[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

Photochemical Studies. XLIX. Ketene and Ketene–Oxygen Mixtures[1]

BY ALEXANDER N. STRACHAN AND W. ALBERT NOYES, JR.

RECEIVED JANUARY 28, 1954

Quantum yields of ethylene and of carbon monoxide formation have been determined in pure ketene at three wave lengths: 2654, 3130 and 3660 Å. Approximately two molecules of carbon monoxide and one of ethylene are formed per quantum at 2654 Å. At 3660 Å. the quantum yields are pressure dependent. The yield of ethylene is always somewhat less than one-half of the yield of carbon monoxide. The addition of small amounts of oxygen reduces the ethylene yield to about two-thirds of the oxygen free value at 2654 and at 3130 Å., but the resultant ethylene yield is independent of oxygen pressure. At 3660 Å. oxygen reduces ethylene formation to about 25% of the oxygen-free value. Carbon dioxide and formaldehyde together with small amounts of acetaldehyde are also formed when oxygen is present. It is possible to suggest two mechanisms which agree with the main facts and to obtain relative rate constants for some of the steps.

The photochemical decomposition of ketene seems to have been investigated first by Norrish, Crone and Saltmarsh.[2] These authors showed that carbon monoxide and ethylene are produced in an approximate ratio of 2:1 and postulated that ethylene is formed by the reaction of methylene radicals with ketene rather than by association of these radicals. This mechanism was at one time disputed[3,4] but appears to be confirmed by recent evidence.[5–8] Further work by Kistiakowsky and his co-workers[5,8] has shown that the ratio of carbon monoxide to ethylene is always somewhat greater than 2:1 and that methylene radicals react with ethylene and with carbon monoxide to form propylene and ketene, respectively. They showed, moreover, that quantum yields increase with decreasing wave length.

The absorption spectrum of ketene[2,9] has a long wave limit between 3700 and 3900 Å. Toward the long wave limit there appear to be bands which may be of the predissociation type but which show no evidence of rotational structure.

A study of the reactions of methylene radicals with oxygen should have considerable interest both in providing rate constants for some of their reactions and possible clues as to their states. It became evident as soon as the present work was started that several aspects of the photochemistry of pure ketene needed elucidation before the behavior with oxygen could be understood. Knowledge of the variations of quantum yields with wave length and with pressure seemed to be essential.

Experimental

Ketene was prepared by pyrolysis of acetone by the method of Williams and Hurd.[10] The crude material was distilled at atmospheric pressure in a Podbielniak low temperature distilling column. The middle fraction, which boiled within ±0.1°, was collected and redistilled, the middle fraction being collected and used. The thermocouple was calibrated by distilling propylene (b.p. 47.7°). Ketene was found to boil at −50°. This boiling point is lower than the previously recorded value (−41°).[11] The ketene was stored at the temperature of liquid nitrogen to prevent slow polymerization. All but 0.06% was absorbed by acetic acid and of the remainder all but 0.01% was absorbed by potassium hydroxide. Thus the ketene was at least 99.9% pure.

Ethylene was a Matheson product stated to be 99.5% pure. Non-condensables were removed at −196°. Carbon dioxide (Ohio Chemical Company) was degassed at −196° and distilled from a bath at −110°. It was absorbed completely by potassium hydroxide. Water was distilled from alkaline permanganate, degassed at −78°, and subjected to low pressure distillation, the middle third being retained. Glacial acetic acid (C.P.) was degassed at −78° and vacuum distilled, the middle third being retained. The purification of diethyl ketone has been described.[12] Oxygen was prepared by heating C.P. solid potassium permanganate and dried by passage through a trap immersed in liquid nitrogen. Reaction with heated copper indicated better than 99.9% purity.

Hanovia Type S100 and General Electric Company Type AH-6 lamps were used. A fairly parallel and uniform beam was achieved by use of a quartz lens of 10 cm. focal length and a stop. The intensity was varied by neutral density filters.[13]

The following color filter combinations were used: (1) Corning glasses 9863 (3 mm.) and 7380 (2 mm.). Transmission from about 3400 to about 4300 Å. with a maximum at 3750 Å.; (2) Corning glass 5840 (3 mm.) and diphenylbutadiene (1.06 mg. in 100 ml. diethyl ether) (4 cm.). Transmission from about 3500 to about 4100 with a maximum at 3700 Å.; (3) Soda glass, short wave limit about 3100 Å.; (4) Pyrex glass, short wave limit about 2800 Å.; (5) Corning glass 9863 (3 mm.), $NiSO_4 \cdot 6H_2O$ (500 g./l. in water) (3 cm.), 2,7-dimethyl-3,6-diazocyclohepta-1,6-diene iodide (100 g./l.) (2 cm.). Transmission from about 2450 to about 2950 Å. with a maximum at 2700 Å. (6) Corning glass 9863 (3 mm.), chlorine gas (300 mm. pressure) (10 cm.). Transmission from about 2200 to about 2950 Å. There is also a slight transmission from about 3700 to about 4200 Å. with a maximum about 3960 Å. The characteristics of most of these filters have been described by Kasha.[14]

A cylindrical quartz cell with plane windows, 20 cm. in length, 2.2 cm. in internal diameter and volume 76 ml. was used. The combined volume of the cell, stirrer and connecting tubing was 218 ml. The light beam filled the cell. Mercury cut-offs were used exclusively and there were no stopcocks in the apparatus. The apparatus was generally of the conventional type used in this Laboratory except for a combined McLeod gage–Toepler pump.

The combined McLeod gage and Toepler pump is shown schematically in Fig. 1. An analysis for a mixture of nitro-

---

[1] This work was supported in part by contract between the Office of Naval Research, United States Navy, and the Department of Chemistry, University of Rochester. The authors wish to express their appreciation to Mr. R. C. Wilkerson, Celanese Corporation of America, Clarkwood, Texas, for performing mass spectrographic analyses.

[2] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *J. Chem. Soc.*, 1533 (1933).

[3] W. F. Ross and G. B. Kistiakowsky, THIS JOURNAL, **56**, 1112 (1934).

[4] R. G. W. Norrish, H. G. Crone and O. D. Saltmarsh, *ibid.*, **56**, 1644 (1934).

[5] G. B. Kistiakowsky and N. W. Rosenberg, *ibid.*, **72**, 321 (1950).

[6] M. Vanpee and F. Grard, *Ann. Min. Belg.*, **49**, 701 (1950).

[7] M. Vanpee and F. Grard, *Bull. soc. chim. Belg.*, **60**, 208 (1951).

[8] G. B. Kistiakowsky and W. L. Marshall, THIS JOURNAL, **74**, 88 (1952).

[9] G. C. Lardy, *J. chim. phys.*, **21**, 353 (1924).

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

[11] F. O. Rice, J. Greenberg, C. E. Waters and R. E. Vollrath, THIS JOURNAL, **56**, 1760 (1934).

[12] K. O. Kutschke, M. H. J. Wijnen and E. W. R. Steacie, *ibid.*, **74**, 714 (1952).

[13] See R. Gomer and W. A. Noyes, Jr., *ibid.*, **71**, 3391 (1949).

[14] M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

gen, oxygen and carbon monoxide will be described. The gage is first evacuated and the mixture to be analyzed allowed to expand into the bulb R. The gas in R is pushed by the mercury into the volume between H and a thread of mercury in K. As the mercury rises in R it also rises in U. The float in L is closed as the mercury rises, thus preventing the rise of the mercury into the capillary K. As the mercury is now lowered a thread of mercury is left at H thus confining the gas between H and K. More gas can now be expanded into R and by sufficient repetition of the operation the gas from the line can be brought effectively between H and K. The float in L can now be held down with a magnet and the amount of gas measured as in an ordinary McLeod gage by raising the level of the mercury to D, E, F and G depending on the pressure.

The threads of mercury are withdrawn from H and K as the mercury is lowered to the level of the valve in L. The tube containing copper and cupric oxide surrounded by a furnace had been evacuated through Q and T and is now cut off by raising the mercury to S. The trap P is immersed in liquid nitrogen and the cut-off at N is opened. The valve in L is closed by removing the magnet and the mercury is raised to E. The gas sample is now confined to the space from D through K and the furnace to the expansion bulb Q. It should be noted that the volume of Q is very large compared to that in the capillary tubing. After several minutes have elapsed to allow for diffusion, the valves in N are closed and the mercury in Q raised to O. Thirty minutes are usually sufficient for the oxygen to be removed by the copper in the furnace and for the carbon monoxide to be oxidized to carbon dioxide by the cupric oxide.

The cut-off is now opened and nitrogen, the only gas remaining, is pumped into the space between H and K with the float in L raised. Its pressure is measured by using R as a McLeod gage. The nitrogen may be discarded through U by removal of the thread of mercury in K. The liquid nitrogen around P is replaced by a Dry Ice-bath and the carbon dioxide formed by combustion of the carbon monoxide is transferred to D and measured. Oxygen is obtained by difference.

Other analytical units can, if necessary, be used in place of the copper–copper oxide tube.

For each run a small quantity of ketene was removed from the storage bulb and degassed three times at −196°. It was allowed to fill the cell to the desired pressure. If oxygen was to be used the ketene was condensed with liquid nitrogen and a measured amount of oxygen introduced. The residual oxygen which did not go into the cell could be measured in the McLeod gage–Toepler pump and subtracted to give the actual amount in the reaction system. A magnetically driven stirrer ensured thorough mixing.

It was found to be impossible to separate ethylene from ketene at −183°. To effect analyses for ethylene the ketene was at first allowed to react with water. Glacial acetic acid proved, however, to be preferable. Carbon monoxide and oxygen could be separated satisfactorily from ketene at −196°. A temperature of −215° (supercooled liquid nitrogen) usually was used to ensure that ethylene was not removed simultaneously. After reaction of the ketene with water or acetic acid, ethylene was removed at −183°. A third fraction volatile at −160° was also measured. This was mainly carbon dioxide, but for some reason it was found impossible to reduce the blank for this fraction to zero. Analyses for carbon dioxide are, therefore, less accurate than those for oxygen, carbon monoxide and ethylene but should be good to about twenty %.

Analytical procedures were checked by adding to ketene known mixtures of oxygen, ethylene and carbon dioxide.

Quantum yield determinations were made in two different wave length regions, *viz.*, about 2700 and about 3700 Å. For the determinations at 2700 Å. diethyl ketone was used as an internal actinometer. The yield of carbon monoxide per quantum was assumed to be unity as it is at 3130 Å.[15] The variations of the light intensity during a run and from one run to the next were measured by a Type 935 General Electric Company phototube and galvanometer.

The photocell–galvanometer combination was used likewise to obtain relative quantum yields at 3700 Å. The spectral response curve of the Type 935 phototube supplied by the General Electric Company was used to convert relative yields to absolute yields at 3700 Å. since no internal actinometer is available at that wave length. From the curve the sensitivity (in terms of equal radiant flux) at 2700 Å. is 78% and at 3700 Å. is 95% of the maximum sensitivity at 3200 Å. For equal numbers of quanta the sensitivity at 3700 Å. will be (95 × 2700)/(78 × 3700) = 0.89 times the sensitivity at 2700 Å. From the actinometer runs at 2700 Å. and this sensitivity factor the absolute magnitudes of quantum yields at 3700 Å. could be obtained.

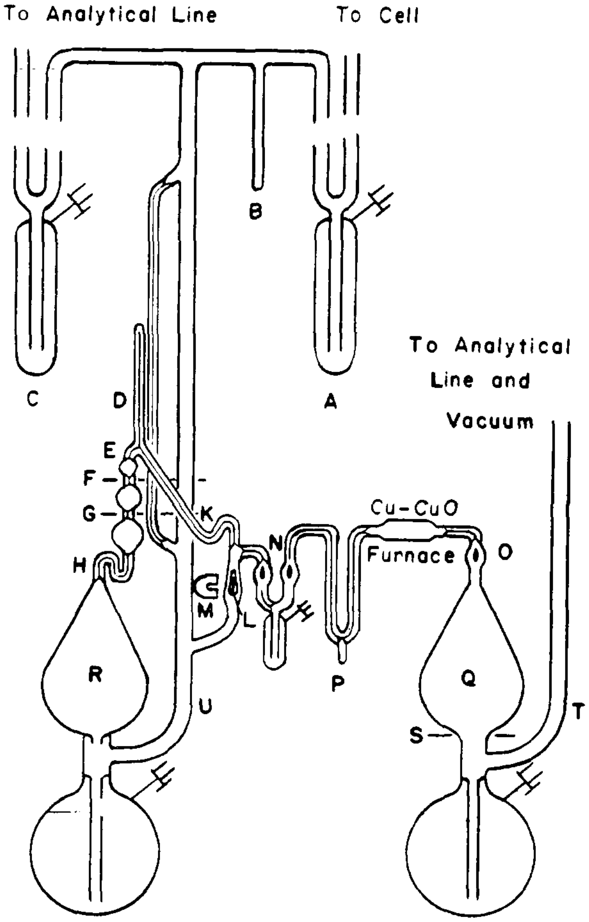

Fig. 1.—Diagram of the combined McLeod gage–Toepler pump.

Results

There was neither measurable thermal decomposition of ketene nor thermal reaction with oxygen at any of the temperatures and pressures used in the present work. There is, apparently, a very slow thermal dimerization or polymerization but the pressure change during blank runs amounted to less than 1% of the total pressure.

The intensity of the S100 Alpine burner was very constant although there was a slow decrease with time, amounting to less than 1% per hour. By interspersing runs with and without oxygen it was possible by interpolation and extrapolation to obtain ratios of rates of product formation with oxygen present to those with no oxygen.

The AH-6 lamp was subject to large fluctuations in intensity. The intensity was measured at frequent intervals with the photocell–galvanometer combination and the mean intensity during a run obtained graphically. Calculations of ratios of rates with oxygen to those without are corrected for

---

[15] W. Davis, Jr., This Journal, **70**, 1868 (1948).

TABLE I

PHOTOLYSIS OF KETENE–OXYGEN MIXTURES

(R (in molecules × 10^{14}/sec.) is the number of molecules of CO formed per second in pure ketene under the same conditions of temperature, pressure and intensity) as for determination of the other rates which are expressed in the same units.)

Lamp-filter comb. and wave l.	Time of run, min.	R	Initial and final O_2 press. mm. × 10^3	R_{CO}/R	$R_{C_2H_4}/R$	R_{O_2}/R	R_{CO_2}/R
$T = 26 \pm 2°$, P (ketene) = 39 mm. unless otherwise specified							
a	60	1.33	54(12)	1.29	0.33	0.62	..
a[a]	30	2.07	57(26)	1.14	..	.60	..
a[b]	30	2.16	100(65)	1.30	..	.60	..
a	60	1.35	158(108)	1.28	.31	.73	..
a	60	1.42	484(440)	1.30	.33	.56	..
a	300	1.29	491(267)	1.30	..	.67	..
b	60	6.15	1037(811)	1.32	.35	.72	.23
a	300	1.16	2127(1881)	1.41	.33	.83	.34
a	60	1.40	2278(2220)	1.28	.31	.82	..
e[c] (2700)	120	1.77	546(460)	1.08	.32	.48	.19
d (2700)	120	2.96	2096(1889)	1.30	.37	.69	.19
d (2700)	120	2.40	20 mm.(20 mm.)	1.33	.32	..	.45
$T = 107 \pm 1°$, P (ketene) = 39 mm. unless otherwise specified							
d (2700)	90	8.23	991(251)	1.39	.30	1.05	.48
d[c] (2700)	45	8.53	1198(677)	1.59	.33	1.42	.61
b	75	5.58	1156(614)	1.64	..	1.36	..
b	90	0.76	1021(925)	1.48	.32	1.47	.67
b	15	5.45	1088(968)	1.59	..	1.52	..
a	60	1.20	1009(888)	1.51	.28	1.75	..
a	60	1.16	1009(904)	1.52	.28	1.58	.80
c	180	0.27	1044(903)	1.83	.17	3.00	1.19
f (3700)	30	2.71	1042(824)	2.02	.05	2.81	1.14
f[d] (3700)	30	1.43	1027(845)	2.54	.11	4.45	2.23
b	10	5.89	103(52)	1.44	.36	0.95	..
b	60	6.08	478(108)	1.53	.32	1.06	..
b	60	5.94	1811(1349)	1.60	.31	1.36	..

Note: The ratios in columns 5–8 are obtained by comparison with blank runs for which the wave length distribution was the same as for the oxygen runs. [a] P (ketene) = 94 mm. [b] P (ketene) = 92 mm. [c] P (ketene) = 143 mm. [d] P (ketene) = 140 mm. Wave lengths are given only in case the radiation was approximately monochromatic.

variations in intensity, but ratios with the AH-6 lamp are subject to greater errors than with the S100 and should not be relied upon to better than ten or possibly even 20%.

Oxygen was not added during runs and hence its pressure decreased continuously. It transpired that any error due to this source is relatively unimportant because of the lack of variation of rates with oxygen pressure.

Formaldehyde and acetaldehyde were determined by the method of Stotz[16] as modified by Erbelding and Walters.[17]

The following symbols are used in the Tables for various lamp-filter combinations: (a) S100 lamp, filter 4 (all wave lengths greater than about 2850 Å.); (b) S100 lamp, no filter (all wave lengths greater than about 2400 Å.); (c) S100 lamp, filter 3 (all wave lengths greater than about 3200 Å.); (d) AH-6 lamp, filter 6 (wave lengths around 2700 Å.); (e) AH-6 lamp, filter 5 (wave lengths around 2700 Å.); (f) AH-6 lamp, filter 1 (wave lengths around 3700 Å.).

Five runs were made at 26 ± 2° with lamp–filter combinations a, b, d and e at pressures of 39 and 143 mm. without oxygen. Rates of CO formation varied from 1.43 to 6.22 × 10^{14} molecules/sec. The ratio of ethylene to carbon monoxide was 0.468 ± 0.006 with no trends apparent. At 107 ± 1° nine runs were made without oxygen and with lamp–filter combinations a, b, c, d and f and pressures of 39 and about 140 mm. The value of $R_{C_2H_4}/R_{CO}$ was found to be 0.453 ± 0.012 with no trends apparent. This ratio is, therefore, essentially independent of temperature, pressure, wave length and rate of carbon monoxide formation. No propylene was found among the products.

Table I presents the data for ketene–oxygen mixtures.

It can be seen from the data in Table I that if the ketene–oxygen reaction is due primarily to radiation of wave length 3130 Å. or shorter the ratio $R_{C_2H_4}/R$ is 0.33 ± 0.01 at 26° and 0.31 ± 0.02 at 107°. This ratio is, therefore, independent of oxygen pressure, of ketene pressure, and of temperature within experimental error. The effect of oxygen is to reduce the rate of ethylene formation to about 70% of the oxygen-free value provided short wave lengths are the main ones causing reaction.

It is evident also from Table I that if the radiation causing reaction is mainly of wave length longer than 3130 Å. (lamp–filter combinations c and f) the ratio $R_{C_2H_4}/R$ is low, *i.e.*, about 0.1 and the rate of ethylene formation is reduced to about 25% of the oxygen-free value. These facts seemed to indicate a fundamentally different behavior at

---

(16) E. Stotz, *J. Biol. Chem.*, **148**, 585 (1943).

(17) W. F. Erhelding and W. D. Walters, unpublished results, University of Rochester. See M. Christie, THIS JOURNAL, **76**, 1979 (1954).

3700 Å. from that at 3130 Å. and shorter wave lengths.

It seemed desirable to make quantum yield determinations in oxygen-free ketene at 2700 and at 3700 Å. Table II shows data obtained at the former wave length at two temperatures, 26 and 107°, and Fig. 2 shows plots of $1/\Phi_{CO}$ *vs.* P (ketene) for 3700 Å. at four temperatures: 26, 27, 107, 154°. The data shown in Fig. 2 were obtained over a range of intensities so that the number of quanta absorbed per second was a minimum of 6.3×10^{14} and a maximum of 156×10^{14}. There was no significant trend in Φ_{CO} with intensity.

TABLE II

QUANTUM YIELDS OF CO FORMATION IN PURE KETENE AT 2700 Å.

Ketene pressure, mm.	Quanta absorbed $\times 10^{-14}$/sec.	R_{CO}, molecules $\times 10^{-14}$/sec.	Φ_{CO}
	$T = 26°$		
39	0.392	0.756	1.93
143	0.780	1.76	2.26
143	1.60	3.45	2.16
	$T = 107°$		
39	0.398	0.770	1.93
143	1.11	2.59	2.33
		Average of all	2.12 ± 0.15

The quantum yield of carbon monoxide formation in pure ketene is 2.0 within experimental error at 2700 Å., and there is probably no significant variation with temperature. There may be a trend with pressure but it scarcely exceeds experimental error. These results are in marked contrast with quantum yields at 3700 Å. (Fig. 1). The latter are very much lower and they decrease at high pressures and increase at high temperatures. These facts show, as do the data in Table I, that there is a marked difference in behavior between short wave lengths and long.

The data in Table I show that oxygen causes an increase in carbon monoxide formation and a decrease in ethylene formation at all wave lengths and temperatures. The rates of oxygen disappearance are such as not to indicate a long chain reaction under any of the conditions used. There is some tendency for the rate of carbon dioxide formation to increase with increase in oxygen pressure, but in no case is this tendency very marked.

For the fifth run at 107° (Table I), R_{HCHO}/R was found to be 0.24 and R_{CH_3CHO}/R to be 0.04. The radiation during this run was polychromatic but that which caused reaction was mainly at 3130 Å. and shorter wave lengths. Under these conditions acetaldehyde is formed in small quantities and the quantum yield of formaldehyde is roughly 0.05.

The conclusions which may be drawn from the mass spectrographic analyses are as follows: (1) More acetic anhydride is formed when oxygen is present than when it is not. This indicates that water is one of the products of the reaction. (2) Formaldehyde and acetaldehyde are formed in small amounts. (3) No formic acid is found. The quantitative determination of formaldehyde and of acetaldehyde would not have been possible by the mass spectrograph due to polymerization and to the necessary conditions for collection and shipping of samples.

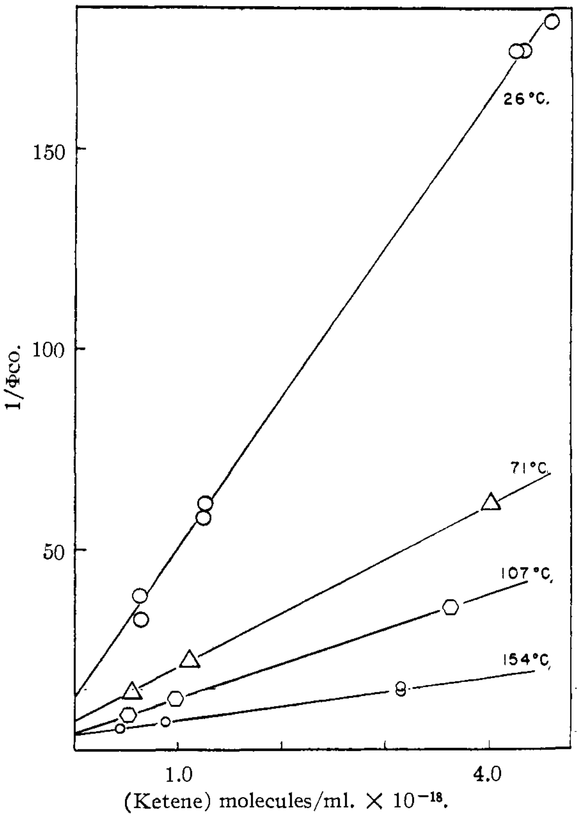

Fig. 2.—Plot of the inverse carbon monoxide quantum yield *vs.* concentration at 3700 Å. and several temperatures.

Discussion

It has been indicated that there are fundamental differences in behavior of either pure ketene or of mixtures of ketene and oxygen between those wave lengths which lie near the long wave absorption limit and those which are much shorter. For this reason it is logical to divide the discussion into three parts: (a) pure ketene at short wave lengths; (b) ketene–oxygen mixtures at short wave lengths; (c) pure ketene and ketene–oxygen mixtures at long wave lengths.

During the early stages of this work the importance of wave length was not fully appreciated and polychromatic radiation was generally used. By comparison of these results with later results obtained with approximately monochromatic radiation it is possible to decide which radiation was mainly responsible for the reaction. Thus these early results have some value in aiding the interpretation.

(a) Pure Ketene at Short Wave Lengths.—Positive proof concerning the nature of the photochemical primary process does not exist, but the accumulation of evidence from all sources,[2–9] including the results of tellurium mirror removal of Pearson, Purcell and Saigh,[18] indicates very strongly that it may be written

$$CH_2CO + h\nu = CH_2 + CO \qquad (1)$$

---

[18] T. G. Pearson, R. H. Purcell and G. S. Saigh, *J. Chem. Soc.*, 409 (1938).

The magnitude of the primary quantum yield is evidently dependent on wave length and at the longer wave lengths is also dependent on pressure (see Table II and Fig. 2). Previous work[2-8] indicates that the principal secondary reaction may be written

$$CH_2 + CH_2CO = C_2H_4 + CO \qquad (2)$$

The results in Table II show the quantum yield of carbon monoxide formation to be about two at 2700 Å. This is the value to be expected if reactions 1 and 2 were the sole ones. Thus the primary quantum yield at 2700 Å. is probably very close to unity, a value not clearly indicated by earlier work.

The reaction $CH_2 + (CH_2)_2CO = C_2H_4 + CH_2CO$ postulated by Kistiakowsky and co-workers[5,8] is not necessary if the quantum yield of carbon monoxide formation is two. Reaction 2 is sufficient to explain ethylene formation. On the other hand, it is necessary to postulate the radical $(CH_2)_2CO$ to explain the formation of compounds of higher molecular weight (see below).

Less than 1% of the ketene was allowed to decompose in each of the experiments herein described. Under these conditions reactions of CH_2 radicals either with ethylene[5] or with carbon monoxide[3] may be neglected. This is confirmed by the absence of propylene in the products. In spite of these facts the average ratio of carbon monoxide to ethylene in the products is 2.20, in excellent agreement with 2.19 found by Kistiakowsky and his co-workers.[5]

The ratio must be due to reactions in addition to 1 and 2 and whose rates are essentially independent both of ketene pressure and of temperature. They may be

$$CH_2 + CH_2CO = (CH_2)_2CO \qquad (3)$$

$$(CH_2)_2CO + CH_2CO = CO + (CH_2)_3CO \qquad (4)$$

Continuation of reactions of the type of 4 could lead to compounds of higher molecular weight with the empirical formula $(CH_2)_nCO$ (crotonaldehyde and/or cyclic ketones may be formed).

The radical formed by 3 may be either CH_2CH_2CO or CH_2COCH_2. Possibly one of the two is responsible for ethylene formation either by direct dissociation or by reactions of the type

$$(CH_2)_2CO + CH_2CO = C_2H_4 + CO + CH_2CO \qquad (5)$$

and the other for compounds of higher molecular weight by the over-all reaction $(CH_2)_2CO + (n - 2)CH_2CO = (CH_2)_nCO + (n - 2)CO$. If $n = 3$, the ratio of the rate of the initial step leading to ethylene to that of the other step would be 10:1. A high value of n means a high value of the ratio. Positive identification of compounds formed in small amounts would be desirable.

Two possibilities must be considered: (1) only one intermediate is formed, and it may react either to give ethylene or to give a polymer; (2) two different intermediates are formed and react, respectively, with ketene to give ethylene and a compound of higher molecular weight.

It should be pointed out that according to the mechanism proposed the quantum yield of ethylene formation may not exceed unity. Indeed, if it is exactly unity, the quantum yield of carbon monoxide must be exactly two, a value which would disagree with the CO/C_2H_4 ratio of 2.2 found experimentally. The nearer $\Phi_{C_2H_4}$ is to unity, the higher the average value of n must be in the formula of the postulated products $(CH_2)_nCO$. The data in Table II are not accurate enough to permit more detailed conclusions to be drawn.

There may be a relationship between one of the two forms of $(CH_2)_2CO$ (possibly CH_2COCH_2) and allene formation found by Kistiakowsky and Marshall.[8] Further work on this point might yield interesting results. (The authors are indebted to Professor Kistiakowsky for this suggestion.)

(b) **Ketene–Oxygen Mixtures at Short Wave Lengths.**—The data in Table I show clearly that whenever oxygen is present and the reaction is due predominantly to wave lengths of 3130 Å. or shorter, the ethylene yield is reduced to about 0.72 of the oxygen-free value and that the yield does not vary either with oxygen pressure, if the oxygen pressure exceeds about 0.01 mm., or with temperature. The carbon monoxide yield is increased about 30% by addition of oxygen at 26° and about 60% at 107°. At both temperatures there may be a slight tendency for the CO yield to increase with oxygen pressure, but the trend is hardly more than experimental error.

The only measured product whose yield seems to increase with oxygen pressure is carbon dioxide, and its yield also increases with increase in temperature.

The formation of large amounts of ethylene in the presence of oxygen is the surprising fact in these results.

The following numbers of molecules are formed or disappear per methylene radical produced in pure ketene: 26°, CO, 2.6; C_2H_4, 0.64; O_2 consumed, 1.4; CO_2, 0.4; 107°, CO, 3.2; C_2H_4, 0.64; O_2 consumed, 2.8; CO_2, 1.2; HCHO, 0.48. These yields are almost constant as long as the ratio CH_2CO/O_2 does not exceed about 500.

These results seem to make inescapable one or the other of the following conclusions: (1) methylene radicals react so rapidly with ketene that their reaction with oxygen is unimportant at the pressures used; (2) methylene radicals react with oxygen so rapidly that their reaction with ketene is unimportant even at the lowest oxygen pressures used. If 1 is accepted, it must be assumed that the radical $(CH_2)_2CO$ reacts with oxygen about one-third of the time and reacts to give ethylene about two-thirds of the time (presumably without consumption of oxygen).

On the assumption that all hydrogen atoms form water a fairly good material balance is obtained both at 26° and at 107°, although slightly more oxygen is consumed than can be accounted for in the products. It is necessary, however, to assume that slightly more than two molecules of ketene disappear per quantum absorbed at 26° and slightly more than three at 107°. This suggests that we are dealing with a short chain reaction with a chain length which increases with temperature. It is possible to write a logical sequence of steps based on the assumption that CH_2 radicals do not react directly with oxygen, that $(CH_2)_2CO$ radicals of one type always give ethylene and that $(CH_2)_2CO$ radicals of the other type react with oxygen to give the other observed products, with additional ketene molecules being involved in the chain. These steps would be purely speculative, and there is no need to pursue the subject further at the present time.

If assumption (2) is accepted, however, so that CH_2 radicals always react with oxygen, it is necessary to assume further that ethylene is formed by

$$CH_2 + O_2 = CH_2O_2 \qquad (6)$$

$$CH_2O_2 + CH_2CO = C_2H_4 + O_2 + CO \qquad (7)$$

Reaction between CH_2O_2 and ketene must also lead to other products, possibly depending on the nature of the intermediate complex.

Kistiakowsky and Rosenberg[5] have estimated the rate constant of reaction (2) to be of the order of magnitude of 10^{-16} ml./molecule sec. The calculation of this constant was based on the assumption that mirror removal is brought about solely by CH_2 radicals. If diradicals such as $(CH_2)_2CO$ may also remove mirrors, 10^{-16} ml./molecule sec. would be a lower limit for the constant of reaction (2).

Reaction (6) must have a rate constant at least 500 times greater than that of reaction (2) if assumption 2 is adopted, *i.e.*, it must have a value greater than 5×10^{-14}. If (6) has zero activation energy, the effective cross section would be about 3×10^{-20} cm.^{2}. If the collision diameter is taken as 4 Å., the steric factor would be of the order of magnitude of 10^{-3}. The value of 2×10^{-4} was found for the reaction of methyl radicals with oxygen.[19]

Thus there seem to be two ways of explaining the reactions in the ketene–oxygen system. One possibly valid objection to assumption 1 can be made. In the absence of oxygen it is necessary to assume that approximately 10% of the methylene radicals react with ketene to give the non-ethylene forming radical, whereas in the oxygen system it would be necessary to assume that approximately one-third of them do this. Further work may distinguish between the two mechanisms provided satisfactory experiments can be devised for the purpose.

It is interesting to note that ethylene is also formed in the presence of nitric oxide.[20]

(c) Pure Ketene and Ketene–Oxygen Mixtures at 3700 Å.—The very marked effect of pressure on the quantum yields in pure ketene is shown in Fig. 2. The equations of the straight lines are all of the form $1/\Phi = a + bP$. Possibly several methods of deriving an expression of this type could be visualized but one is much more plausible than the others

$$CH_2CO + h\nu = CH_2CO' \qquad (8)$$

$$CH_2CO + CH_2CO' = 2CH_2CO \qquad (9)$$

$$CH_2CO' = CH_2 + CO \qquad (10)$$

$$CH_2CO' = CH_2CO\ (+\ h\nu?) \qquad (11)$$

followed by reactions of the methylene radicals already discussed. Since the CO/C_2H_4 ratio is independent of pressure, temperature, intensity and wave length, it may logically be assumed that methylene radicals once formed will react in the same way at 3700 Å. as at shorter wave lengths. Thus by assumption of the steady state one finds

$$I_a/R_{CO} = 1/\Phi_{CO} = (1/2)(1 + (k_{11}/k_{10}) + k_9(CH_2CO)/k_{10}) \qquad (12)$$

where I_a = number of quanta absorbed/ml. sec., R_{CO} = rate of formation of CO in molecules/ml. sec., 2 = number of CO molecules produced per methylene radical formed in the primary process at 2700 Å., Φ_{CO} = quantum yield of carbon monoxide formation. Equation 12 is of the right form to fit the straight lines in Fig. 2. (NOTE: Even higher pressures than those shown in Fig. 2 were investigated at 26°. These points fall on the same linear plot.)

Reaction 11 must be included because of the very low quantum yields at 3700 Å. These are much lower than those reported previously for this wave length.[3]

The intercepts found from equation 12 are $1/2$ $(1 + k_{11}/k_{10})$ and the slopes $(k_9/2\ k_{10})$. It is seen that both the slope and the intercept increase with temperature. If the rate constants are all written in the form $k = a \exp(-E/RT)$

$$k_9/2k_{10} = (a_9/2a_{10}) \exp\ (-(E_9 - E_{10})/RT)) \qquad (13)$$

and it is possible to calculate $E_9 - E_{10}$ from a plot of the logarithm of the slope *vs.* $1/T$. The result is $(E_9 - E_{10}) = -4500 \pm 300$ cal. per mole. Similarly $(a_9/a_{10}) = (4 \pm 2) \times 10^{-20}$ ml./molecule. If reaction 9 has a steric factor of unity, a_{10} is about 10^{10} sec.$^{-1}$. This is an upper limit.

If $E_9 = 0$, $E_{10} = 4500$ cal. per mole would be the activation energy for dissociation of active molecules. This is of the same order of magnitude as that estimated for a similar step in acetone.[21]

The data necessitate two unimolecular methods of disappearance of CH_2CO', *viz.*, (10) and (11). Possibly (11) results in fluorescence but if so the emitted light has a wave length so close to that of the absorbed radiation that it could not be detected. Further work on this point would be desirable. In any case the intercepts provide a method of determining $k_{10}/(k_{10} + k_{11})$. A plot of $\ln\ (2i^{-1})$ *vs.* $1/T$ should have a slope proportional to $E_{10} - E_{11}$ (i = intercept in Fig. 2). The intercepts cannot be determined with sufficient accuracy to permit good determination of this activation energy difference but it proves to be slightly less than $E_{10} - E_9$. There may be, therefore, a slight activation energy (perhaps 1000 cal.) for reaction 11.

Two runs were made at 107° at 3700 Å. with added oxygen. Oxygen at this wave length markedly reduces the yield of ethylene, carbon monoxide is greatly increased, carbon dioxide is formed, and the oxygen consumption is relatively large. These facts indicate a different reaction at this wave length from that at 2700 Å. The obvious conclusion is that the active molecules react with oxygen

$$CH_2CO' + O_2 = (\text{no ethylene}) \qquad (14)$$

The small amount of ethylene formed in the presence of oxygen could be due either to some stray

---

[19] F. B. Marcotte and W. A. Noyes, Jr., *Discussions Faraday Soc.*, No. 10, 236 (1951).

[20] M. Burton, T. W. Davis, A. Gordon and H. A. Taylor, THIS JOURNAL, **63**, 1956 (1941).

[21] W. A. Noyes, Jr., and L. M. Dorfman, *J. Chem. Phys.*, **16**, 788 (1948).

radiation of shorter wave lengths or to competition between (10) and (14). If it is assumed that there is no stray radiation an estimate can be made of k_{14}/k_9. This gives 323 and 316 for the two runs. Thus if every collision of an activated molecule with oxygen is effective in preventing formation of methylene radicals, the steric factor for the deactivation by ketene must be not greater than 0.003. This would make $a_{10} = 3 \times 10^7$ sec.$^{-1}$, rather than 10^{10} as given above.

A second method may be used to estimate k_{14}/k_9. From the data in Table II it is found that 2.8 oxygen molecules are consumed for each ethylene molecule formed at 2700 Å. The remaining oxygen must be consumed by reaction 14 and the reactions which follow it. If it is assumed that only one oxygen molecule is used as a result of (14) one can obtain k_{14}/k_{10} and combine this with k_9/k_{10} to obtain k_{14}/k_9. The two runs give 77 and 54, respectively. Of the two methods the second seems to be based on the more doubtful assumptions.

One may take a_{10} to be not more than 10^8 sec.$^{-1}$ so that $k_{10} < 10^8 \exp(-4500/RT)$. At 107° $k_{11}/k_{10} \sim 8$ (Fig. 2) and $E_{10} - E_{11} \sim 3500$ cal./mole. Hence $a_{11} < 10^7$ sec.$^{-1}$ and the mean life will be greater than 10^{-7} sec. A calculation of the mean life based on the integrated absorption coefficient gives 3×10^{-6} sec.[22] The approximate agreement between the mean lifetimes obtained by the two methods may be fortuitous but does suggest the desirability of a more careful investigation of the spectrum and possible fluorescence of ketene vapor. These mean lifetimes would be compatible with existence of rotational structure in the ketene spectrum.

More detailed work will be necessary to establish the nature of the reaction of excited ketene molecules with oxygen but it may be said with considerable certainty that such a reaction does occur.

The results presented in this paper do not establish conclusively the detailed mechanism of the reactions of methylene radicals with oxygen largely because the lack of variation of the results with experimental conditions prevents use of the customary methods of competitive reactions. It may be concluded that in the case of ketene, and probably also for other molecules, it is necessary to exercise considerable care in experimental procedure and in interpretation to be sure that reactions of active molecules with oxygen are not confused with reactions of radicals.

(22) We are indebted to Mr. H. K. Dice and Dr. O. V. Luke of the Celanese Corporation of America, Clarkwood, Texas, for permission to use absorption coefficients obtained in their research laboratory by Messrs. J. S. Hill and R. C. Wilkerson. The calculation of the mean life was made by Mr. Richard Holroyd at the suggestion of Professor A. B. F. Duncan.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM LABORATORY OF MOLECULAR STRUCTURE AND SPECTRA, DEPARTMENT OF PHYSICS, THE UNIVERSITY OF CHICAGO]

The Aromatic Carbonium Ions[1]

BY C. REID[2]

RECEIVED FEBRUARY 1, 1954

The spectra of a number of aromatic hydrocarbons dissolved in liquid hydrogen fluoride containing boron trifluoride have been examined. Two kinds of absorption bands have been observed and are attributed (1) to the aromatic carbonium ions RH^+ and (2) to the complexes $R:BF_3$. The carbonium ions are subdivided into two groups with spectra centered at about 4,000 and 4,800 Å., respectively, and a tentative explanation for these is put forward. Photochemical changes have also been observed on irradiation of some of the polycyclic carbonium ions and are discussed.

Introduction

The fact that the more basic, polynuclear hydrocarbons dissolve in strong sulfuric acid, and that even the less basic ones, benzene, toluene, etc., will dissolve in anhydrous hydrofluoric acid, in the presence of boron trifluoride, is well-known.[3a,b] Differences in basicity have been used as a mode of separation of these hydrocarbons.[3]

Nevertheless, data on the "carbonium ions" which are formed, it is thought by the addition of a proton to the hydrocarbon—which thus acts as a base—are very scanty, although some spectra of sulfuric acid solutions of the more basic hydrocarbons have been published.[4] The experimental work here described shows that in fact the phenomena occurring in HF–BF_3 solutions are quite involved, addition compounds of BF_3 and hydrocarbon sometimes forming as well as the carbonium ion, which may itself react to form further products.

Experimental

Absorption.—Anhydrous HF (Mathieson C.P.) and dry boron trifluoride (from the same source) were distilled through Teflon tubes directly into the absorption cell which was kept at −80° during the distillation and subsequently. In some of the earlier runs the HF was distilled from a small copper cell and the middle fraction only used. However, no difference in transmission could be detected between this material and that distilled directly from the supply cylinder. It showed no trace of the absorption band at 2800 characteristic of SO_2, and was assumed substantially free of that material. BF_3 was distilled into the cell through a cold trap kept at −100° by a pentane-bath. It was assumed

---

(1) This work was assisted by the Office of Ordnance Research under Project TB2-0001 (505) of Contract DA-11-022-ORD-1002 with the University of Chicago.

(2) On leave of absence from the University of British Columbia, Vancouver, B. C., Canada, which is presently the correct address.

(3) (a) M. Kilpatrick and F. E. Luborsky, THIS JOURNAL, **75**, 577 (1953), and references given there; (b) D. A. McCaulay, B. H. Shoemaker and A. P. Lien, *Ind. Eng. Chem.*, **42**, 2103 (1950).

(4) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172 (1952), and references therein.