

All pressures in Tables 1, 2, and 3 are expressed in mm. of mercury in the reaction volume of 125 c.c. and at 13°.

In view of the interest in the mechanism by which carbon is formed in this reaction, the structure of the deposit was investigated with the aid of an electron microscope. The carbon particles were found to be fairly uniform in size, the average dimensions being about 500 Å, though most of them form agglomerations of large size. A few of the smaller particles showed definite diffraction patterns characteristic of graphitic structure and the whole deposit closely resembled those obtained from smoky acetylene flames.

Determination of Quantum Yield.—The effect of nitrogen in reducing the total decomposition under otherwise identical conditions suggests that, in the absence of nitrogen, the quantum yield must be in excess of the value found under ordinary conditions, which is of the order of unity.

The measurement of quantum yields in a flash decomposition such as this presents several new problems, but recent work by Christie and Porter (in course of publication) has shown that the methods of uranyl oxalate actinometry are applicable to the high intensities obtained with the flash discharge and that the quantum yield is unchanged. This makes possible the determination of the quantum yield of keten decomposition at high intensity, but the usual technique, of measuring the reduction in oxalate decomposition when a second cell containing the keten is interposed between the oxalate and the lamp, is unsuitable, owing to the fact that it involves the measurement of a small difference in two small decompositions. The method used, though more involved, is capable of greater accuracy. The quantity determined is the number of keten molecules decomposed divided by the total number of quanta absorbed in the region between 2000 and 4000 Å, it being impossible to obtain the high decomposition required by using a smaller wave-length range.

It was necessary to use a different optical arrangement, which gave an approximately parallel beam of light, for these experiments. The flash lamp was of the same dimensions as before but was in the shape of a conical helix surrounded by a paraboloidal reflector. The reaction vessel, through which the parallel light passed, was cylindrical, 2 cm. long and 7 cm. in diameter, and had quartz windows. Measurements of the percentage decomposition of 0·005M-oxalate in this cell were made, and then without changing the position, the decomposition of keten at 30 mm. pressure produced by a flash of the same energy was also measured. The extinction coefficients of keten under these conditions were measured between 2000 and

4000 Å by means of a Beckman spectrophotometer and are given in Fig. 3, since quantitative measurements for the gas do not appear in the literature. The energy distribution of the flash discharge between these wave-lengths, which is also required in the calculation, has been measured and is given elsewhere along with further details of the methods of actinometry (Christie and Porter, *loc. cit.*).

The results obtained, for two similar determinations with 30 mm. pressure of keten were : (1) oxalate decomposed = 5·30%, keten decomposed = 18·7%, ϕ_k = 6·8; (2) oxalate decomposed = 5·38%, keten decomposed = 17·6%, ϕ_k = 6·3.

No allowance is made for the change in absorption caused by the decomposition of keten; this and most other errors of the method are such as to make the above values of the quantum yield a minimum. It is therefore established that, even when the decomposition is only 18%, the quantum yield is over 6, and we should expect that if higher decompositions could be obtained in this sytem even higher values of ϕ would be found.

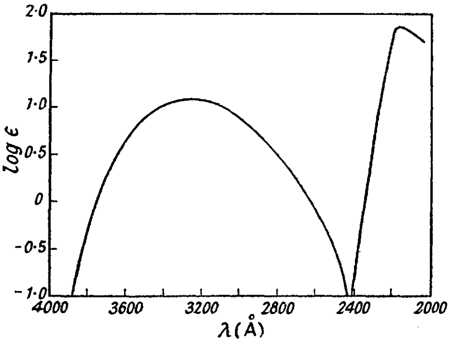


FIG. 3. *Extinction curve of keten gas : ε = decadic molar extinction coefficient (l. mole^{-1} cm.$^{-1}$).*

DISCUSSION

The photolysis of keten at normal intensities has been shown to proceed by the following mechanism (Norrish, Crone, and Saltmarsh, *J.*, 1933, 1533; *J. Amer. Chem. Soc.*, 1934, **56**, 1644; Ross and Kistiakowsky, *ibid.*, p. 1112; Vanpee and Grard, *Ann. Mines Belg.*, 1950, **49**, 37; Kistiakowsky and Rosenberg, *J. Amer. Chem. Soc.*, 1950, **72**, 321) :

$$CH_2{:}CO + h\nu = CH_2 + CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

$$2CH_2 = C_2H_4 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

$$CH_2 + CH_2{:}CO = C_2H_4 + CO \quad . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

It seems that the relative importance of reactions (2) and (3) depends on concentration, as might be expected, and, although the recent work quoted above supports reaction (3), the results of mirror experiments indicate that this reaction is accompanied by a considerable activation energy or steric factor (Pearson, Purcell, and Saigh, *J.*, 1938, 409; Norrish and Porter, *Discuss. Faraday Soc.*, 1947, **2**, 97).

Unless very high intensities are used, the effect of intensity on this reaction will simply be to alter the quantum yield, owing to competing reactions (2) and (3), but otherwise the mechanism and products remain unchanged. At very high intensities, such as those used in this investigation, several new possibilities arise.

(1) The concentration of intermediates may become comparable with that of the stable reactants or products. In the case of keten this is only an extreme case of the concentration effect considered above and cannot, by itself, produce any other effect than a reduction in the quantum yield if reactions (1), (2), and (3) only are considered.

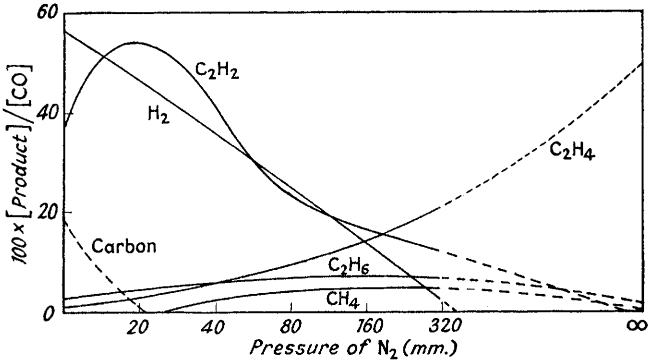
(2) The primary act may be changed by the simultaneous absorption of more than one quantum by the same molecule. The probability of this happening under the present experimental conditions is about 10^{-5} if each molecule absorbs, on an average, one quantum per flash. This is too small to make a significant contribution.

(3) Adiabatic reaction : the calculated time taken for the centre of a reaction vessel, 2 cm. in diameter and filled with nitrogen at 1 mm. pressure, to begin cooling is 0·3 millisec.,

and proportionately longer at higher pressures. As the duration of the flash is 1·5 millisec., the process will proceed nearly adiabatically for pressures greater than 10 mm. of mercury.

A cursory examination of the results in Tables 1, 2, and 3 suggests that the adiabatic effect, resulting in a rise in the temperature of the system, is playing a very important part. There are two ways in which the addition of an inert gas affects the kinetics of an ordinary photochemical reaction; first, it may act as a third body to facilitate recombination of atoms and radicals, and secondly, it may prevent diffusion of these bodies to the wall. These effects are insufficient in themselves to explain any of the observed phenomena, and a third effect, the increased thermal capacity of the system, must be invoked before it is possible to account for the effect of nitrogen in decreasing the quantum yield and restoring the products to those obtained at low intensity. The products are entirely as would be expected if a large temperature rise accompanies photolysis. The thermal decomposition of ethylene is known to give mainly acetylene and hydrogen as products, which is in accordance with our analysis at low nitrogen concentrations. The products from the runs 54—59, which were all carried out under the same conditions apart from the pressure of nitrogen, are plotted in Fig. 4 as a function of the nitrogen pressure, the concentrations being expressed as percentages of the carbon monoxide formed, which is equal to the keten decomposed. Although the percentage decomposition is nearly 90 in each case, the products show a gradual transition from ethylene to its pyrolysis products as the nitrogen is decreased. An extrapolation to " infinite " nitrogen concentration, corresponding to zero temperature rise, will be expected to lead to the normal products of isothermal photolysis, as indicated. Similarly, at lower light intensity, comparison of the products in runs 30, 31, 32, 35, 34, and 46 shows the same effect and, in addition, a marked decrease in the amount of decomposition as the nitrogen is increased. If the reaction at high nitrogen dilution is to be identified with the normal photolysis, this implies that the quantum yield is greatly increased as the nitrogen is reduced and even if, in run 46, conditions are such that the " normal " quantum yield of unity is reached, in runs 30, 31, and 32 the quantum yield must be about 9.

FIG. 4. *Products of photolysis of keten (expressed as percentage of carbon monoxide) as a function of nitrogen pressure. Original keten pressure* = 10 *mm.* Hg.



The energy which is liberated as heat in a photochemical reaction arises in three ways : (1) Excess energy of the dissociation products; (2) degraded electronic energy; (3) heat of reaction of intermediates formed in the primary act. Too many values are uncertain, and too little is known about the mechanism at higher temperatures, to make an accurate estimate of the total heat liberated, but, for the purpose of discussion, a total figure of 100 kcal./g.-mol. of keten decomposed is probably of the right order. The resulting temperature rises, calculated for the series in Table 1, are as follows, it having been assumed that the decomposition at the highest dilution represents the true primary photochemical decomposition :

Run	30, 31, 32	35	34	46
Maximum temp.	800°	650°	500°	200°

In experiments such as 54 and 58, the effective specific heat is no longer that of nitrogen or keten, but is determined by the degree of dissociation. The temperature must be greatly in excess of that reached in the above experiments and is probably comparable with the temperature of hydrocarbon flames.

Studies of the pyrolysis of keten have been complicated by the rapid polymerisation to diketen and it is likely that, in the work of Akeroyd (*loc. cit.*) and Williamson (*J. Amer. Chem. Soc.*, 1934, **56**, 2216), who found respectively carbon dioxide and allene, and methane, as major products, the pyrolysis of diketen played an important part (Hurd and Williams, *ibid.*, 1936, **58**, 962). The nearest approach to our conditions was obtained by Muller and Peytral (*Compt. rend.*, 1933, **196**, 279) who pyrolysed keten in a flow system at 115°, in a platinum tube 2 mm. in diameter, the contact time being 2—3 millisec. They found as products : C_2H_4 21·8, C_2H_2 2·7, CO 63·9, CH_4 9·1, and H_2 2·5% as well as some carbon and polymer. Except for the absence of ethane, these are the same products as found by us.

We conclude, therefore, that comparisons with work on the thermal decomposition of keten under similar conditions, approximate estimations of the temperature rise, the nature of the products formed, the quantum-yield determinations and the effect of intensity, pressure, and especially the addition of inert gas, are all in accord with our explanation of the high-intensity reaction in terms of adiabatic heating. A more detailed consideration of the individual experiments, although it cannot lead to a complete elucidation of a mechanism as complex as this, shows that the main scheme of reactions may be represented as follows :

(*a*) Some radical disproportionation at relatively low temperatures, *e.g.*,

$$2CH_2 = CH_3 + CH \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

followed by formation of small amounts of ethane and acetylene by recombination, and of methane by

$$CH_3 + C_2H_4 = CH_4 + C_2H_3, \text{ etc.} \quad . \ . \ . \ . \ . \ . \ . \quad (5)$$

(*b*) Radical-chain decomposition of keten, probably by

$$CH_3 + CH_2{:}CO = C_2H_5 + CO \quad . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

$$C_2H_5 = C_2H_4 + H \quad . \ . \ . \ . \ . \ . \ . \ . \quad (7)$$

$$H + CH_2{:}CO = CH_3 + CO \quad . \ . \ . \ . \ . \ . \ . \ . \quad (8)$$

giving quantum yields increasing with temperature, the activation energy of reaction (7) being 43 kcal. (Steacie, " Atomic and Free Radical Reactions," Reinhold, 1946, p. 96).

(*c*) Removal of methane by

$$CH_2 + CH_4 = C_2H_6 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (9)$$

(*d*) Dehydrogenation of hydrocarbons by Rice–Herzfeld mechanisms :

$$C_2H_6 + H = C_2H_5 + H_2 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (10)$$

$$C_2H_5 = C_2H_4 + H \quad . \ . \ . \ . \ . \ . \ . \ . \quad (11)$$

$$C_2H_4 + H = C_2H_3 + H_2 \quad . \ . \ . \ . \ . \ . \ . \ . \quad (12)$$

$$C_2H_3 = C_2H_2 + H \quad . \ . \ . \ . \ . \ . \ . \ . \quad (13)$$

(*e*) Decomposition of acetylene to carbon and hydrogen.

At higher temperatures the dehydrogenations may proceed directly without the radical chain, but, unless our temperature estimations are greatly in error, a radical-chain mechanism is necessary to explain the observed rate at lower temperatures.

The Mechanism of Carbon Formation.—Although many of the individual reactions given are better studied in other ways, the mechanism of carbon formation in the homogeneous gas phase is a problem which is inevitably associated with a complex set of experimental conditions, and the production of carbon by flash photolysis is a relatively simple one. It has the great advantage that the system may be heated homogeneously to a very high temperature, comparable with that obtained in flames, and then quenched rapidly to room temperature. The products found, after heating to different temperatures, are therefore a valuable guide to the overall mechanism by which solid carbon is formed, and the system is entirely free from the heterogeneous complication introduced when the gas is heated by the wall of the vessel.

If solid carbon is formed, it is clear that polymerisation must occur at some stage, and most recent theories have been based on the postulate that the hydrocarbon first polymerises to large molecules, probably mainly aromatic ones, which are subsequently dehydrogenated. The analyses of the products in this work are quite contary to this theory. As the decomposition is increased and, consequently, a higher temperature attained, the products show a definite transition from ethane, *via* ethylene and acetylene, to solid carbon without the intermediate formation of any detectable amount of higher hydrocarbons. It is true that analyses of the solid always show some hydrogen present, but this is probably explained as polymerisation occurring at, or near to, the relatively cold wall. In all cases where this hydrogen could be estimated accurately, it was less than 1% of the total products and much less than the carbon or acetylene present. The important point is that, in spite of the rapid quenching, which results in the retention of an appreciable amount of all the intermediate products and keten, even when large amounts of carbon are formed, the amount of higher hydrocarbons formed is so small as to be undetectable in the gas phase. The experimental evidence supporting this statement is as follows :

(1) The carbon and hydrogen balances, especially at the higher decomposition when more accurate analyses were possible, show that the amount of hydrocarbons higher than C_2 must be very small.

(2) Combustion analyses on the hydrocarbon fractions corresponded to C_2 hydrocarbons to within 5%.

(3) Infra-red analysis of the products showed a just detectable amount of propylene present, corresponding to a very small fraction of the ethylene and acetylene.

(4) Ultra-violet spectroscopic examination of the products of many experiments showed aromatic hydrocarbons such as benzene, toluene, and naphthalene to be absent, the sensitivity of the test being such that less than 0·1 mm. would have been detectable.

In addition to this evidence, the analyses in runs (*e.g.*, 31, 32, 52, 53) where a large amount of carbon is formed show that nearly all the remaining hydrocarbon present is acetylene. This is also shown clearly in Fig. 4, where, although acetylene only is present in significant amounts at low nitrogen pressures, the carbon formation has just begun, with a consequent decrease in acetylene concentration. There can therefore be no doubt that acetylene is an essential intermediate in carbon formation from the more saturated hydrocarbons.

The detail of the last stage (*e*) of carbon formation from acetylene was avoided in the above reaction scheme, but we can now say, in view of these considerations, that it does not involve the formation of a *stable* higher hydrocarbon polymer. Two possibilities remain :

(1) Chain dehydrogenation of acetylene to C_2 radicals by the process

$$H + C_2H_2 = C_2H + H_2 \qquad (14)$$

$$C_2H = C_2 + H \qquad (15)$$

or perhaps direct thermal decomposition of acetylene to C_2 and hydrogen, followed in either case by polymerisation of C_2 radicals.

(2) A simultaneous polymerisation and dehydrogenation. This subject will be developed elsewhere in connection with other work on the reactions of acetylene and the chemistry of C_2. It is significant that the particle size in these experiments is within the range found in flames, and the high temperature and radical concentration, as well as the rate of the overall reaction, are very similar in the two cases. It seems probable that the reactions leading to carbon formation are not very different from those occuring in flames, the oxygen playing the same part as a free radical in the initial steps.

The Spectrum of Methylene.—As a result of the investigations reported here it became clear that, at high decompositions, the methylene-radical concentration would be low owing to the high temperature and consequent high reaction rate. In the light of this information, further attempts to obtain its absorption spectrum have been made recently, the temperature rise being reduced by excess of nitrogen or carbon dioxide. If the lifetime of methylene under the conditions of the experiment was comparable with the duration of the flash, a concentration, estimated from the amount of decomposition, of several mm. of methylene would have been obtained. Nearly all the commonly occurring free-radical spectra have now been obtained by the method of flash spectroscopy (Porter, *loc. cit.*), and it is fairly certain that if methylene had a discrete absorption, corresponding to a fully allowed electronic transition, in the region between 2300 and 5000 Å it would have been detected with a methylene pressure of considerably less than 1 mm., the absorption path being 1 m. in length. In view of the long life of methylene found in mirror experiments in the presence of keten, it appears that methylene has no allowed transition to a stable electronic state in this region or, alternatively, that its association to ethylene occurs bimolecularly without the necessity of a third body and with a collision yield greater than 10^{-3}.

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