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The Photolysis of Methyl Iodide*,†

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The photolysis of methyl iodide by 2537A radiation has been investigated under varying conditions of light intensity, temperature, iodine removal by rotating silver vanes and added carbon dioxide. Methane production is independent of temperature in the range 40°–100°C, directly dependent on the light, nearly independent of efficiency of iodine removal and is inhibited by carbon dioxide. Ethane production increases rapidly as the efficiency of iodine removal is increased. It is argued that methane results from the reaction, with iodide, of "hot" methyl radicals produced in the primary reaction. Ethane is formed from the association of cold methyl radicals. A possible decrease in ethane production with increase in temperature can be accounted for by the reaction of CH_3+I_2 having an activation energy of $\sim$1 kcal.

THE continuous absorption band with a maximum at 2500A exhibited by methyl iodide, first observed by Herzberg and Scheibe[1] has been interpreted by Goodeve and Porret.[2] On the basis of calculated and observed extinction coefficients, the band is shown to be complex involving transitions to two separate upper states. One band leads to dissociation giving an excited iodine atom ($^2P_{\frac{1}{2}}$) and an unexcited methyl; the other band gives products neither of which is excited. From the data given by Goodeve and Porret it appears that at 2537A, absorption in the band resulting in an unexcited iodine atom is extremely small compared to the absorption resulting in the excited iodine. Taking the energy of the $C-I$ bond as 54 kcal. and the excitation energy of the iodine as 22 kcal., conservation of momentum requires that the absorption of 112 kcal./mole by CH_3I will result in methyl radicals with 32 kcal. excess energy. It is not at all obvious in the previous studies of methyl iodide photolysis that sufficient attention has been paid to the fact that these methyl radicals are "hot," nor has its bearing on their ultimate fate as methane and ethane been investigated. To this end a careful study of these products under varying conditions of temperature, light intensity, iodine removal and added carbon dioxide has been made.

EXPERIMENTAL

The purification of methyl iodide as usually recommended in the literature includes drying with P_2O_5. If any alcohol is present such a treatment could give ether and acetal which would remain in the final product. Merck methyl iodide was therefore freed from iodine and oxygen compounds by passage through a column, 30 cm long and 9 mm diameter, packed with 200 mesh silica gel. The effluent was fractionally distilled through a vacuum-jacketed column, 75 cm long and 15 mm in diameter, packed with 3 mm diameter glass spirals, using a 20 to 1 reflux ratio. The entire distillate came over at 42.3°C but only the middle third fraction was used. This was stored at room temperature in the absence of air in a Pyrex bulb closed with a stopcock greased with a fluorocarbon oil.[3] Two pieces of copper wire served to pick up traces of iodine which might be formed on standing. After six months' storage the liquid remained colorless and the wire showed no evidence of corrosion.

The purification procedure was checked with the aid of a Baird Associates infra-red recording spectrophotometer. By comparing spectrograms of the purified CH_3I with those of CH_3I containing known added amounts of impurities, the product was shown to contain less than 0.2 percent oxygen containing impurities. It may be stated here that the bands reported by Courtoy[4] at 1182 and 1167 cm^{-1} do not belong to methyl iodide but probably to dimethyl ether as an impurity in his sample.

The reaction vessel was 500 cc spherical flask of fused silica. It was attached to the system through a ball joint. A Pyrex enclosed magnetic stirrer to which vanes of silver foil were fastened was operated by a rotating horseshoe magnet. The stirrer was introduced through a ground joint in the neck of the reaction vessel, the vanes being coiled on the stirrer axis. During rotation the vanes spread out and served not only to effect iodine removal and thus alter the stationary methyl radical concentration but also to maintain good mixing of the contents of the reaction flask.

The light source was a low pressure mercury arc, Hanovia SC 2537. To remove 1849A radiation a 2 mm filter of Corning 791 glass was interposed between the lamp and reaction vessel. The lamp was in the shape of a rectangular grid covering an area approximately 10 by

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[1] G. Herzberg and G. Scheibe, Zeits. f. physik Chemie. **B7**, 390 (1930).

[2] D. Goodeve and C. F. Porret, Proc Roy. Soc. **A165**, 31 (1938).

[3] Because of the solubility in methyl iodide other greases were not found satisfactory. Perfluorolube oil FC-334, with a boiling point 190–210°C at 10 mm was supplied through the courtesy of the Jackson Laboratories, E. I. du Pont de Nemours, Inc.

[4] C. Courtoy, Ann. Soc. Sci. Bruxelles, Ser I, **60**, 122 (1946).

15 cm. The diameter of the quartz tubing was 8 mm. A Sola constant voltage transformer maintained an input voltage of 110 volts to a Variac supplying 38 volts at 1.0 amp. to a 5000 volt, 1.32 kva transformer which operated the lamp. An aluminum reflector was placed behind the lamp and the whole was housed in a large box which prevented drafts affecting the lamp performance while permitting sufficient ventilation to prevent overheating. The relative position of the lamp and reaction vessel was carefully reproduced for all runs.

The filling manifold was a Pyrex tube one end of which led to the reaction flask while the other end led to a U-trap in series with a conventional high vacuum pump system. The U-trap immersed in liquid nitrogen prevented mercury vapor from diffusing into the reaction vessel. The filling manifold carried a number of freeze-out bulbs. Prior to each run, a portion of the methyl iodide, purified as described above, was frozen on the walls of one of these bulbs immersed in CO_2-methanol mush and thoroughly degassed by evacuation after repeated thawing and refreezing. The residual pressure above the methyl iodide after freezing in liquid nitrogen was less than 1 micron as read on a Pirani gauge connected to the filling manifold and less than 10^{-5} mm as read on a McLeod gauge on the vacuum manifold side of the U-trap.

The bulb containing the degassed methyl iodide was now immersed in water at 20°C and opened to the previously evacuated reaction vessel thermostated at 40°C. After attainment of the 331 mm equilibrium pressure of methyl iodide (as measured on a nickel diaphragm gauge attached to the reaction vessel through a Kovar metal to Pyrex seal) the reaction vessel was closed and the oven temperature raised to the desired value. The gauge now served to indicate the average temperature as well as the pressure in the reaction vessel provided room temperature was high enough to prevent condensation in the tubing external to the oven.

After irradiation, the reaction vessel was opened to a bulb immersed in secondary-butyl chloride mush at $-131°C$. Products volatile at this temperature could diffuse through a U-tube safety trap also at $-131°C$ and were frozen out in a trap immersed in solid nitrogen obtained by pumping on liquid nitrogen until the pressure was reduced to 15 mm or less. The residual CH_3I was thawed and refrozen at least four times and a total of at least one half hour was allowed for the diffusion of products.

In the runs with added CO_2, the CH_3I-CO_2 mixture was frozen out at -145 to $-150°C$. This temperature was obtained by passing dry tank nitrogen at an appropriate rate into the low temperature bath immersed in liquid nitrogen. Blank runs with synthetic mixtures of methane, ethane, ethylene, carbon dioxide, and methyl iodide served to check the efficiency of the method of product recovery.

The products frozen out in the solid nitrogen trap were vaporized and transferred by means of a Toepler pump to a 60 cc gas cell fitted with rock salt windows. The infra-red absorption by the contents was then measured in the range 2–16μ using the Baird instrument already mentioned. CH_4 absorption at 7.7μ, C_2H_6 at 6.8μ, C_2H_4 at 10.6μ and C_2H_2 at 7.3μ were used for the analysis. The spectrogram obtained for the products from a given run was matched against those given by known amounts of pure gases under the same optical conditions of the spectrophotometer. In this way variations in the resolution of the instrument due to adjustments of the optical system during the course of the research were not of significance. The values obtained in this way for methane are good to ± 1 mm. The values for ethane are good to ± 5 mm since the band at 6.8μ is not strong but has the advantage that it does not appreciably overlap the methane bands.

RESULTS

The results obtained are tabulated in Table I. A direct comparison with the six runs reported by West and Schlessinger[5] is difficult because of the considerable differences in the quantity and composition of the product gas obtained by them in different experiments under nearly identical conditions. The relative ratios of methane and ethane found in presence and absence of silver are in approximate agreement. The ethylene yields reported by West and Schlessinger are surprisingly high especially since Jungers and Yeddanapalli[6] have shown that methyl radicals from the photolysis of methyl iodide induce polymerization in ethylene. The error probably arises from the use of fuming sulfuric acid as the quantitative absorbent for ethylene.

The present results are much more self-consistent. Complete reproducibility of results is, however, hardly to be expected in view of several uncontrollable variables including stirring speed, aerodynamic shape of the silver vanes and extent of reaction of iodine on the silver surface. The rate of iodine fixation probably decreases as the silver surface becomes progressively covered with silver iodide during a run. Such variables affecting the iodine concentration and hence also the methyl radical concentration might be expected to affect both the methane and ethane yields. That methane formation is nearly constant when corrected to 100 percent area of illumination is significant suggesting that methane is formed from methyl radicals whose concentration depends only on the amount of light absorbed and is independent of other variables. Such would be the "hot" radicals produced in the primary act of light absorption. The variability in ethane yield, on the other hand, and especially its obvious dependence on stirring speed suggests that it must result from "cold" methyl radicals.

This conclusion is amply verified by the results in Table I which may be summarized as follows: (1) The

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[5] W. West and L. Schlessinger, J. Am. Chem. Soc. **60**, 961 (1938).

[6] V. C. Jungers and L. M. Yeddanapalli, Trans. Faraday Soc. **36**, 483 (1940).

TABLE I. Results of photolysis of methyl iodide by 2537A light, (initial pressure CH_3I, 331 mm measured at 40°C inside reaction vessel)

Run No	Conditions and remarks	Percent area of illumination[a]	Temp °C	Time hr.	mm pressure in infra-red analytical cell[b] @25°C C_2H_6	CH_4	C_2H_4	C_2H_2	Av. rates corrected to 100 percent area of illumination $\frac{\Delta(C_2H_6)^b}{\Delta t}$	$\frac{\Delta(CH_4)^b}{\Delta t}$
1	Ag present (2 leaves), moderate stirring	100	40	16	135	50	trace	trace	8.4 mm/hr	3.1 mm/hr
2	Ag present (2 leaves), moderate stirring	100	100	8	60	24	trace	—	7.5	3.0
3	Ag present (1 leaf), stirrer jammed part way through run	50	40	16	31	24	trace	—	3.9	3.0
4	Ag present (2 leaves), stirrer also jammed	50	40	16	31	25	trace	—	3.9	3.1
[c]5	No Ag, no stirring, reaction vessel gradually fogged with decomposition products during run	50	40	(*ca.* 2 weeks)	~30	~300	trace	trace		
6	Ag present (2 leaves), rapid stirring	50	40	16	130	24	trace	trace	16.3	3.0
7	Ag present (2 leaves), no stirring	50	40	16	20	24	trace	—	2.5	3.0
8	No Ag, no stirring	50	40	16	trace	20	—	—	—	2.5
9	No Ag, no stirring	50	100	16	trace	19	—	—	—	2.4
10	No Ag, CO_2 (331 mm @ 40°C), added	100	40	16	trace	25	—	—	—	1.6
11	No Ag, no stirring	100	40	16	trace	38	—	—	—	2.4
12	No Ag, CO_2 (331 mm @ 40°) added	100	40	16	trace	21	—	—	—	1.3
13	No Ag, CO_2 (662 mm @ 40°C) added	100	40	16	trace	16	—	—	—	1.0
14	Ag present (2 leaves), stirring, 700–900 rpm	100	40	16	135	47	trace	trace	8.4	2.9
15	Ag present (2 leaves) stirring, 700–1000 rpm	100	100	16	82	50	trace	—	5.1	3.1

[a] In the experiments indicated, 50 percent of the Corning 791 Filter was made opaque by coating with a thin layer of Aquadag and scraping away alternate $\frac{1}{16}$-inch strips

[b] Pressures of products refer to pressures inside the analytical cell which has approximately 0.1 the volume of the reaction vessel

[c] With the exception of run No. 5, fogging of the reaction vessel with decomposition product (i.e. CH_2I_2, I_2, C_2H_4 polymer?) was negligible, in that only a very slight film was noticeable on the walls after the run. Prior to the next run, this was burned off at red heat in air. In the runs without silver small quantities of a brown liquid (i.e CH_2I_2, I_2) deposited in the tubing external to the oven. In the runs with silver much smaller amounts of this liquid product were deposited.

apparent activation energy for methane formation in the presence and absence of silver is zero in the temperature range 40°–100°C; (2) In the absence of silver, ethane yield is negligible, while in presence of silver ethane is formed in amounts up to five times that of methane, dependent on stirring conditions. In the apparatus used, rapid stirring with silver foil increased ethane formation by as much as four times that with the foil stationary; (3) The presence of silver increases methane formation by about 25 percent of the methane yield in the absence of silver, and stirring with the silver is without effect; (4) The presence of CO_2 cuts down the rate of methane formation. Quantitatively the effect is represented by the equation:

$$\left[\frac{\Delta[CH_4]}{\Delta t}\right]_{CO_2\ \mathrm{present}} = \frac{[CH_3I]}{[CH_3I]+\alpha[CO_2]}\left[\frac{\Delta[CH_4]}{\Delta t}\right]_{CO_2\ \mathrm{absent}}$$

relating the rates of methane production in presence and absence of CO_2 to the partial pressures of CH_3I and of CO_2. The value of the constant α may be calculated from runs 10, 11, 12 and 13 and gives an average value of 0.67; (5) The effect of temperature on ethane production is not large in the range studied. The effect, if any, as judged from runs 14 and 15 may be to decrease the ethane yield as the temperature increases.

DISCUSSION

Accepting the primary reaction to be:

$$CH_3I \rightarrow CH_3^* + I(^2P_{\frac{3}{2}}) \tag{1}$$

in which for 2537A radiation, CH_3^* represents a methyl radical with excess energy amounting to 32 kcal. per mole, the above results necessitate the following reactions to account for the products.

$$CH_3^* + CH_3I \rightarrow CH_4 + CH_2I \tag{2}$$

$$CH_3^* + M \rightarrow CH_3 + M \tag{3}$$

$$CH_3 + CH_3 = C_2H_6 \tag{4}$$

$$I + I = I_2 \tag{5}$$

$$CH_3 + I_2 \rightarrow CH_3I + I. \tag{6}$$

Reaction (2) as the sole source of methane seems necessary on the basis of (a) zero activation energy for its production (b) independence of iodine fixation by silver and (c) inhibition by CO_2. If normal methyl radicals reacting with methyl iodide produced methane one would expect by analogy with other similar reactions an energy of activation of up to 8 kcal. The temperature range covered should have been ample to show any such effect. Furthermore, since the stationary concentration of normal methyl radicals must be highly dependent on the efficiency of iodine fixation by silver, the independence of the latter in the methane production rules out any reaction of the normal radicals. Finally the value of 0.67 for α previously found now has an obvious interpretation meaning that CO_2 is 67 percent as effective as methyl iodide in cooling a "hot" methyl radical by collision.

As additional support of the above argument there may be cited the work of Ogg, reported by Williams and Ogg,[7] on the effect of an inert gas in the photolysis of a mixture of methyl iodide, iodine, and hydrogen chloride. The inert gas inhibited the reaction of methyl radicals with hydrogen chloride to form methane in favor of the iodine reaction. Williams and Ogg conclude that the methane is produced from hydrogen chloride almost entirely by reaction with hot methyl radicals. Phibbs and Darwent[8] have also presented evidence for the presence of hot methyls in mercury dimethyl photolysis.

That the quantum yield of methane production in methyl iodide photolysis is as low as 0.003 requires that reaction (2) has a low probability factor of this order. This however, is not unreasonable even for a "hot" reaction since, in the case considered, it is necessary for three translational and three rotational degrees of freedom to disappear and be replaced by at least five vibrations in the collision complex. Unless the reactants at the instant of collision are so orientated that the necessary transfer can be easily accomplished, reaction (2) will not occur and the "hot" radical will merely lose kinetic energy in the collision, that is, reaction (3) occurs. It is obvious in this connection that the most probable collision site on the methyl iodide molecule will be the comparatively large iodine atom rather than the small hydrogen atoms; reaction (3) preferred over (2).

The stationary concentration of "hot" methyl radicals is thus given essentially by reactions (1) and (3) and is seen to be constant at fixed illumination, independent of iodine concentration. The rate of methane production should therefore be independent of iodine concentration and should be the same in the presence and absence of silver. The small increase in methane yield in the presence of silver can be ascribed to the reaction:

$$CH_3^* + C_2H_6 \rightarrow CH_4 + C_2H_5$$

since appreciable amounts of ethane are then present. Alternatively, there is the possibility of a disproportionation reaction:

$$2CH_3 \rightarrow CH_4 + CH_2,$$

it being true that small amounts of ethylene are found when silver is present.

A methyl radical having lost its excess energy by reaction (3) will, in the absence of silver, most probably react with iodine to reform methyl iodide. If iodine can be removed sufficiently rapidly by fixation as silver iodide, the methyl radical concentration will be able to build up to the point where reaction (4) becomes appreciable. The tremendous dependence of ethane yield on iodine pick-up thus has a ready explanation. It may be remarked here that ethane production by a Walden inversion type reaction:

$$CH_3 + CH_3I \rightarrow C_2H_6 + I$$

seems unlikely since it obviously does not occur to any noticeable extent as a "hot" reaction and should not therefore be expected as a "cold" reaction.

The effect of temperature on the ethane yield is not too reliable in view of the great dependence of ethane on stirring conditions. This dependence was not too well realized in the earliest experiments. In runs 14 and 15 great care was exercised to reproduce so far as possible the iodine fixation. Stirring speeds were measured with a stroboscopic tachometer at the start and finish of each run, with the results indicated in Table I. It may be significant therefore that the ethane yield is less at the higher temperature as runs 1 and 2 would also indicate. If it is true that the steady state concentration of iodine was the same in runs 14 and 15, calculation by the usual steady state method shows that an energy of activation of about 1 kcal for reaction (6) would be sufficient to account for the observed decrease in ethane. Despite the inconclusiveness of this value it is of interest to compare it with the value estimated by Andersen and Kistiakowsky[9] namely 0.5±0.5 kcal.

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[7] R. Williams and R. A. Ogg, J. Chem. Phys. **15**, 696 (1947).

[8] M. K. Phibbs and B. de B Darwent, Trans. Faraday Soc. **45**, 541 (1949)

[9] H. G. Andersen and G. B Kistiakowsky, J. Chem. Phys. **11**, 6 (1943).