

A graph, showing a comparison of results with those of other investigators, is given.

The value of the heat of reaction for the dissociation of calcium hydride is found to be 51,100 calories at 1100°K.

A brief discussion is given of the mechanism of the reaction.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE OXIDATION OF FREE ALKYL GROUPS. PHOTO- OXIDATION OF GASEOUS METHYL IODIDE

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One of the greatest difficulties facing most investigations connected with the oxidation of gaseous organic compounds such as the hydrocarbons, is the occurrence, at the relatively high temperatures which have previously been necessary, of numerous incomplete side reactions. These side reactions mask the fundamental processes, making complete elucidation of reaction mechanisms from kinetic studies almost impossible. However, it can be shown that the photochemical oxidation of alkyl halides, occurring at 0°, is essentially the oxidation of free alkyl groups and an investigation of the photo-oxidation of methyl iodide, the simplest member of the series, seemed to promise some information regarding the fundamental processes of hydrocarbon oxidation.

Previous workers studying the action of light on alkyl halides dealt with the liquids, and have, for the most part, come to conflicting conclusions. Donnan and Burke¹ and Stobbe and Schmidt² found that oxygen was necessary for decomposition of ethyl iodide as determined by the production of iodine. Job and Empschwiler³ found that oxygen was not necessary for the decomposition of either ethyl or methyl iodides. In the former case they were able to obtain what was believed to be a photochemical "threshold" of reaction at 4100 Å., which was ascribed to the fact that the energy of this wave length coincided with the then accepted value for the C-I linkage. More recently, Iredale⁴ has determined the quantum yield of ethyl iodide decomposition in the absence of oxygen. This he finds to be unity, as measured by the iodine liberated, and therefore concludes that the primary process is the separation of an ethyl group and an iodine atom. Work on gaseous methyl iodide has been confined to its absorption spectrum, first studied by Herzberg and Scheibe.⁵ The absorption is con-

¹ Donnan and Burke, *J. Chem. Soc.*, 85, 574 (1904).

² Stobbe and Schmidt, *Z. Wiss. Phot.*, 20, 57 (1920).

³ Job and Empschwiler, *Compt. rend.*, 179, 52 (1924).

⁴ Iredale, *J. Phys. Chem.*, 33, 290 (1929).

⁵ Herzberg and Scheibe, *Trans. Faraday Soc.*, 25, 716 (1928); *Z. physik. Chem.*, [B] 7, 390 (1930).

tinuous above 2000 Å., terminating in a short wave limit at 3000 Å. According to the band spectra theories of Franck and his co-workers⁶ this indicates decomposition as the primary act of light absorption. Since the band in question is characteristic of the C-I linkage it may be safely assumed that the electronic excitation concerns an electron which goes to make this bond, and therefore that the decomposition is into a methyl group and an iodine atom. Mills and Iredale⁷ have also studied the band and show that its long wave limit corresponds to the latest value for the C-I linkage, and come to the same conclusion. Absorption spectra taken by us before the publications of Herzberg and Scheibe are in agreement with these statements and indeed led to the present investigation.

Experimental

The reaction was followed by observing changes in pressure at constant volume as recorded on a mercury manometer. The cylindrical reaction vessel was of clear fused quartz, 50 mm. in diameter, 130 mm. long and having a volume of 240 cc., with two plane, circular, polished windows fused onto either end. This was fitted into a metal tank in such a way that one window was flush with the outer side of the tank, the latter being filled with ice and water to maintain a temperature of 0°. In this way the window was free from any condensation of iodine on the inside and the disturbing effects on the light intensity of ice or other foreign matter was eliminated. This would not have been possible had the vessel been totally immersed in ice water. Oxygen was taken directly from a tank, dried over calcium chloride and stored in a large bulb, from which samples could be admitted to the reaction vessel. Methyl iodide (Merck and Company) was distilled once, *in vacuo*, and kept under its own pressure, as a perfectly colorless liquid. The source of illumination was a mercury vapor lamp of the Kromayer type, so arranged that it could always be returned to exactly the same position after tilting to start the arc.

Experimental Results

The Action of Light on Methyl Iodide in the Absence of Oxygen.—Pure methyl iodide vapor undergoes a very slow decrease in pressure when illuminated for long periods and only small amounts of iodine are freed. For example, in Expt. 8, Table II, 80 mm. of methyl iodide was illuminated for six hours with a light intensity which, in the subsequent experiments with oxygen, gave a pressure decrease of 6 mm. per minute. The decrease in pressure after six hours was only 5.5 mm., iodine liberated being equivalent to 1.4 mm., and residual gas pressure when frozen out by carbon dioxide snow only about 10 mm. A series of experiments in which the change in pressure and the amount of permanent gas formed were

⁶ Franck and co-workers, *Trans. Faraday Soc.*, 21, 536 (1925).

⁷ Mills and Iredale, *Nature*, Oct. 1930, p. 604.

measured simultaneously showed an approximate parallelism between the decrease in total pressure and the increase in residual gas (Table I).

TABLE I
DECOMPOSITION OF METHYL IODIDE

Time of illumination, minutes	$-\Delta p$, mm.	P residual gas, mm.
50	0.7	0.6 ^a
50	.6	.6
70	.7	.7

^a 20 mm. of hydrogen present.

Budde Effect.—Immediately upon illumination, the pressure of the methyl iodide increased in a manner similar to the Budde effect in chlorine.⁸ The increase is proportional to the total pressure up to about 100 mm., but appears to fall off somewhat above this pressure. Thus, we were able to obtain increases up to 2 mm. at 80–100 mm. of methyl iodide, while only 1.2 mm. was observed at 110–120 mm. This effect was also obtained in the presence of oxygen, especially when the latter was in high concentration, as can be seen from the curve in Fig. 1.

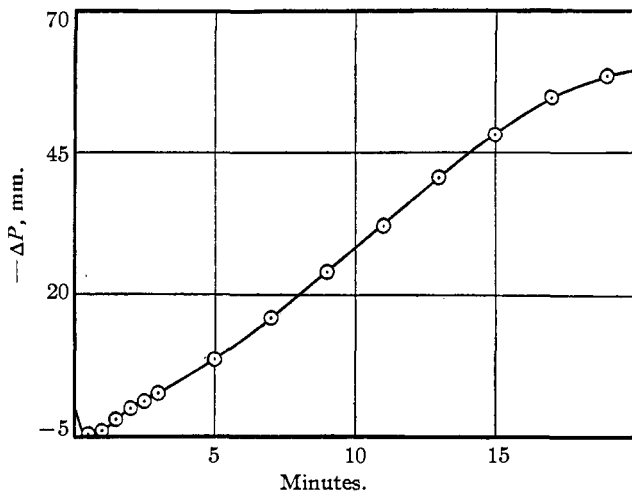


Fig. 1.—Typical experimental curve, ΔP plotted against time.

The Action of Light on Methyl Iodide in the Presence of Oxygen.—With oxygen present, the reaction velocity increases over a hundred-fold, thus becoming sufficiently rapid to permit of kinetic measurements. Iodine is liberated and upon reaching its vapor pressure of 0.03 mm. at 0°, condenses on the walls. This pressure of iodine does not absorb sufficient light to have any further photochemical influence upon the reaction. There is a variation in the total pressure decrease accompanying the re-

⁸ Kistiakowsky, "Photochemical Processes," Chemical Catalog Co., 1928, p. 138.

action from a value slightly lower than the initial pressure, at low methyl iodide pressures, to about 20% greater at high methyl iodide pressures.⁹ That iodine does not enter into the constitution of the final oxidation products was demonstrated by carrying a number of runs to completion and titrating the free iodine with *N*/10 thiosulfate. These values, together with the initial pressures of methyl iodide and oxygen, the total pressure decrease, and the value of the iodine titrations expressed in mm. of methyl iodide in the reaction vessel (1 mm. = 1.41×10^{-5} mole), are given in the first five columns of Table II. The values in the last column were calculated from the equation on page 1694.

TABLE II
IODINE TITRATIONS

P_{CHI_3}	P_{O_2}	$N/10$ thiosulfate, cc.	$-\Delta P$, obs.	$-\Delta \text{CHI}_3$	$-\Delta P$, calcd.
37.2	263.0	5.24	39.6	37.2	41.9
59.8	308.2	7.85	66.5	55.6	65.2
98.2	110.8	14.05	123.2	102.8	118.1
14.7	111.6	2.07	13.2	14.7	14.7
108.5	17.7	5.15	38.0	36.5	39.6
101.7	106.1	13.70	125.6	98.5	122.7
101.0	100.0	13.95	126.7	99.0	121.1
80.1	0.0	0.18	5.5	1.4	...
104.0	98.0	4.25	34.2	30.2	33.1 ^a
102.3	20.0	2.45	16.4	17.4	16.6 ^a
51.0	52.6	0.69	4.8	4.9	4.9 ^a

^a ΔP calcd. obtained from $-\Delta \text{CHI}_3$, since these runs were not carried to completion

The general course of the reaction is shown by the $-\Delta P/T$ curve (Fig. 1). After a small immediate expansion, the reaction proceeds rapidly for a few seconds, then slows up for several minutes before proceeding at an almost uniform rate, finally slowing down to zero when the reaction is complete. For high initial pressures of methyl iodide and oxygen, the period of uniform pressure decrease is of long duration but at low initial concentrations it practically disappears.

Identification and Analysis of Reaction Products. (a) **Noncondensable Gaseous Products.**—105.0 mm. of methyl iodide and 38 mm. of oxygen were illuminated until reaction was complete and the gaseous products slowly pumped off through a liquid air trap. No difference in pressure was observed when the liquid air was replaced by carbon dioxide-ether mixture and, when the trap was allowed to return to room temperature, the condensate exerted a pressure less by only 4 mm. than its pressure before evacuating. Hence, the hydrogen, carbon monoxide, ethane or methane formed in the reaction amounted to less than 4 mm.

⁹ The highest pressure of methyl iodide studied was 110 mm., since its vapor pressure is 141 mm. at 0° and condensation of liquid in the capillary leads to the reaction vessel introduced errors between these pressures.

(b) **Condensable Gaseous Products.**—About 1 cc. of product condensable in liquid air was collected from about fifteen experiments in which 100 mm. of methyl iodide and 60 mm. of oxygen were allowed to react to completion. This liquid was carefully distilled, giving first a fraction boiling at 38–40°, slightly colored by iodine, then a colorless mobile liquid came over between 40 and 43°, identical in appearance, solubility and smell with a sample of pure methylal.¹⁰ The vapor density, as measured by the Victor Meyer method, using 0.0185 g. of liquid, gave a value 52.5 for the molecular weight. Although the correct molecular weight of methylal is 76, pure methylal is partially hydrolyzed at 100° and 0.060 g. has an apparent molecular weight of 61.1. The condensate was soluble in water and did not smell of formaldehyde but gave the characteristic *p*-nitrophenylhydrazone of formaldehyde upon warming with an acid solution of *p*-nitrophenylhydrazine. The aqueous extract of the liquid from a flowing system, when treated with dilute resorcinol solution and poured over concentrated sulfuric acid, gave the reddish layer, tinged with purple and covered with a white, cloudy layer, characteristic of formaldehyde and methylal. Water was shown to be a constituent of the condensate by the fact that it turned anhydrous copper sulfate blue. Therefore, it was concluded that the condensable gaseous products of the reaction consist of methylal and water.

(c) **Solid Products.**—After having removed the gaseous and liquid products, the reaction vessel was washed out with ether to remove iodine. A white solid remained on the walls which was insoluble in water, alcohol or ether, but which reacted vigorously with concentrated nitric acid. Upon warming, the deposit evaporated, producing a powerful odor of formaldehyde.

(d) **Determination of Methylal, Iodine and Paraformaldehyde.**—Methylal was determined by collecting in a liquid air trap and titrating with thiosulfate after treating with a known excess of iodine. The iodine and paraformaldehyde formed were weighed in the vessel, the iodine determined by titration and paraformaldehyde obtained by difference.

TABLE III

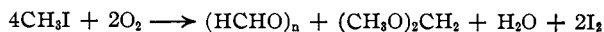
ANALYSIS OF THE REACTION PRODUCTS

$P_{\text{CH}_3\text{I}}$, 101.0 mm.; P_{O_2} , 100.0 mm.; vol., 240 cc.; temp., 0°; time, 200 minutes

Product	Gram molecules 10 ⁴	
	At beginning	At end
CH ₃ I	14.24	..
I ₂	...	14.02
(CH ₃ O) ₂ CH ₂	...	3.29
(HCHO) _n	...	3.47

¹⁰ Boiling point of pure methylal 42–43°, Timmermans and Martin, *J. chim. phys.*, 25, 411 (1928).

Therefore, the total process may be represented as



Polymerization of Formaldehyde and Synthesis of Methylal.—Formaldehyde was observed to polymerize both thermally and photochemically when introduced into the reaction vessel at 0° . The gas was produced by warming paraformaldehyde contained in a side tube. Figure 2 shows the general course of the reaction with formaldehyde alone, in the dark and in the light, and in the presence of methyl iodide or oxygen. A quantitative study of the polymerization was precluded owing to the varying rates

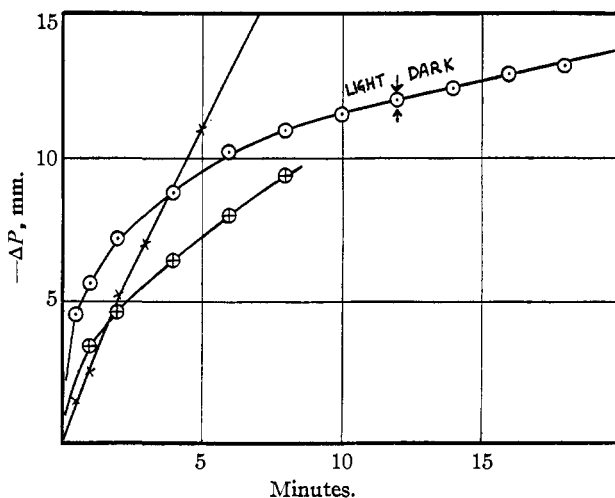


Fig. 2.— $\Delta P/T$ curves for polymerization of formaldehyde alone (dotted circles), for formaldehyde and oxygen (crosses) and for formaldehyde and methyl iodide (crossed circles).

at which the window became covered with polymer and to other undetermined factors such as the presence of small amounts of water vapor.¹¹ Thus, when the reaction vessel had been heated and evacuated for a long time, the velocity of polymerization of formaldehyde was lower, but when a small amount of methyl alcohol was introduced and allowed to react with formation of methylal and water, both the light and the dark polymerizations were greatly accelerated. According to the work of Bowen and Tietz,¹² acetaldehyde, in the presence of oxygen, partly reacts and partly polymerizes when illuminated with ultraviolet light. Formaldehyde should show similar properties, for Henri and Schou¹³ find that below 2700 Å., predissociation bands and continuous absorption occur, while

¹¹ Cf. Trautz and Ufer, *J. prakt. Chem.*, **113**, 105 (1926); Tropsch and Roelen, *Abhandl. Kennt. Kohle*, **7**, 175 (1925).

¹² Bowen and Tietz, *J. Chem. Soc.*, 234 (1930).

¹³ Henri and Schou, *Z. Physik*, **49**, 778 (1928).

above 2700, the bands show discontinuous, fine structure. Actually, the rate of polymerization is so great compared with the rate of oxidation that only polymerization is observed. However, Bredig and Goldberger¹⁴ observed photochemical decomposition at 80°. Thus, 32.0 mm. (0.0135 g.) of formaldehyde and 104.0 mm. of oxygen gave 104.9 mm. of residual gas and 0.0150 g. of paraformaldehyde. The residual gas was slowly pumped off through a liquid-air trap but no condensate formed.

Formaldehyde and methyl alcohol condense together in the dark at 0°, giving methylal and water as the principal products. The reaction is so extremely rapid that only an approximate idea of the amounts of gas introduced could be obtained. The form of the $-\Delta p/T$ reaction curve appears in Fig. 3.

Kinetic Studies

Variation of Rate of Oxidation of Methyl Iodide with Light Intensity.

The influence of varying light intensities was studied by measuring the rate after the induction period was over and a steady speed obtained. By interposing blackened copper gauze screens which had previously been calibrated on a visual photometer, it was possible to reduce the light intensity to known fractions. Table IV contains the results obtained in this manner and which point to a linear proportionality of reaction rate and light intensity to within 10%.

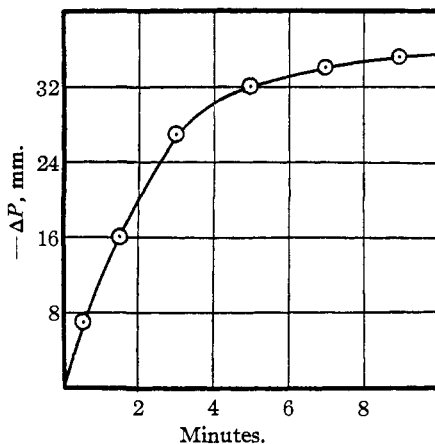


Fig. 3.— $\Delta P/T$ curve for condensation of formaldehyde and methyl alcohol.

TABLE IV
DEPENDENCE ON LIGHT INTENSITY

% light intensity	$-\Delta P$ in mm.				$-dx/dt$	$-\frac{dx/dt}{\% \text{ intensity}}$
	2 min.	5 min.	7 min.	10 min.		
100	0.6	2.1	3.3	5.1	5.60	5.60
50	0.7	1.4	1.9	2.6	2.50	5.00
35	0.5	0.9	1.4	2.2	1.83	5.23
29	0.3	0.8	1.2	2.1	1.70	5.86
100	1.0	2.9	4.1	5.3	5.60	5.60

Quantum Yield.—An attempt was made to determine an approximate quantum yield of the oxidation process. A normal solution of monochloroacetic acid, which Rudberg¹⁵ has shown to have a quantum yield of unity in the region around 2500 Å., was placed in a cell of 1 cm. thickness,

¹⁴ Bredig and Goldberger, *Z. physik. Chem.*, 110, 521 (1924).

¹⁵ Rudberg, *Z. Physik*, 24, 247 (1924).

in front of the reaction vessel. The relative rates of reaction were obtained for the cell filled with this solution and with distilled water. After having done this, the reaction vessel itself was filled with chloroacetic acid of such a concentration as to absorb the same fraction of light as the 1 cm. cell, illuminated for a given time with the arc running as before, and the resulting hydrochloric acid titrated with standardized silver nitrate and ammonium thiocyanate. Using these observations, the quantum yield was calculated as follows

$$\frac{\text{Molecules}}{h\nu} = \frac{-\frac{dp}{dt} \times 1.41 \times 10^{-5} \times 6}{\frac{\text{Moles HCl}}{\text{hr.}} \times \frac{V_{\text{H}_2\text{O}}}{V_{\text{ClCH}_2\text{COOH}}}} = \frac{4.72 \times 1.41 \times 6 \times 10^{-5}}{1.0 \times 10^{-4} \times \frac{4.65}{2.70}} = 2.3$$

where $-dp/dt$ is the maximum rate of methyl iodide consumption in mm./10 minutes obtained from Tables V and VI, 1.41×10^{-5} is the number of moles/mm. in the reaction vessel, $V_{\text{H}_2\text{O}}$ and $V_{\text{ClCH}_2\text{COOH}}$ rates with the small cell in front of the reaction vessel, filled with water and chloroacetic acid, respectively.

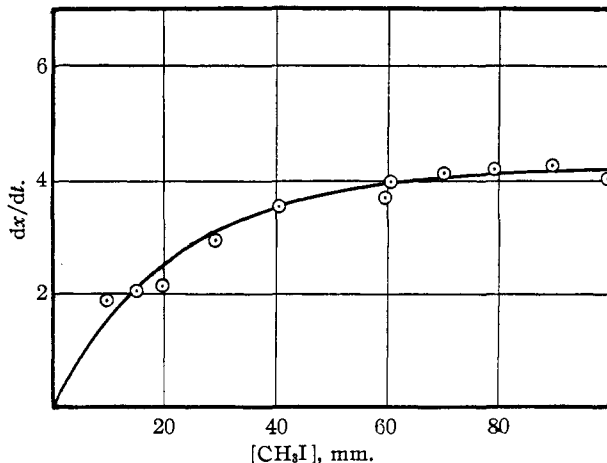


Fig. 4.—Variation of reaction rate with methyl iodide concentration, at constant oxygen concentration (100 mm.).

A value of 2 molecules/ $h\nu$ for the oxidation process would give, according to the relative rates of the oxidation and decomposition of methyl iodide, a value of 0.02 for the quantum yield of the latter.

Variation with Methyl Iodide and Oxygen Concentrations.—In all the kinetic measurements, every effort was made to maintain uniform light intensity for each series of experiments, and constant conditions throughout the whole series. The uniformity of the light intensity during a series of experiments was checked by repeating one of the earlier experiments at the end, and if no change in rate occurred, then the light intensity was

assumed to have remained constant. When an appreciable fall in intensity was detected, that series was discarded. Manometer readings were taken every minute for the first five minutes, then every five minutes and the results of each experiment plotted as $-\Delta P$ against time. The slope of the portion of these curves after the induction period was measured and ex-

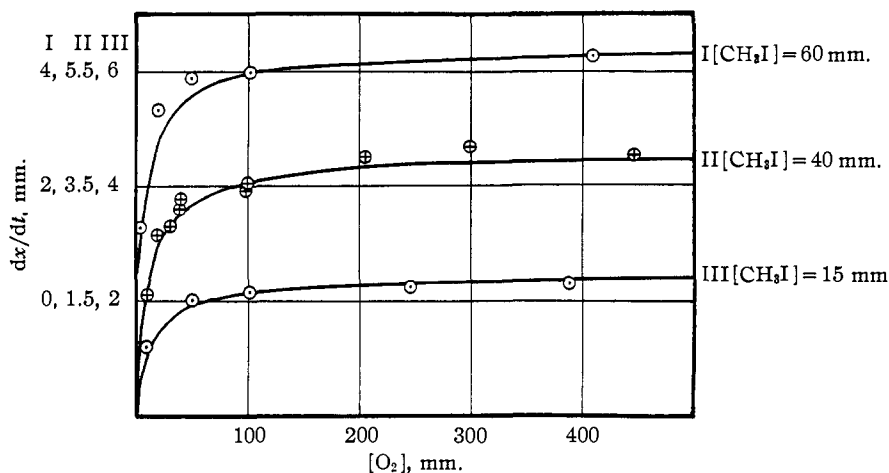


Fig. 5.—Variation of reaction rate with oxygen concentration at constant methyl iodide concentration.

pressed as mm. change/ten minutes. Table V contains the results obtained for varying concentrations of methyl iodide and constant oxygen concentration, while the relation between rate and methyl iodide concentration is illustrated graphically in Fig. 4. Taking the light intensity of this series as standard, the intensity of each subsequent series was compared with the standard intensity at 100 mm. of oxygen. Results for varying oxygen concentrations and constant methyl iodide concentrations appear in Table VI and Fig. 5.

TABLE V
DEPENDENCE OF RATE ON METHYL IODIDE CONCENTRATION

No.	CH_3I , mm.	O_2 , mm.	$-\Delta P$				$d\rho/dt$	I/I_0	dx/dt	K
			5 min.	10 min.	20 min.	30 min.				
D1	9.9	100.7	0.9	1.8	3.6	5.0	1.88	1.00	1.88	5.68
D4	19.8	102.7	.7	1.9	3.9	6.1	2.15	1.00	2.15	3.98
D5	29.1	100.2	.9	2.1	4.8	7.3	2.95	1.00	2.95	4.44
D2	59.7	100.2	1.0	2.8	6.1	9.9	3.70	1.00	3.70	4.42
D6	70.1	101.0	1.0	2.7	7.1	11.0	4.13	1.00	4.13	4.81
D3	79.2	101.6	1.0	2.5	6.3	10.9	4.20	1.00	4.20	4.82
D7	89.6	100.4	1.0	2.5	6.8	11.1	4.25	1.00	4.25	4.83
D8	99.5	107.4	1.5	3.8	7.6	11.6	4.03	1.00	4.03	4.53

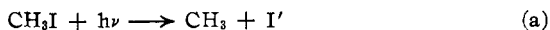
The figures under dx/dt are obtained by dividing the values under $d\rho/dt$ by the ratio of the light intensities which appear under I/I_0 .

TABLE VI
DEPENDENCE OF RATE ON OXYGEN CONCENTRATION

No.	CH ₃ I. mm.	O ₂ . mm.	5 min.	10 min.	$-\frac{\Delta P}{20 \text{ min.}}$	30 min.	$\frac{dp}{dt}$	I/I_0	$\frac{dx}{dt}$	K
J4	15.0	10.1	0.6	1.4	3.2	5.1	1.90	1.52	1.25	5.46
J6	15.6	11.2	0.6	1.4	3.2	5.0	1.82	1.52	1.20	4.85
J1	15.5	50.7	1.4	2.6	4.6	6.4	2.30	1.52	1.51	3.63
J8	15.2	101.2	0.5	2.7	5.3	8.6	3.25	1.52	2.14	4.73
J5	15.1	245.9	-.8	0.8	4.3	7.5	3.40	1.52	2.24	4.62
J3	15.7	388.1	-.4	1.3	4.1	8.2	3.48	1.52	2.30	4.56
C6	40.1	10.4	.0	0.5	1.5	2.6	1.60	1.00	1.60	4.11
C4	40.0	19.6	.5	1.6	4.4	6.8	2.65	1.00	2.65	5.07
C5	41.8	31.3	.1	1.3	4.0	6.8	2.80	1.00	2.80	4.53
C9	39.2	39.3	.9	2.3	4.9	8.1	3.27	1.00	3.27	5.05
C2	40.1	39.4	.4	1.7	4.7	7.8	3.10	1.00	3.10	4.79
C1	39.5	41.3	.3	1.5	4.8	7.7	3.27	1.00	3.27	4.99
C3	38.8	98.7	.0	1.0	4.0	7.5	3.42	1.00	3.42	4.58
C11	40.7	100.2	.7	2.4	5.6	9.1	3.54	1.00	3.54	4.68
C10	40.0	204.9	1.2	2.6	5.9	10.7	4.00	1.00	4.00	4.99
C7	39.4	299.3	0.8	2.3	5.8	9.9	4.18	1.00	4.18	5.02
C12	40.8	446.8	.9	2.7	6.6	10.7	4.05	1.00	4.05	4.89
C8	39.3	614.2	.1	2.0	5.9	10.0	4.00	1.00	4.00	4.80
I3	61.6	5.3	0.5	1.8	4.0	6.0	2.30	1.78	1.29	4.53
I2	61.6	21.0	1.7	3.8	10.5	16.2	5.95	1.78	3.33	5.59
I4	60.5	50.3	1.6	4.2	10.5	17.3	6.95	1.78	3.89	5.14
I1	60.6	102.5	2.2	5.6	12.7	20.5	7.10	1.78	3.98	4.73
I6	60.5	103.0	1.3	3.8	10.1	17.5	7.00	1.78	3.92	4.66
I5	59.7	409.1	-0.7	2.9	10.8	18.1	7.60	1.78	4.26	4.67

Theoretical Discussion

Decomposition of Methyl Iodide.—Since the absorption spectrum of methyl iodide is continuous, we may assume that the primary process of light absorption is



The rate of this reaction will be proportional to the number of quanta absorbed in unit time. From the absorption laws, then

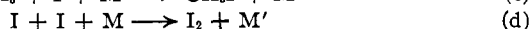
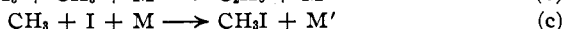
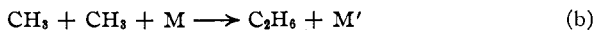
$$-\frac{d[\text{CH}_3\text{I}]}{dt} = I_1(1 - e^{-[\text{CH}_3\text{I}]\alpha_1 d}) + I_2(1 - e^{-[\text{CH}_3\text{I}]\alpha_2 d}) + \dots$$

where I_1, I_2 , etc., are the intensities of the various lines of the mercury arc, α_1, α_2 , etc., are the absorption coefficients of methyl iodide for these lines, both expressed in appropriate units, and d is a constant, being the length of the vessel. Within the accuracy of our experiments, we are justified in taking as an approximation

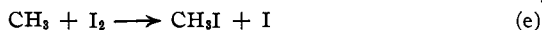
$$-\frac{d[\text{CH}_3\text{I}]}{dt} = I(1 - e^{-[\text{CH}_3\text{I}]\alpha})$$

where I and α are over-all wave lengths, d being included in α , and $[\text{CH}_3\text{I}]$ is expressed in mm. of mercury.

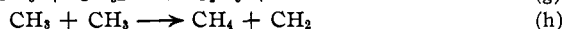
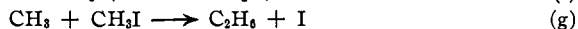
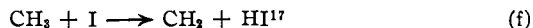
In the absence of oxygen, the following reactions may take place



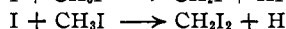
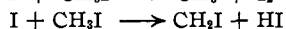
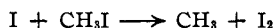
The above processes involve collision either with a third molecule or with the wall (M). It must, however, be noted that any iodine atom colliding with the wall will probably be adsorbed or "cleaned up" as, for instance, is the case with hydrogen atoms, there to combine with other iodine atoms already absorbed. Bonhoeffer and Farkas¹⁶ have found this to be the case in the photochemical decomposition of hydrogen iodide at low pressures. As soon as iodine molecules have been formed, the following two body process may occur



and the bimolecular reactions



are also possible. In addition, the presence of iodine on the walls will effectively reduce the probability of occurrence of the wall reaction (b) which can then only take place as a three-body process in the gas phase, for the probability of two methyl groups recombining on a surface of iodine will be much less than the probability of their combination with iodine itself. On the other hand, the reactions



are thermally impossible ($\text{H}-\text{I} = 69 \text{ Cal.}$; $\text{C}-\text{H} = 120 \text{ Cal.}$; $\text{I}-\text{I} = 35 \text{ Cal.}$; $\text{C}-\text{I} = 68 \text{ cal.}$).¹⁷ The very low rate of formation of permanent gas and of free iodine when pure methyl iodide is illuminated indicates that the processes (b) and (g) must be of relatively infrequent occurrence. Therefore, methyl groups will, for the most part, reform methyl iodide by reason of reactions (c) and (e) and the remainder will form ethane according to (b) and (g) with (f) and (h) occurring as a subsidiary reaction. Also, the probability of (g) occurring must be extremely small; otherwise, owing to the relatively high concentration of methyl iodide as compared with iodine, there would be a rapid formation of ethane and consequently a high rate of pressure decrease.

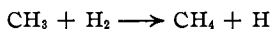
From one point of view, methyl may be regarded as a pseudo halogen and reaction (g) could, therefore, be considered as an elementary replacement of I by CH_3 . However, the fact that every "Elementarprozess" does not

¹⁶ Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

¹⁷ The second hydrogen atom stripped from a carbon atom has a heat of linkage of only 30 k. cal., Mecke, *Z. Elektrochem.*, **36**, 595 (1930).

occur on every collision, even when energetically possible, has become recognized during the past year. Kistiakowsky¹⁸ has shown, for example, that oxygen atoms do not react with hydrogen molecules. The subject has been summarized by Franck and Rabinowitsch.¹⁹

In a paper which has just appeared, Hartel and Polanyi²⁰ have described a series of reactions of this type which, although exothermic, have an activation energy, and, therefore, do not go on every collision. Among those considered by them are the reaction of sodium atoms with alkyl halides, and methyl groups with hydrogen molecules. They find that the activation necessary for the exothermic reactions of sodium with methyl halides varies from 0 with methyl iodide to >25 Cal. with methyl fluoride, showing that it is a specific property of each reaction. In the case of methyl plus a hydrogen molecule, they give an activation energy of 8 Cal. In some experiments with methyl iodide and hydrogen in light, we found no effect on the rate of decomposition as measured by permanent gas formed, which would have been the case had the reaction



been a probable one. An activation energy of 8 Cal. is equivalent to 10^6 collisions per reaction at 0° .

Methyl Iodide and Oxygen.—The photochemical oxidation of methyl iodide proceeds sufficiently rapidly to allow determinations of the rate of removal of methyl iodide to be made, and of the influence of such factors as light intensity, concentration of reactants, etc., upon this rate. Results obtained from a series of such measurements are set forth in the experimental part above. It is evident from Figs. 4 and 5, that the variation in the reaction rate follows fixed rules, which must have their origin in those fundamental chemical processes whose aggregate effect makes up the measured reaction. If, then, we can construct a mechanism of fundamental reactions, based on sound theoretical considerations, which will take account of all the observed phenomena and whose kinetic equation affords a complete description of the dependence of the reaction rate upon its physical parameters, then we can assume that mechanism to represent the true state of affairs, at least to the extent of our present knowledge.

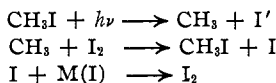
For all practical purposes, the mechanism need only be concerned with reactions which make an appreciable contribution to the total rate of reaction. Now, all those reactions which we considered in the photochemical decomposition of methyl iodide, may be taken as occurring in the oxidation process also, but fortunately the greater part of them can be omitted from our kinetic considerations. Thus all reactions involving the formation of methane or other permanent gases (reactions b, f, g and h)

¹⁸ Kistiakowsky, *THIS JOURNAL*, **52**, 1868 (1930).

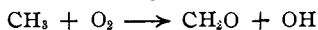
¹⁹ Franck and Rabinowitsch, *Z. Elektrochem.*, **36**, 794 (1930).

²⁰ Hartel and Polanyi, *Z. physik. Chem.*, [B] **11**, 97 (1930).

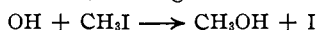
can be neglected because experiment shows them to be over a hundred times slower than the oxidation process. Reaction (c) has been shown to be extremely improbable as a wall reaction and its extremely infrequent occurrence in the gas phase does not warrant its inclusion in our kinetic treatment, leaving only three of these processes which can materially affect the rate of oxidation.



In the presence of oxygen, methyl may react in the following way

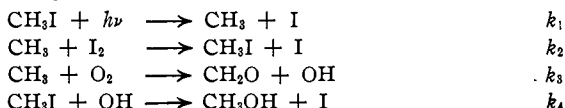


Now, the possible three-body reaction of OH with CH₃ or I, can be neglected as being extremely infrequent, while reactions between OH and I₂ or O₂ are thermally improbable, leaving



to account for the removal of hydroxyl groups.

Since the rate of formation of iodine molecules from the atoms does not affect the rate of removal of methyl iodide, and, assuming that the formaldehyde and methyl alcohol formed will not play any part in these reactions, we have only to consider the following reactions to determine the rate of removal of methyl iodide



Therefore

$$-\frac{d[\text{CH}_3\text{I}]}{dt} = k_1 I_0 (1 - e^{-\alpha[\text{CH}_3\text{I}]}) - [\text{CH}_3][\text{I}_2]k_2 + [\text{CH}_3\text{I}][\text{OH}]k_4$$

Assuming stationary concentrations of OH and CH₃, we can equate their respective rates of formation and removal as follows

$$\text{OH: } [\text{CH}_3][\text{O}_2]k_3 = [\text{CH}_3\text{I}][\text{OH}]k_4 \quad (1)$$

$$\text{CH}_3: \quad k_1 A = [\text{CH}_3][\text{I}_2]k_2 + [\text{CH}_3][\text{O}_2]k_3 \quad (2)$$

$$\text{where } A = I_0 (1 - e^{-\alpha[\text{CH}_3\text{I}]})$$

Therefore

$$[\text{CH}_3] = \frac{[\text{CH}_3\text{I}][\text{OH}]k_4}{[\text{O}_2]k_3}$$

whence

$$\frac{[\text{CH}_3\text{I}][\text{OH}]k_4}{[\text{O}_2]k_3} = \frac{A k_1}{[\text{I}_2]k_2 + [\text{O}_2]k_3}$$

But, from Equations 1 and 2

$$k_1 A - [\text{CH}_3][\text{I}_2]k_2 = [\text{CH}_3\text{I}][\text{OH}]k_4$$

and consequently

$$\begin{aligned} -\frac{d[\text{CH}_3\text{I}]}{dt} &= 2[\text{CH}_3\text{I}][\text{OH}]k_4 \\ &= \frac{2 A k_1 [\text{O}_2]k_3}{[\text{I}_2]k_2 + [\text{O}_2]k_3} \end{aligned}$$

Now, it is evident from Table II that for the initial part of the reaction, that is, the portion considered in the kinetic measurements, $-d[\text{CH}_3\text{I}]/dt$ is approximately equal to $-dP/dt$ and

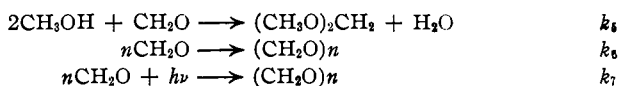
$$\frac{dx}{dt} = \frac{2I_0 (1 - e^{-\alpha[\text{CH}_3\text{I}]})[\text{O}_2]}{\frac{k_2}{k_3} [\text{I}_2] + [\text{O}_2]}$$

assuming k_1 to be equal to unity.

It is to be noted that at high oxygen concentrations this mechanism gives a quantum yield of 2, in terms of methyl iodide oxidation per quantum, which is the experimentally determined value.

Furthermore, even if we consider the total reaction, which will yield a slightly larger pressure decrease than corresponds to methyl iodide removed, as can be seen from the higher values in Table II, we can show that the kinetic equation remains essentially the same.

The formaldehyde and methyl alcohol react in the following ways



Assuming stationary concentrations of formaldehyde and methyl alcohol, we arrive at the equations

$$\text{CH}_3\text{OH: } [\text{CH}_3\text{I}][\text{OH}]k_4 = [\text{CH}_3\text{OH}]^2[\text{CH}_2\text{O}]k_5 \quad (3)$$

$$\text{CH}_2\text{O: } [\text{CH}_3][\text{O}_2]k_3 = \frac{[\text{CH}_3\text{OH}]^2[\text{CH}_2\text{O}]k_5}{2} + k_7A' + [\text{CH}_2\text{O}]^n k_6 \quad (4)$$

Equation 4 assumes the form it does if the rate of removal of formaldehyde by the methylal reaction is only half that of an equal volume of methyl alcohol, as we have shown to be true.

By a reasoning similar to that used above it may be shown from (1), (2), (3) and (4) that

$$\begin{aligned} \frac{d(\text{CH}_2\text{O})}{dt} &= \frac{d(\text{CH}_3\text{OH})}{dt} = \frac{d[(\text{CH}_3\text{O})_2\text{CH}_2]}{dt} \\ &= \frac{2d(\text{CH}_2\text{O})_n}{dt} = \frac{k_1A[\text{O}_2]k_3}{[\text{I}_2]k_2 + [\text{O}_2]k_3} \end{aligned} \quad (5)$$

Since the total pressure decrease must be proportional to the sum of these rates, we have again

$$-\frac{dP}{dt} = K \frac{k_1A[\text{O}_2]k_3}{[\text{I}_2]k_2 + [\text{O}_2]k_3}$$

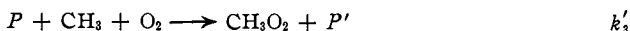
and, therefore, the rate of pressure decrease is proportional to the rate of decrease of methyl iodide concentration. Approximate values for the constants α and k_2/k_3 were derived from the experimental results and, using these figures, the value of K was calculated and appears in the last column of Tables V and VI.

$$-\frac{dP}{dt} = \frac{K (1 - e^{-0.047[\text{CH}_3\text{I}]})[\text{O}_2]}{12.3 + [\text{O}_2]} \quad (6)$$

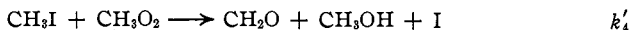
Curves appearing in Figs. 4 and 5 were obtained theoretically from this equation and the experimental points plotted for purposes of comparison.

The constant 12.3 is equal to $k_2/k_3[I_2]$ and since $[I_2] = 0.03$ mm., $k_2/k_3 = 410$. Therefore, if methyl reacts with iodine on every collision, only one collision in about every four hundred between methyl and oxygen can be fruitful. Since this reaction is strongly exothermic, this is another elementary reaction which does not go on every collision, such as we have already discussed on page 1700. A more general discussion of the relative collision efficiencies of these reactions will be included in a forthcoming paper.

Besides the mechanism involving intermediate production of free hydroxyl groups, which is given above, another alternative mechanism is possible. The comparative inefficiency of the collisions between methyl and oxygen suggests the possible intervention of a third body and, indeed, the number of collisions of this type would be roughly of the same order as the number of efficient collisions between methyl and oxygen. The theory of intermediate peroxide formation, which has received considerable support in the case of hydrocarbon oxidation,²¹ at once suggests itself and requires the following scheme of reaction: methyl iodide would be dissociated according to reaction (1) above and would be formed by reactions (2) above. Since the formation of a peroxide would necessitate a three-body process, we have



where P represents the total pressure



while formaldehyde and methyl alcohol would be removed by reactions (5), (6) and (7) of the previous scheme, and by precisely the same reasoning that was used to derive Equation 6, we can obtain the equation

$$-\frac{dP}{dt} = \frac{K(1 - e^{-\alpha[CH_3I]})[O_2]}{\frac{k'_2[I_2]}{k'_3[P]} + [O_2]} \quad (7)$$

According to this, increase in total pressure at low oxygen concentrations should increase the reaction velocity. Thus, comparing 50 mm. of methyl iodide and 10 mm. of oxygen, with 50 mm. of methyl iodide, 10 mm. of oxygen and 40 mm. of nitrogen, as predicted from Equation 7, the respective rates ought to be in the ratio of 1:2.35. Actually, we find by experiment that they are as 1:0.9. It would seem then, that the photochemical oxidation of methyl iodide is to be represented by the hydroxyl scheme and kinetic Equation 6, rather than by the peroxide scheme and Equation 7.

²¹ Lewis, *J. Chem. Soc.*, 58 (1930); Brunner and Rideal, *ibid.*, 1162 (1928); Thompson and Hinshelwood, *Proc. Roy. Soc. (London)*, A125, 277 (1929); Callendar, *Engineering*, 123, 147, 182, 210 (1927); Fort and Hinshelwood, *Proc. Roy. Soc. (London)*, A125, 218 (1930).

Without wishing to lay too much stress upon this conclusion, the writers would point out that such a "hydroxyl" scheme is at least as probable a mechanism of hydrocarbon oxidation as a peroxide scheme, especially when it is considered that hydrocarbons generally do not react appreciably with oxygen until they reach temperatures at which dissociation begins to occur.

One of the authors (R. S.) wishes to express his indebtedness to the Commonwealth Fund for a Fellowship which enabled him to take part in the research.

Summary

1. Gaseous methyl iodide decomposes extremely slowly when illuminated with ultraviolet light, and exhibits a Budde effect similar to that obtained with chlorine.

2. The photo-oxidation of gaseous methyl iodide has been shown to be essentially an oxidation of free methyl groups.

3. Iodine, paraformaldehyde, methylal and water are practically the sole products of reaction.

4. The kinetics of the process have been investigated and found to agree with the theoretically derived mechanism.

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THE OXIDATION OF IODIDE ION BY PERSULFATE ION. IV. KINETICS OF THE REACTION IN HIGHLY DILUTE AQUEOUS SOLUTION

BY CECIL V. KING AND MORRIS B. JACOBS

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Introduction

A combination of Brönsted's equation for the velocity of a bimolecular ionic reaction and the Debye-Hückel limiting expression for the activity coefficient of an ion (in water at 25°) leads to the expression

$$\log k = \log k_0 + z_A z_B \sqrt{\mu} \quad (1)$$

where k is the velocity constant observed and k_0 that at zero ionic strength. Introduction of the Debye-Hückel expression necessitates velocity measurements at very low salt concentrations to test this expression; previously only three ionic reactions have been measured at concentrations below $\sqrt{\mu} = 0.14$ and two others below $\sqrt{\mu} = 0.25$. An excellent summary of this work has been given by Livingston¹ and we have reproduced his plot of $(\log k - \log k_0)$ against $\sqrt{\mu}$ for the various reactions, including for comparison (in black circles, Fig. 1) some of our measurements on the persulfate-iodide reaction.

¹ Livingston, *J. Chem. Ed.*, 7, 2887 (1930).