where K is the dissociation constant at temperature t, and $K_{\max.}$ is the maximum value of the dissociation constant at the temperature Θ. P has the same value (5×10^{-5}) for most of the acids studied. For the first dissociation constant of phosphoric acid equation (7) becomes

$$\log K_1 + 2.0304 = -5 \times 10^{-5}(t + 18)^2 \qquad (8)$$

The values of pK_1, calculated from this relation, agree very well with those determined experimentally, as can be seen from the data in Table II. From equation (5) it follows that the corresponding heat of ionization expressed in calories is

$$\Delta H = -4.58 \times 10^{-4}T^2\,(T - 255.1) \qquad (9)$$

where T is the temperature in degrees absolute.

Lugg[8] (see also Sherrill and Noyes[9] and Abbott and Bray[2]) has recalculated earlier conductance data in accordance with modern theory and has estimated that pK_1 at 18° is 2.09, a value which agrees excellently with that of 2.096 derived from the present measurements. Jowett and Price[10] report that pK_1 at 37.5° is 2.188 in agreement with the value of 2.185 given here.

TABLE II

THE CONSTANTS USED IN THE CALCULATIONS AND THE RESULTS

t°C.	A	E_0[13]	pK_1 (obs.)	pK_1 (calcd.)
0.3	0.487	0.23618	2.048	2.0472
12.5	.496	.22993	2.076	2.0769
25	.506	.22239	2.124	2.1229
37.5	.519	.21383	2.185	2.1844
50	.534	.20436	2.260	2.2616

Summary

1. The first dissociation constant of phosphoric acid has been determined over the temperature range of 0 to 50°.

2. The variation of the dissociation constant with the temperature conforms closely to the empirical equation proposed by Harned and Embree[11] for the dissociation of weak acids and bases.

3. The heat of ionization for the first step in the ionization of phosphoric acid is given as a function of the temperature.

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[13] Harned and Ehlers, THIS JOURNAL, **55**, 2179 (1933).

NEW HAVEN, CONNECTICUT RECEIVED MARCH 1, 1934

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF HARVARD UNIVERSITY]

The Photochemical Decomposition of Ketene

BY WILLIAM F. ROSS AND G. B. KISTIAKOWSKY

A few years ago one of the present writers photographed the ultraviolet absorption spectrum of ketene ($H_2C{=}C{=}O$), described previously by Lardy,[1] under moderately high dispersion preliminary to an attempt at its analysis. The spectrum, however, was found to be continuous to its limit at 3700 Å. with 10 mm. pressure in a 2-meter tube, possessing only faint, regularly and closely spaced, maxima which hardly deserve the name of bands. A predissociation and disruption of ketene molecules was thus clearly indicated, with CO and CH_2 being the most likely products of decomposition. The present work was undertaken in order to test this supposition and, eventually, to develop a method of producing free methylene radicals.

Experimental

Ketene was prepared from acetone which had previously been refluxed with potassium permanganate and distilled from anhydrous potassium carbonate. An adaptation of previous methods[2] was used, in which acetone was refluxed over a coil of glowing platinum wire. The gaseous products passed through a trap at −50°, removing final traces of acetone, and then through two traps at −78°, in which the ketene was condensed. The system was thoroughly swept with oxygen free nitrogen before each preparation. The apparatus was made completely from glass, a paraffin–vaseline mixture being used for the several necessary stopcocks. Four or five cc. of ketene could be prepared in this manner within an hour.

This product was purified by five fractional distillations in which the more volatile and the heavier portions were discarded. Thus prepared, ketene could be kept at −78° in the presence of several mg. of hydroquinone for two weeks or more without appreciable polymerization. Small amounts of inert gas were found when analyzing both this pure ketene and the products of the light

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[1] Lardy, *J. chim. phys.*, **21**, 353 (1924).

[2] Hurd and Cochran, THIS JOURNAL, **45**, 3095 (1923).

reaction. It is believed that these gases, mostly nitrogen and some saturated hydrocarbons, were not removed during the fractionation because of their solubility in liquid ketene. They amounted at most to only 5–6% of the total gas volume, however.

A cylindrical quartz cell of 20 cc. capacity connected directly to a quartz spiral manometer of the Bodenstein type and indirectly through a stopcock to an automatic Sprengel pump was used for all runs except the quantum yield determinations to be discussed separately. This cell was immersed in a constant temperature water-bath with a window of crystal quartz. The type of mercury vapor lamp described by Forbes and Heidt[3] was employed.

The analytical portion of the apparatus was modeled after that reported by Bone and Wheeler,[4] and was set up completely of glass without rubber connections. Ketene was determined by absorption in aqueous alkaline solution; other gases in the usual manner.

For the quantum yield determinations a cylindrical quartz cell, 28 cc. in volume, attached to a constant volume mercury manometer was used. The optical system consisted of a constant pressure mercury arc and a quartz monochromator,[5] for the use of which we wish to express our indebtedness to Professor G. S. Forbes and Dr. L. J. Heidt. The absolute light sensitivity of the linear thermopile-galvanometer assembly was determined with the aid of the quinine–chromic acid reaction[5] using the technique there described. For these measurements we are greatly indebted to Mr. W. H. Avery. The slight variations in light intensity and the percentage light absorption of ketene were measured at frequent intervals during illumination. Corrections were made for light reflection on quartz–air interfaces and for the dark reaction. Pressure changes were measured with a cathetometer, all readings being taken with the cell in a liquid bath at constant temperature. During illumination the cell was in air, placed immediately behind the exit slit of the monochromator. Between experiments B and C of Table II a new galvanometer for the thermopile and a new mercury lamp were installed and the absolute energy factor was determined anew using both the uranyl oxalate and the quinine sulfate reactions as actinometers. This new factor should be more accurate than that used in experiments A and B. To make sure that the results with the 3660 Å. line were not due to stray light, a light filter for this wave length was placed behind the exit slit of the monochromator but this did not appreciably change the fraction of light absorbed.

Results.—The decomposition of ketene was found to be accompanied by pressure increase, the gaseous products being exclusively carbon monoxide and ethylene. In addition, a solid film was found to be deposited gradually on the walls during illumination. This film was quite transparent to the 3130 Å. line but absorbed considerably the 2537 line of the mercury arc.

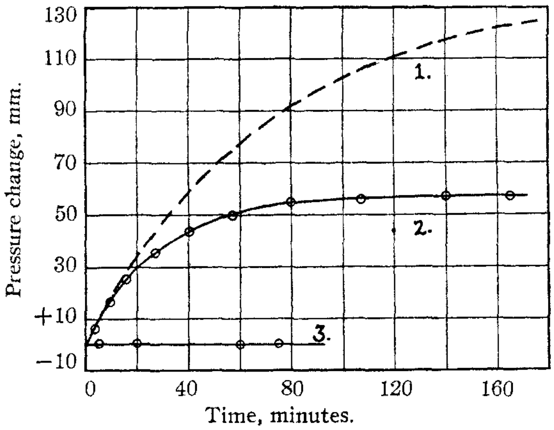

Fig. 1.—1, Hypothetical pressure change; 2, a typical run with Red-Purple Corex A filter; 3, a run with Red-Purple Ultra filter.

Using a calibrated wire screen the rate of initial pressure change was found to be proportional to the incident light intensity. The reaction behind a 3 mm. thick window plate glass or a 4.6 mm. Red-Purple Ultra filter (transmitting 90% of the 3660 Å. line but almost none of the 3130 Å.) is immeasurably slow. Behind a 4.3 mm. Red-Purple Corex A filter the rate is reduced some 40%. Figure 1 shows two typical runs, while in Table I are presented data for six experiments essential for the interpretation of the reaction mechanism. The dotted line in Fig. 1 shows the hypothetical rate of pressure change if this were proportional to the light energy absorbed by ketene. Table II presents the data of quantum yield determinations. Only the initial stages of the reaction were used here for which, as Table I shows, the ratio $P_{CO}/\Delta p$ is very nearly two. In computations of the quantum yield it was

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[3] Forbes and Heidt, THIS JOURNAL, **53**, 4349 (1931).

[4] Bone and Wheeler, *J. Soc. Chem. Ind.*, **27**, 10 (1908); Dennis, "Gas Analysis," The Macmillan Co., New York, 1929, p. 103.

[5] Forbes, Heidt and Boissonnas, THIS JOURNAL, **54**, 960 (1932).

therefore assumed that for each mm. pressure change two mm. of ketene was decomposed.

TABLE I

ANALYSIS OF REACTION PRODUCTS

All pressures in mm. mercury

No.	1	2	3	4	5	6
Temp., °C.	4.3	5.3	4.7	90.0	5.3	3.9
$P_{C_2H_2O}$ initial	301.3	272.7	312.3	289.2	108.3?	45.6
$P_{C_2H_4}$ initial	0	0	0	0	204.2	284.5
Time of illumination, min.	77	205	15.5	15.5	120	118
Δp	64.1	57.1	19.7	17.3	−0.4	−4.7
P_{CO} final	198.7	194.3	42.0	45.2	54.4	38.5[a]
$P_{C_2H_4}$ final	63.1	59.5	21.8	20.7	194.0	
$P_{C_2H_2O}$ final	103.1	76.1	268.2	240.7	53.8	
$P_{CO}/\Delta p$	3.15	3.27	1.93	2.18		

[a] This determination made by freezing out with liquid air.

TABLE II

QUANTUM YIELD DETERMINATIONS

Experiment number	A				B				
Wave length, Å.		3130		3130	3130		3130		3660
Condition	Dark	Light	Dark	Light	Light	Dark	Light	Dark	Light
Time, min.	120	125	145	88	120	95	103	68	121
Initial pressure of ketene, mm., 20°	348				375				
Pressure change	−1.61	+6.39	−1.74	+3.81	+4.83	−2.07	+4.65	−1.89	−0.48
Corrected light reaction, mm./min.		+0.064		+0.056	+0.065		+0.070		+0.021
Fraction of light absorbed		0.60		0.60	0.65		0.65		0.24
Einsteins absorbed per minute × 10^7		1.73		1.73	1.86		1.86		1.58
Quantum yield		1.17		1.03	1.11		1.19		0.42

Experiment number	C					D		
Wave length, Å.		3130		3130			3660	
Condition	Dark	Light	Dark	Light	Dark	Dark	Light	Dark
Time, min.	77	120	70	142	104	165	150	80
Initial pressure of ketene, mm., 20°	363					316		
Pressure change	−0.74	+3.71	−0.54	+4.31	−0.68	−1.33	−0.15	−0.58
Corrected light reaction, mm./min.		+0.039		+0.038			+ .007	
Fraction of light absorbed		.46		0.46			.23	
Einsteins absorbed per minute × 10^7		1.25		1.25			.99	
Quantum yield		0.97		0.98			.21	

Interpretation of the Results.—The following facts stand out clearly in the data presented above: when only ketene is present in the illuminated zone the reaction yields quantitatively carbon monoxide and ethylene in the theoretical ratio; the quantum yield in the light of 3130 Å. is very near unity. The reaction, as measured by pressure increase, stops before all of the ketene has been consumed. This, as the experiments with added ethylene clearly show, is due to the presence of this gas. In the later stages of the reaction a solid polymer is formed which must have the composition $(CH_2)_n$, since all of the original ketene is accounted for either as free carbon monoxide or as undecomposed ketene (see Table I) and since no hydrogen has ever been found among the products and no deposits of free carbon have been observed. Although the polymerization involves stoichiometrically only ethylene, it is directly due to the decomposition of ketene, since runs with ethylene alone showed no measurable polymerization, as was to be expected since our arc was run hot.[6]

The primary reaction upon absorption of light energy is undoubtedly

$$H_2C{=}CO \longrightarrow H_2C + CO$$

occurring through a "predissociation" mechanism without the agency of collisions. In this respect ketene behaves analogously to many aldehydes[7] which also yield carbon monoxide on illumination. The difference is that in aldehyde molecules the process consists of the breaking of a single carbon–carbon bond with an accompanying transfer of a hydrogen atom, while in ketene a double carbon bond must be broken. The energy of quanta in the spectral region investigated ($\geqq$80 Cal.) is not sufficient for the latter step so additional energy must be derived from the "resonance" energy of

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(6) Olson and Meyers, THIS JOURNAL, **48**, 389 (1926).

(7) Norrish and Kirkbride, *J. Chem. Soc.*, **135**, 1529 (1932); also forthcoming paper by John A. Leermakers.

carbon monoxide formed in the decomposition.[8] This description of the primary process is essentially the same as suggested very recently by Norrish and his collaborators.[9] In the interpretation of secondary reactions we must, however, disagree with them. The quantum yield with the 3130 Å. line being unity, the reaction

$$H_2C{=}CO + CH_2 = \longrightarrow CO + C_2H_4$$

cannot occur to any significant extent. It requires probably a considerable activation energy, so the methylene radicals must react with each other to form ethylene. The latter reaction predominates even at 90°, since the rate of carbon monoxide formation is increased by only a few per cent. over the temperature range 5 to 90°.

The slowing down and, finally, the complete discontinuance of pressure increase is to be attributed to the reaction of methylene groups with ethylene, the ultimate product being the solid polymer. The exact mechanism of this reaction cannot be decided now, but it appears that ethylene is required only in the initial stages of the polymerization and that later more methylene radicals are added to the intermediate product, which is probably formed by the reaction of methylene radicals with one ethylene. This is substantiated by the observation (Expts. 5 and 6, Table I) that altering the ratio of concentrations of methylene[10] to ethylene more than three-fold results in only a slightly increased ethylene consumption.

The value of the quantum yield in light of 3660 Å. wave length (Table II) is admittedly not very accurate on account of the slowness of the light reaction as compared with the dark rate. There is no doubt, however, that the quantum yield is here less than unity since the total light energy absorbed with this wave length is nearly the same as with the 3130 Å. line, but the light reaction is very slow, barely distinguishable from the dark reaction. Quite in agreement with this is also the almost complete absence of observed reaction with the Red-Purple Ultra Filter mentioned previously.

The most plausible explanation of the decreasing quantum yield is that at longer wave lengths, near the end of the absorption spectrum where the banded structure is more pronounced, predissociation becomes less probable. Then, at least some of the molecules lose their energy before decomposition, probably by collision, since no fluorescence was noticeable in ketene vapor.

The photochemical decomposition of ketene presents a very convenient method of producing free methylene radicals and opens up the possibility for a study of their chemical reactions. As the present work shows they appear to differ from methyl radicals in one respect at least: they combine readily in a bimolecular reaction to form ethylene although almost all work on free methyl has shown that no ethane is formed even under conditions very similar to those described here. Further work is planned on this aspect of the investigation.

Summary

1. The decomposition of ketene proceeds with wave lengths below 3700 Å., yielding carbon monoxide and ethylene.

2. The quantum yield is near unity at 3130 Å., which, together with the diffuse structure of the spectrum, suggests that the primary reaction is a decomposition into carbon monoxide and free methylene, the latter combining to form ethylene.

3 In the presence of ethylene there occurs a polymerization of methylene groups with the formation of a solid polymer.

4. Near the long wave length end of the absorption spectrum the quantum yield falls off.

CAMBRIDGE, MASSACHUSETTS RECEIVED MARCH 5, 1934

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[8] Pauling, *J. Chem. Phys.*, **1**, 608 (1933).

[9] Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

[10] This is almost proportional to the ketene concentration when light absorption is slight, and methylene reacts chiefly with ethylene as in the case of Expts. 5 and 6.