methyl iodide in dioxane was obtained 3 g. of pure ether, after the crude product had been treated with sodium-potassium alloy to remove unsaturated impurities.[16] The substance was a fragrant, colorless oil that did not solidify at −15° and did not decolorize bromine in carbon tetrachloride. Its physical constants were: boiling point 88–90° at 2 mm.; d^{20}_{4} 1.048; n^{20}_{D} 1.5483.

Anal. Calcd. for $C_{12}H_{16}O$: OCH_3, 16.3. Found: OCH_3, 16.7.

The potassium alkyls derived from isopropylbenzene, phenylcyclohexane, and phenylcyclopentane were made by the action of sodium–potassium alloy upon the corresponding methyl ethers in dry ether.[17] The yields of alkyl were in no case greater than about 50%, as determined by treatment of the reaction mixture with carbon dioxide and isolation of the resulting carboxylic acids. In the case of the potassium derivative of phenylcyclohexane, the yield was especially low (about 7–15%). This was at least partially due to the extreme slowness of the reaction between the ether and the alloy. The potassium derivatives of diphenylmethane, triphenylmethane, and 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane were prepared by the action of the potassium derivative of isopropylbenzene (prepared as above) upon the appropriate hydrocarbon. In all cases, the alkyls were treated with carbon dioxide, and the resulting acids were isolated and identified. All of these acids have been previously described, except for the one derived from the trixylylmethane.

3,3′,3″,5,5′,5″-Hexamethyltriphenylacetic Acid.—Carbonation of the bright orange-red potassium derivative of 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane yielded the corresponding acid. This formed small colorless plates melting at 276–281° with decomposition.

Anal. Calcd. for $C_{26}H_{28}O_2$: C, 83.82; H, 7.54; neut. equiv., 372. Found: C, 83.95; H, 7.75; neut. equiv., 375.

Comparison of Acid Strengths

Since all the alkyls which contained only one phenyl group per molecule were of nearly the same color (a dark reddish brown) the reactions could not be followed by the colorimetric method. The reaction mixtures were therefore carbonated, and the resulting acids were isolated and identified by melting point, mixed melting point, and neutral equivalent.[18]

In this way, it was found by direct comparison that phenylcyclohexane is a weaker acid than isopropylbenzene and phenylcyclopentane, that isopropylbenzene is a weaker acid than phenylcyclopentane, triphenylmethane and trixylylmethane, and that phenylcyclopentane is a weaker acid than diphenylmethane. Diphenylmethane has already been found by Conant and Wheland[3] to be a weaker acid than triphenylmethane. In all of these cases, the reactions went to completion, to within the limits of the method of analysis. On the other hand, the potassium derivative of phenylcyclopentane did not react appreciably with either phenylcyclohexane or isopropylbenzene; and the potassium derivative of neither triphenylmethane nor trixylylmethane reacted at an observable rate with the other hydrocarbon.

The micro-analyses reported in this paper were performed by Dr. T. S. Ma.

Summary

The following order of decreasing acid strength has been established: diphenylmethane > phenylcyclopentane > isopropylbenzene > phenylcyclohexane. Triphenylmethane and 3,3′,3″,5,5′,5″-hexamethyltriphenylmethane could not be compared with each other, but both are stronger acids than isopropylbenzene.

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[16] *Cf.* ref. 12, p. 19.

[17] Ziegler and Thielmann, *Ber.*, **56**, 1740 (1923); *cf.* also ref. 12, p. 20.

[18] The procedure for the carrying out of the experiments is described in ref. 3.

CHICAGO, ILLINOIS RECEIVED AUGUST 20, 1941

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Photolysis of Ketene in the Presence of Hydrogen and Methane

BY CHARLES ROSENBLUM[1]

When gaseous ketene is irradiated[2] with ultraviolet light from a quartz–mercury vapor arc, the pressure increases and the gas phase is found to contain ethylene and carbon monoxide. For short exposures these gases are present in the ratio $2CO/1C_2H_4$, whereas after longer exposures, or if ethylene is added initially, the ratio increases[2] due to polymerization of unsaturated hydrocarbon. To account for these results, mechanisms involving the primary formation of free methylene radicals have been proposed.

The evidence for the formation of free methylene radicals from ketene and other sources has been reviewed by Barrow, Pearson and Purcell.[3] As regards ketene, it is known that its ultraviolet absorption spectrum,[2,4] in the 2600–3700 Å. wave length region consists of diffuse bands characteristic of predissociation into molecular fragment; and the photochemical investigations mentioned

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[1] Present address: Merck and Co., Inc., Rahway, N. J.

[2] (a) Norrish, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); (b) Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

[3] Barrow, Pearson and Purcell, *Trans. Faraday Soc.*, **35**, 880 (1939).

[4] Lardy, *J. Chim. Phys.*, **21**, 353 (1924).

indicate that light absorption by the unsaturated ketone is followed by rupture into carbon monoxide and the biradical methylene. Perhaps the most direct demonstration is due to Pearson, Purcell and Saigh,[5] who employed the mirror technique to prove that methylene radicals could be produced by photodissociation of ketene and that, in the latter medium, the radicals were quite stable.

Other sources of methylene radicals are of course available[6]; but they offer certain experimental difficulties or are complicated by involving chain reactions as shown by quantum yields which differ from unity, with attendant increase in the number and variety of products. Ketene photolysis does not appear to possess chain characteristics, and the extent of decomposition is readily revealed by the carbon monoxide production, so that·it constitutes a most convenient means of investigating the chemical properties of methylene radicals. The investigations of Pearson, Purcell and Saigh[5] have eliminated nitrogen, ketene and ether vapors as reactants since their use as diluents markedly increases the life of methylene radicals; and Paneth and Lautsch[7] have been unable to detect any reaction of methylenes with carbon or benzoic acid. On the other hand, methylene radicals are known to react with other methylene radicals to form ethylene, and with ethylene[2,8] itself to yield polymeric unsaturates; reaction with diazomethane[9] is assumed to explain the high quantum yield for decomposition of this compound; the absence of methylene during the thermal decomposition of methane[10] under certain circumstances is attributed to interaction between these substances; combination with carbon monoxide[11,12] has long been known; and reactions with nitric oxide,[8] oxygen[9,13] and hydrogen[9,14,15] have been reported.

The early experiments[14] of the present author on the photo-reaction of ketene in the presence of hydrogen unfortunately involved high light intensities and exposures long enough to produce more than 85% ketene decomposition, so that no information concerning the early stages of the reaction was forthcoming. The principal purpose of this paper is to discuss in detail the behavior of ketene subjected for different time intervals to ultraviolet light of different intensities in the presence and absence of hydrogen. A number of experiments involving the addition of methane and ethylene to the ketene will also be reported.

Experimental

Materials.—Ketene was prepared by pyrolysis of purified[2] acetone by refluxing over an electrically heated[16] glowing platinum or nichrome wire supported in an appropriate lamp[17] which led to a water-cooled reflux condenser. During the preparation the system was flushed occasionally with nitrogen. The exit gases passed through several traps maintained at −50 to −60° to collect uncondensed acetone, and then through a trap at −78° which retained most of the ketene. Purification of the product was effected in two stages. As a preliminary, the liquid ketene was subjected to repeated vacuum fractional distillation from one container kept at −70° to another immersed in liquid air. Permanent gases were removed by freezing the ketene and pumping. Samples obtained in this manner contained about 5.5% of hydrocarbon impurity, and were used for the earlier communication[14] as well as in several of the experiments to be discussed. Fractionation with refluxing[18] was the method adopted for the second stage of purification. By means of a four-foot column packed with cracked glass beads, with a still head temperature of −90° and a pot temperature of about −50°, it was possible to bleed off a middle fraction containing 1% and less of hydrocarbon impurity. Frequent analyses were performed to ascertain the extent and nature of the impurity, which was always taken into account when calculating the material balance sheets. In every case the impurity was a hydrocarbon mixture which was at least 75% unsaturated (judging from hydrogenation over nickel) and contained an average of about three carbon atoms per molecule (as determined by cracking to methane in the presence of hydrogen).

Hydrogen was prepared by electrolyzing a 15% potassium hydroxide solution, or tank hydrogen of electrolytic origin was used. In either case the gas was circulated repeatedly over a glowing platinum wire and through a liquid air trap before use. Passing this hydrogen into a heated (≃300°) chamber containing cupric oxide, and freezing out the water formed, left only negligible amounts of residual gases.

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(5) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

(6) (a) Methane: Kassel, THIS JOURNAL, **54**, 3949 (1932); Belchetz and Rideal, *ibid.*, **57**, 1168 (1935); *cf.*, however, Rice and Dooley, *ibid.*, **56**, 2747 (1934); (b) diazomethane: Norrish and Kirkbride, *J. Chem. Soc.*, 119 (1933); Rice and Glasebrook, THIS JOURNAL, **56**, 2381 (1934); Barrow, Pearson and Purcell, see above; (c) methylene dihalides: Gregory and Styles, *Trans. Faraday Soc.*, **32**, 724 (1936); Bawn and Dunning, *ibid.*, **35**, 185 (1939); Bawn and Milsted, *ibid.*, **35**, 889 (1939).

(7) Paneth and Lautsch, *J. Chem. Soc.*, 380 (1935).

(8) Burton, Davis, Gordon and Taylor, THIS JOURNAL, **63**, 1956 (1941).

(9) Norrish and Kirkbride, *J. Chem. Soc.*, 119 (1933).

(10) Belchetz, *Trans. Faraday Soc.*, **30**, 170 (1934); Belchetz and Rideal, THIS JOURNAL, **57**, 1168 (1935).

(11) Staudinger and Kupfer, *Ber.*, **45**, 501 (1912).

(12) Rice and Glasebrook, THIS JOURNAL, **56**, 2381 (1934).

(13) Gregory and Styles, *Trans. Faraday Soc.*, **32**, 724 (1936).

(14) Rosenblum, THIS JOURNAL, **60**, 2819 (1938).

(15) Bawn and Milsted, *Trans. Faraday Soc.*, **35**, 889 (1939).

(16) Hurd, THIS JOURNAL, **45**, 3095 (1923); Williams and Hurd, *J. Organic Chem.*, **5**, 122 (1940).

(17) Herriot, *J. Gen. Physiol.*, **18**, 69 (1934).

(18) Rice, Greenberg, Waters and Vollrath, THIS JOURNAL, **56**, 1760 (1934).

Ethylene was obtained by fractional distillation of tank ethylene. The product used analyzed by catalytic hydrogenation as 100.5 ± 0.5% unsaturated and contained 2.03 ± 0.02 carbon atoms per molecule (shown by cracking to methane). These figures give an idea as to the reliability of the hydrocarbon analysis. Ethane was prepared from this ethylene by hydrogenation over reduced nickel, the volume of unreacted hydrogen being measured as a check on the completeness of the reaction. Methane was obtained by cracking some of the above ethane in an excess of hydrogen over nickel at about 270°, freezing out any uncracked ethane, and removing the excess hydrogen by combustion over hot copper oxide.

Apparatus and Procedure.—The essential features of the apparatus have been described in a previous publication.[19] Gaseous ketene obtained from a stock supply, stored in the liquid state at −78° to diminish polymerization, and at all times protected from stopcock grease by mercury seals, was introduced into a highly evacuated cylindrical quartz reaction vessel (diameter of 2.7 cm.; 22 cm. long) of known volume (131 cc. including dead space) and the pressure (always about 100 mm.) observed on a closed end mercury manometer. Measured quantities of other gases were added when desired, and the reaction chamber was exposed to light from a hot Cooper–Hewitt quartz–mercury arc placed at a distance of 6 cm. from the vessel. Between vessel and lamp was interposed a hydrogen–mercury vapor filter[20] for mercury resonance radiation as an additional precaution against the formation of hydrogen atoms in experiments involving hydrogen. Exposures of ten minutes or forty-five minutes duration were made at several radiation intensities obtained by operating the mercury lamp at different wattages maintained constant to within 10% by manual regulation of a slide wire resistance. During most of the experiments, the arc was run at 250 watts (approximately 3.4 amps. and 73 volts) or at 490 watts (about 6.3 amps. and 77 volts); and an hour was allowed for the lamp to overcome major fluctuations before any actual irradiation was begun. The greater part of the work was done at ordinary temperatures, with no attempt being made to thermostat the system since the extent of ketene photodissociation does not change appreciably[2,14] between 4 and 200°. Due to the heat from the arc, the reaction vessel was at a temperature of 45–50°.

Analytical Methods.—At the conclusion of an experiment the final gas mixture was fractionated and the several components analyzed. Two Toepler pumps were needed to facilitate the transport of gases between the reaction vessel, the Ramsay buret used for measuring volumes of all gases other than ketene, the storage containers of these gases, and the chambers containing reduced nickel and cupric oxide utilized in the analytical procedure. Permanent gases (not frozen at liquid air temperature) were pumped into the buret, and the remaining gas sent into an alkali absorption chamber to remove the ketene, after which the hydrocarbon residue was collected for analysis. The final ketene could be determined as the difference between the amounts of ketene plus hydrocarbon, and the hydrocarbon recovered. However, because of the tendency for ketene to polymerize and to dissolve in traces of grease or hydrocarbon polymerization product, a more reliable value is obtained by subtracting the carbon monoxide from the ketene taken initially. This deficiency averaged 1.5% of the initial ketene, the maximum polymerization being observed as less than 4% in experiment 2.

The permanent gas fraction was transferred to a chamber containing granular cupric oxide at 300–310° for combustion of hydrogen and carbon monoxide. First methane was pumped off through a liquid air trap and measured, then the carbon dioxide was removed at −78°. The amount of hydrogen was obtained by difference.

The hydrocarbon analysis was based upon the work of Morikawa, Trenner and Taylor[21] and has been used frequently in this Laboratory.[19,26a] It involved a determination of the degree of unsaturation and of the average chain length by catalytic hydrogenation[22] and cracking to methane over nickel. No attempt was made to fractionate into components because the volume of gas formed as a rule was only about three cubic centimeters.

Results

Presence of Hydrogen.—The results of experiments at ordinary temperatures (45–50°) with and without hydrogen, using purified ketene containing 1% or less of hydrocarbon impurity, are recorded in Table I. The exposure time, intensity of light source, and the initial and final compositions of gas mixture are given, as well as the degree of unsaturation (% uns.) and the average number of carbon atoms (C_x) per molecule of hydrocarbon (HC). All quantities are expressed as 10^{-4} mole. The exact amount of hydrocarbon impurity in the various ketene samples is not recorded. It varies between 0.04–0.07 × 10^{-4} mole; and because the impurity is practically completely unsaturated, it will have no sensible effect on the extent to which the gaseous reaction products are saturated. Furthermore, its effect on the C_x determination does not exceed 5% of a theoretical C_2 hydrocarbon. The column headed Δn gives the over-all change in the number of moles during the reaction, a positive value signifying an increase in volume. The "deficiency" columns give the carbon shortage in the gas phase, and the ratio of the carbon and hydrogen deficiencies as indicated by a material balance of all components analyzed. It represents the formation of non-volatile polymer for which the H/C ratio is given. In preparing such a balance sheet, the gaseous hydrocarbon was treated as a paraffin

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[19] Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

[20] Morikawa, Benedict and Taylor, *ibid.*, **5**, 212 (1937).

[21] Morikawa, Trenner and Taylor, This Journal, **59**, 1103 (1937).

[22] The hydrogenation and cracking were carried out at about 265° in one operation instead of in two stages. Tests on ethylene showed that equally reliable analyses could be obtained provided that a sufficient quantity of hydrogen was present to prevent carbonization.

TABLE I

EFFECT OF HYDROGEN

			Initial moles × 10^4		Final moles × 10^4									Deficiency[b]	
Expt.	Time, min.	Watts	Ketene	H_2	Ketene, meas.	Ketene,[a] diff.	H_2	CO	CH_4	HC	% Uns.	C_x	Δn[b] × 10^4	C × 10^4	H/C
1	10	243	7.02	...	5.69	5.69	0	1.327	0	0.628	99+	2.40	+0.58	0	..
2	45	250	7.29	...	3.23	3.50	0.011	3.792	0.005	1.617	100	2.47	+1.54	0.13	2.00
3	10	489	7.19	...	3.79	3.82	0	3.370	.003	1.357	100	2.31	+1.28	.52	1.96
4	10	251	7.31	15.81	5.83	5.86	15.428	1.454	.012	0.696	55	2.39	+0.26	.02	..
5	45	249	7.23	6.70	3.41	3.56	6.033	3.672	.020	1.436	61.2	2.45	+ .72	.38	2.47
6	45	252	7.19	15.73	3.14	3.31	14.447	3.881	.083	1.448	28.3	2.43	+ .19	.48	2.64
7	10	481	7.13	15.78	3.40	3.54	14.707	3.588	.026	1.410	34.8	2.40	+ .28	.45	2.58
8	10	497	7.18	33.65	3.45	3.52	32.244	3.663	.042	1.493	18.0	2.36	+ .06	.36	2.64
9	45	472	7.28	15.78	1.20	1.39	13.637	5.888	.136	1.920	10.4	2.64	− .15	.90	2.64

[a] Final ketene calculated by subtracting CO from initial ketene. [b] Calculated on the basis of final ketene (diff.).

containing a quantity of olefin equivalent to the hydrogen disappearing during the catalytic hydrogenation.

Experiments 1–3 with ketene alone yield substantially the same results as have been found by other workers in that a volume increase occurs and that prolonged irradiation causes the formation of a non-volatile polymer. It is to be noted in addition that an increased light intensity (Expt. 3) likewise favors polymerization to a product which in each case has the empirical formula $(CH_2)_n$. The direct cracking of the gaseous hydrocarbon shows that ethylene is not the sole product, but that higher unsaturated hydrocarbons are produced simultaneously, probably as a result of intermediate stages in the polymerization process.

The photochemical decomposition of ketene in the presence of hydrogen (Expts. 4–9) is in some respects similar to the behavior of ketene alone. Prolonged irradiation and increased light intensity yield more condensed polymer, and again the gas phase contains higher hydrocarbons. However, the greatly diminished (and even negative) volume increase shows that a new reaction has occurred, and inspection of the analytical data reveals that hydrogen has disappeared, and that the gaseous hydrocarbon is to a considerable extent saturated. The longer the exposure (Expts. 4 *vs.* 6; 7 *vs.* 9) and the higher the lamp intensity, (Expts. 4 *vs.* 7; 6 *vs.* 9) the more saturated is the gaseous hydrocarbon, and increasing the initial hydrogen has a similar saturating effect. Furthermore, one must conclude from the calculated carbon and hydrogen deficiencies that the polymeric residue is a saturated hydrocarbon with an empirical formula $C_1H_{2.3-2.6}$. The appearance of small amounts of methane is another feature of the reaction in the presence of hydrogen; and again the gaseous product contained higher hydrocarbon. Incidentally it was ascertained that mercury photosensitization did not enter as a factor in these experiments. Mixtures of ethylene and hydrogen irradiated for an hour at room temperature and at 200° failed to show any signs of reaction, the reactants being recovered intact.

Finally it should be emphasized that the hydrogen disappearing during a reaction is exactly equivalent to the total quantity of saturates appearing in the form of methane, higher gaseous hydrocarbons, and condensed polymer.

Presence of Hydrocarbons.—A number of experiments were performed in the presence of methane, ethane and ethylene in an effort to learn how hydrocarbons produced during the ketene photodecomposition influenced the course of the reaction. Preliminary data obtained after forty-five minutes of irradiation are summarized in Table II. These experiments were carried out at 45–50° except 12B which was performed at 200°.

In every case the presence of hydrocarbons, whether added for experimental purposes or present initially as impurity in the ketene sample, tended to increase the carbon deficiency, *i. e.*, the amount of polymer formation. The effect of initial ethylene has already been noted[2,8] and is here confirmed even when hydrogen is present. A pronounced polymerization occurred also when ethane was added, though these data are not presented. As one would expect, the condensed polymers are unsaturated, except for the polymer formed in the presence of hydrogen which appears to contain some saturated hydrocarbon. These experiments indicate that methylene radicals, in common with ethyl and methyl radicals, hydrogen atoms and excited atoms, are able to polymerize hydrocarbons. The operation of this property of CH_2 radicals in ethylene diminishes

TABLE II

EFFECT OF METHANE AND ETHYLENE (45 MINUTES OF IRRADIATION)

		Initial moles × 10^4		Final moles × 10^4									Deficiency		Moles × 10^4	
Expt.[a]	Watts	Ketene	HC	Ketene, meas.	Ketene, diff.	H_2	CO	CH_4	HC	% Uns.	C_x	$\Delta n \times 10^4$	C $\times 10^{-4}$	H/C	$-\Delta CH_4$	$-\Delta$Uns.
10A	251	7.27	7.247 CH_4	3.76	3.85	0.026	3.420	6.850	1.596	76.4	2.33	+1.14	0.38	2.00	0.397	0.376
11B	360	7.91	4.631 CH_4	2.95	3.10	0	4.81	4.37	2.123	77.0	2.37	+1.39	1.48	1.90	.26[c]	.37
12B (200°)	236	7.91	3.75 CH_4	3.90	4.06	0.026	3.85	3.64	1.195	83.7	2.50	+0.66	2.39	2.00	.11	.08
13A	254	7.29	3.615 C_2H_4	3.54	3.57	0.019	3.720	0.007	4.329	100	2.07[b]	+0.69	2.12	1.98	...	..
14A	247	7.17	3.594 C_2H_4 15.72 H_2	3.77	3.89	14.809	3.275	0.027	4.128	81.1	2.37	−0.43	0.94	2.23	...	..

[a] A indicates that pure ketene was employed. B means that the ketene contained about 5.6% or about 0.47×10^{-4} mole of hydrocarbon impurity. This will attach some doubt to the HC figures, but will in no way affect the value of $-\Delta CH_4$. [b] This value is an average based on a mass spectrographic analysis of the gaseous hydrocarbon. The formation of higher hydrocarbons is thus directly demonstrated. [c] In experiment 11B, the CH_4 may be high by as much as 0.08 due to an accident during the combustion of non-condensable (in liq. air) gases. This would account for the apparent discrepancy between $-\Delta CH_4$ and $-\Delta$Uns.

the extent of reaction with hydrogen (compare experiments 6 and 14A).

In the presence of methane, an additional reaction occurs which resembles that with hydrogen. Methane disappears, and the gaseous hydrocarbon (HC) becomes partly saturated, these changes being represented in Table II by $-\Delta CH_4$ and $-\Delta$Uns., respectively. The latter quantity is calculated on the assumption that no saturated hydrocarbon is polymerized, which is reasonable in view of the 2/1 ratio of hydrogen to carbon deficiencies. It is evident that the disappearance of methane is accompanied by formation of an equivalent quantity of saturated hydrocarbon. The negative temperature coefficient may be only apparent since the light intensities and quantities of methane employed were not strictly comparable. Furthermore an increased production of methane at higher temperatures has not been ruled out.

Extent of Ketene Decomposition.—Besides the experiments already reported, a large number were performed with impure ketene. In every case the % decomposition/*EI* was quite constant for similar experimental conditions. The average for ten-minute experiments at about 45° was 0.079 ± 2% when *EI* ≃ 250 watts, and 0.099 ± 4% when *EI* ≃ 490 watts, four experiments being involved in each group. For the forty-five minute exposures, the average "yields" were: (a) 0.203 ± 5% for nine runs at about 45° and an *EI* ≃ 250 watts, (b) 0.175 ± 3% for three runs at 45° and ≃ 470 watts, and (c) 0.209 ± 5% for three runs with a lamp energy input of 250 watts but at a temperature of 200°. The writer is not convinced that the intensity effect shown by the ten-minute exposures is genuine, and not due to fluctuation in lamp intensity during irradiation, occasional small differences in the relative positions of lamp and reaction vessel, or different amounts of polymer deposition. Actually, with the forty-five minute runs, the percentage decomposition is less at the higher lamp intensity, though this may be due to a depletion of the ketene in the reaction vessel (> 80% decomposed) or to partial absorption[2] of effective radiation by polymeric deposit on the walls of the reaction chamber. For any given intensity, however, the ketene decomposition seems to be unaffected by the nature of the reaction which proceeds subsequent to light absorption, whether it be ethylene formation by ketene alone, polymerization in the presence of added hydrocarbon or impurity, or reaction with methane and hydrogen to produce saturates.

Discussion

Presence of Hydrogen.—Existing evidence for the formation of methylene radicals when ketene is irradiated already has been presented briefly. Since ketene itself is thermally stable[23] to well above 400°, and since blanks on hydrogen–ketene mixtures maintained at 200° for several hours excluded any dark reaction, it is reasonable to attribute the photo-reactions observed in the presence of added gases to these methylene radicals. This is strongly supported by the observations that the amount of ketene decomposed under comparable conditions is independent of the nature of the reaction which follows light absorption. This indicates that the formation of carbon monoxide from ketene is a first order reaction, which can be only

$$CH_2CO \xrightarrow{h\nu} CH_2 + CO \qquad (1)$$

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(23) Williamson, THIS JOURNAL, 56, 2216 (1934).

The photoreaction of ketene alone may be represented by the over-all reaction

$$2CH_2CO \xrightarrow{h\nu} C_2H_4 + CO \qquad (2)$$

which is followed by formation of the condensed polymer $(CH_2)_n$. Actually, however, the ethylene probably results from a bimolecular collision of radicals as proposed by Ross and Kistiakowsky[2]

$$2CH_2 \longrightarrow C_2H_4 \qquad (3)$$

The condensation of non-volatile polymer may result from a succession of reactions such as

$$C_2H_4 \xrightarrow{CH_2} C_3H_6 \xrightarrow{CH_2} \cdots C_nH_{2n} \qquad (4)$$

starting with ethylene produced in the reaction. This is in accord with the observed effect of time, initial ethylene, and light intensity on the degree of polymerization. An increase in lamp intensity (expts. 2 *vs.* 3) increases the concentration of methylene, with resultant increased polymerization. The higher hydrocarbons present in the gas phase would simply represent an intermediate step in the polymerization process, such as has been considered reasonable by a number of other investigators.[8,24] Since the gaseous hydrocarbon mixture formed from ketene alone is completely unsaturated, it seems likely that even the higher hydrocarbon present is an olefin and not a cycloparaffin as has been suggested recently.[8] No such statement can be made with certainty however for the condensed polymer. Furthermore, since the average carbon number per molecule is 2.31–2.47, the gaseous product is chiefly ethylene.

The presence of hydrogen during exposure to ultraviolet light changes the entire complexion of the reaction. The existence of saturates among the gaseous and the non-volatile hydrocarbons, as well as the net pressure changes, requires an additional overall reaction such as

$$nCH_2CO + H_2 \longrightarrow nCO + C_nH_{2n+2}; \qquad (5)$$

and the gaseous product probably contains considerable quantities of ethane because the average chain length varies from about 2.4 to 2.6. More specifically it seems reasonable to account for the saturated products (other than methane) and the disappearance of hydrogen by assuming an interaction between methylene radicals and hydrogen such as

$$CH_2 + H_2 \longrightarrow CH_3 + H \qquad (6)$$

This can be followed by

$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (7)$$

and

$$CH_3 \xrightarrow{CH_2} C_2H_5 \xrightarrow{CH_2} \text{----} C_nH_{2n+1} \qquad (8)$$

The recombination of methyl radicals to form ethane is known to occur at ordinary temperatures even in a large excess of hydrogen,[19,25] and could easily account for the formation of saturates. Polymerization could occur through the agency of successive reactions as are represented by equation (4) and (8). Such a sequence would be terminated by disproportionation or recombination,[26] which may involve a hydrogen atom. Since the carbon and hydrogen shortages indicate the formation of saturated condensed hydrocarbon, sequence (8) seems to be more probable. The possible presence of cyclic hydrocarbons in the polymeric product is not very likely since the ratio of hydrogen to carbon exceeds two, and the fact that the formation of saturates involves the disappearance of an equivalent quantity of hydrogen eliminates this possibility as regards the gas phase since the production of cycloparaffins would yield a saturated product requiring no hydrogen utilization.

The reaction between methylene radicals and hydrogen may of course be more complicated than is represented by equation (6). It is conceivable that a trimolecular collision such as

$$2CH_2 + H_2 \longrightarrow 2CH_3 \text{ or } C_2H_6 \qquad (9)$$

occurs.

Actually the methylene radicals are not completely monopolized by the hydrogen. Table I reveals that a considerable part of the gaseous hydrocarbon remains unsaturated even when hydrogen is present, the degree of unsaturation being greater for lower initial hydrogen pressures and for shorter periods of exposure to light. A greater concentration of CH_2's, such as is produced when a higher lamp intensity is employed, would favor an increase in the quantity of unsaturates since reaction (3) is second order with respect to methylene while reaction (6) is only first order. This expectation can be verified by comparing experiment 6 (252 watts, forty-five minutes, 54% decomposition) with experiment 7 (481 watts, ten minutes, 50.3% decomposition). In both cases about 50% of the ketene is decomposed, yet a more unsaturated gaseous hydrocarbon is produced in the latter experiment which involved the greater light intensity. This is what

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[24] Lenher, THIS JOURNAL, **53**, 3752 (1931); Kassel, *ibid.*, **54**, 3949 (1932); Steacie, *Chem. Reviews*, **22**, 371 (1938).

[25] Cunningham and Taylor, *J. Chem. Phys.*, **6**, 359 (1938).

[26] (a) Moore and Taylor, *ibid.*, **8**, 396 (1940); (b) Beeck and Rust, *ibid.*, **9**, 480 (1941).

one would expect if the methylene radicals took part in two competing reactions such as (3) and (6).

It should be noted that reaction (9) is also second order with respect to CH_2 radicals; and if this reaction rather than (6) were responsible for the formation of saturates, then the hydrocarbons formed in experiments 6 and 7 should have been equally saturated. The fact that a difference was found would argue against the three body collision.

Since ethylene is formed, reactions (3) and (6) can be followed either by

$$C_2H_4 + H \longrightarrow C_2H_5 \qquad (10)$$

which is a very efficient "sink" for hydrogen atoms,[27] or by an interaction between ethylene and methyl radicals.[26b,28] The nature of the products recalls the results obtained by Taylor and Hill[27] from the mercury photosensitized reaction between ethylene and hydrogen.

The small quantities of methane which are produced even at ordinary temperatures may have as a source a number of obvious reactions, such as

$$CH_3 + H \longrightarrow CH_4 \qquad (11)$$
$$CH_3 + H_2 \longrightarrow CH_4 + H \qquad (12)$$
$$CH_2 + H_2 \longrightarrow CH_4 \qquad (13)$$

or even an interaction of methyl radicals with hydrocarbons.[29] Although methyl radicals at room temperature recombine to form ethane even in the presence of hydrogen, a small amount of methane is also produced; and this effect is much more pronounced at higher temperatures.[19,25] A comparable production of methane from ketene plus hydrogen suggests the presence of methyl radicals in this reaction and supports the operation of equation (12). It should be noted that if the methane resulted directly from equation (13), then the yield of methane should be greater when the methylene radical concentration is greater. Referring again to experiments 6 and 7 in which equivalent amounts of ketene have been decomposed at different wattages, we note that less than one-third as much methane is formed in experiment 7 than in 6, this in spite of the fact that the lamp intensity employed in 7 was about twice that in 6. This is contrary to expectations based on a direct combination of methylenes with hydrogen, and tends to exclude equation (13) as a significant source of methane. That the amount of methane is always small relative to the other hydrocarbons also argues against (13).

Mention should be made of the single experiments of Norrish and Kirkbride[6] and Bawn and Milsted[6] involving methylene and hydrogen, in both of which more methane was produced than was found with ketene. The former investigators, however, used diazomethane photodecomposed at room temperature, decomposition being carried to completion. Differences in experimental conditions coupled with the chain nature of the reaction and the fact that considerable quantities of methane are formed even when hydrogen is absent would tend to discredit any comparison with the ketene experiments. Nor is the report of Bawn and Milsted to the effect that hydrogen reacts with methylenes (from methylene halides plus sodium vapor) to form a product which is 92% methane in any way contradictory to the results here presented, since their experiments were performed at 300°, and the present author has already cited[14] the increased methane production at high temperatures.

Presence of Methane.—It is conceivable of course that methane does result from a direct combination of CH_2 and H_2, only to undergo a further reaction with methylenes to form methyl radicals

$$CH_4 + CH_2 \longrightarrow 2CH_3 \qquad (14)$$

This mechanism would equally well account for the formation of saturated hydrocarbons. The above reaction has usually been thought[5,6a] to take place readily only at elevated temperatures. Actually, Table II shows that the reaction occurs at ordinary temperatures, though less easily than the reaction of CH_2 with hydrogen. Obviously the equivalence between hydrogen disappearance and increase in saturation is best interpreted as an interaction between methylene radicals and methane to yield saturated hydrocarbons such as ethane.

This does not mean, however, that reaction (14) is necessarily an important factor in the photodecomposition in the presence of hydrogen since the amount of methane ordinarily present is never very great. Furthermore, the increased production of methane with time tends to contradict the supposition that first methane is formed by direct combination, only to experience further reaction

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(27) Bates and Taylor, This Journal, **49**, 2438 (1927); Taylor and Hill, *ibid.*, **51**, 2922 (1929); Rice and Herzfeld, *ibid.*, **56**, 284 (1934).

(28) Rice and Sickman, *ibid.*, **57**, 1384 (1935); Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937).

(29) Smith and Taylor, *J. Chem. Phys.*, **7**, 390 (1939).

with methylene radicals. Such a sequence of processes would build up a certain concentration of the intermediate methane which would then decrease as ketene is depleted. Actually the amount of methane increases as the reaction progresses.

Presence of Ethylene.—The experiments with initial ethylene confirm the findings of other workers in that the hydrocarbon deficiency indicative of higher polymer formation is considerably increased. Not only is this observed when ethylene is added to ketene alone (expts. 2 and 13) but a similar effect is obtained by adding ethylene to a ketene-hydrogen mixture (expts. 6 and 14), probably due in both cases to the greater concentration of the easily polymerized ethylene. However, it should be noted that when ethylene and hydrogen are added simultaneously (no. 14), the deficiency is less than when hydrogen is absent (expt. 13). This is comprehensible if one assumes that saturated hydrocarbons are more difficult to polymerize than unsaturates. Furthermore, the addition of ethylene (expt. 14) diminishes the quantity of methane resulting from interaction (expt. 6) of hydrogen and methylene, probably because the ethylene acts as a trap for methyl and methylene radicals.

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Summary

1. The extent of photodecomposition of ketene by ultraviolet light at about 45° appears to be independent of the nature of subsequent reactions, thus supporting the supposition that methylene radicals are produced as a result of light absorption.

2. In the presence of hydrogen the gaseous hydrocarbon is to a considerable degree saturated, the quantity of saturates increasing with time of exposure and higher initial hydrogen pressures. Simultaneously a saturated condensed polymeric product is formed. The hydrogen utilized is equivalent to the methane, higher saturated hydrocarbon and polymer present. The formation of saturates has been attributed to a reaction between hydrogen and methylenes to yield methyl radicals and hydrogen atoms, which is considered to proceed simultaneously with the recombination of methylenes to yield ethylene.

3. Saturates are formed also in the presence of methane, at the expense of the latter just as in the case of hydrogen. This is attributed to a reaction between methylene radicals and methane to form methyl radicals. The principal effect of ethylene is to increase the amount of condensed polymer.

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[CONTRIBUTION FROM THE COLLEGE OF ST. THOMAS]

The Activity Coefficients of the Undissociated Part of Weak Acids. II. Oxalic Acid

BY W. D. LARSON AND W. J. TOMSICEK

In the first paper[1] of this series, we showed that it is possible to determine the activity coefficients of undissociated molecules of weak acids by an e. m. f. method. It was found that there were only small changes in these coefficients up to an ionic strength of about 0.3.

The present study extends the method to a dibasic acid, which is considerably stronger as an acid than the acetic acid studied previously. In addition we have determined incidentally the standard e. m. f. of the mercury–mercurous oxalate electrode at 25°. For the purpose at hand, we have studied the e. m. f. at 25° of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2C_2O_4(s)},\ \mathrm{H_2C_2O_4}\ (c) \mid \mathrm{H_2} \qquad (1)$$

Materials and Apparatus.—Mercury, water, and hydrogen were treated as in the previous work.[1] Oxalic acid was a C. P. product, recrystallized twice from distilled water. Mercurous oxalate was prepared by precipitation from approximately 0.1 *N* solutions of mercurous nitrate and potassium oxalate. Oxalate was kept in excess. The precipitate was carefully washed by decantation and allowed to air-dry in a dark cupboard. It was then placed in a desiccator over calcium chloride for several weeks before use.

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[1] Larson and Tomsicek, THIS JOURNAL, **61**, 65 (1939).