[Contribution from the Department of Chemistry, University of Notre Dame]

Hot Radical Reactions in the Photolysis of Methyl Iodide Vapor[1]

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The photolysis of methyl iodide vapor at 2537 Å. has been investigated with particular concern for the mode of production of methane and ethane. It has been shown that the rate of methane production is strictly linear with time, is independent of temperature, is unaffected by iodine added initially and is decreased by addition of various unreactive gases. These facts support the view that methane is exclusivly a hot radical reaction product. The rate of production of ethane is initially comparable to that for methane, but decreases with extent of photolysis or with initially added iodine to a limiting value 0.075 times the rate for methane. This limiting rate is temperature independent, and is decreased by addition of unreactive gases as with methane. It is concluded that this ethane is also the product of a hot radical reaction. Quantum yields for methane and ethane have been determined as well as the efficiencies of various moderators.

Introduction

Previous investigations[2-5] have shown that in the photolysis of methyl iodide vapor at 2537 Å., methane is the product of a hot radical reaction. The process (equation 2, below) is regarded as a consequence of the excess energy (*ca.* 40 kcal.) imparted to the methyl radical in the primary act (equation 1, below). In agreement with this view, the rate of methane formation has been found to be independent of iodine concentration and of temperature, and to be decreased by the addition of unreactive gases (moderators).

Ethane is also a product of this photolysis, but in this case it has not been clear whether it arises from a thermal or a hot radical reaction (3 or 5 below). In the present work the rates of production of methane, ethane and iodine have been carefully measured as functions of pressure, temperature, iodine concentration and various moderators and reactive substances have been added to obtain a more detailed picture of the reaction of hot methyl radicals.

The results of this investigation have been interpreted in the framework of the following mechanism, which is not inconsistent with those of previous investigators.

$$CH_3I + h\nu \longrightarrow \mathbf{CH_3} + I \qquad (1)$$
$$\mathbf{CH_3} + CH_3I \longrightarrow CH_4 + CH_2I \qquad (2)$$
$$\mathbf{CH_3} + RH \longrightarrow CH_4 + R \qquad (2a)$$
$$\mathbf{CH_3} + CH_3I \longrightarrow C_2H_6 + I \qquad (3)$$
$$\mathbf{CH_3} + CH_3I \longrightarrow CH_3 + CH_3I \qquad (4)$$
$$\mathbf{CH_3} + M \longrightarrow CH_3 + M \qquad (4a)$$
$$CH_3 + CH_3 \longrightarrow C_2H_6 \qquad (5)$$
$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (6)$$
$$CH_3 + I \longrightarrow CH_3I \qquad (6a)$$
$$CH_2I + I_2 \longrightarrow CH_2I_2 + I \qquad (7)$$
$$I + I + M \longrightarrow I_2 + M \qquad (8)$$

The symbol $\mathbf{CH_3}$ refers to a methyl radical with excess energy (hot radical) capable of undergoing reactions 2 or 3 in its first few collisions, but subject to thermalization by non-reactive collisions represented by 4. At small concentrations of iodine process 5 may lead to significant production of ethane, but in the presence of sufficient iodine process 6 is considered to be the exclusive fate of thermal methyl radicals. Process 2a represents the possibility of hot methyl radical reactions with added reagents such as hydrogen, methane, etc.

Experimental

Materials.—Methyl iodide, Mallinckrodt analytical reagent grade, was purified by fractional distillation, retaining the middle third. It was stored over copper wire under vacuum and outgassed before each use. Its purity was confirmed by mass spectrometric analysis and the most significant impurity was found to be dimethyl ether, present at less than 0.5%.

Iodine, Rascher and Betzold C.P. grade, was resublimed before use. Production of iodine in photolysis was determined by titration to a starch–iodine end-point with standard thiosulfate.

Hydrogen iodide was prepared by passing hydrogen gas first over molten iodine at 150°, then over platinized asbestos at 350°. The product was purified by passage through traps cooled in salt–ice and Dry Ice–acetone slush. The product was collected by condensation at liquid air temperature and pumped to remove non-condensable gases.

Hydrogen, helium, neon, argon, nitrogen and methane were obtained from the Matheson Co. and freed of oxygen by passage over copper at 700°. Deuterium (>99.5 mole %) was obtained from the Stuart Oxygen Co.[6] and methane-d_4 (2 mole % of methane-d_3) from Tracerlab.[6]

Apparatus.—The light source in all experiments was a Hanovia SC2537 mercury resonance lamp, enclosed in a metal box and ventilated with an air stream to maintain a temperature of 50 ± 1°.

In the majority of the experiments the reaction vessel, a cylindrical Vycor (Corning #7910) tube of 17 mm. diameter and 40 ml. volume, was placed in a reproducible position in the center of the lamp helix. The use of Vycor serves to remove the 1849 Å. line.

Unless otherwise noted, the sample temperature was 50°. In some experiments a quartz jacket was placed around the sample within the helix and steam, ice-water, or water of controlled temperature was circulated through the jacket. Some experiments were performed with the reaction cell held in a reproducible position external to the lamp housing, in which case the temperature was that of the room.

Procedure.—After vigorous evacuation the reaction cells were filled and pressures measured on a conventional vacuum line. The reaction cell was sealed off from the line with a breakoff provided for entry after irradiation. The reaction mixture was brought to temperature before irradiation.

After irradiation the reaction cell was attached to the vacuum line and cooled in frozen acetone (−94°). The volatile products were removed and measured in a modified Saunders–Taylor apparatus and then subjected to mass spectrographic analysis. The condensable products were taken up in a small volume of potassium iodide solution and titrated with thiosulfate.

All mass spectrometric analyses were made on a Consolidated 21–103A mass spectrometer. The C^{12}-C^{13} isotope ratio in methane was determined directly from the mass 16 and 17 peaks. In some experiments only the methane–ethane ratio was determined, in which case the volatile products were admitted directly to the mass spectrometer.

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(1) Taken from the doctoral dissertation of R. D. Souffie, June, 1955. Presented at the 128th meeting of the American Chemical Society, Minneapolis, Minn., Sept. 11–16, 1955.

(2) R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950).

(3) F. P. Hudson, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **21**, 1894 (1953).

(4) R. B. Martin and W. A. Noyes, Jr., This Journal, **75**, 4183 (1953).

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(6) By authorization of the U.S.A.E.C.

Results

The results of photolysis of methyl iodide vapor alone at 50° and 2537 Å. are shown in Fig. 1 in which the yields of methane, ethane and iodine are given as functions of time under constant intensity of irradiation. Within the precision of measurement, methane is produced at a constant rate and ethane and iodine are equal. In all cases the extent of decomposition of the sample, initially present at 150–200 mm., was less than 5%. No ethylene was detected.

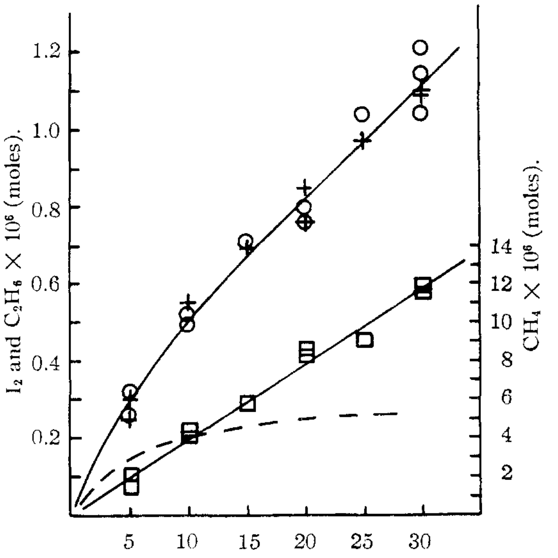

Fig. 1.—Photolysis of methyl iodide: ○, ethane; +, iodine; □, methane; ---, computed thermal ethane.

In Fig. 2 the methane–ethane ratio is shown as a function of time. It appears that this ratio is increasing toward a limiting value. In the same figure are given the results of experiments with iodine added initially for which a constant methane–ethane ratio of 13.4 ± 0.1 is obtained. A series of similar experiments in which the initial pressure of methyl iodide was *ca.* 60 mm. instead of 200 gave the same ratio. This ratio was also found to be independent of temperature in the presence of added iodine for seven determinations over the range 28–100°. A determination at 0° gave a lower ratio of 10.5, but this is attributed to the low vapor pressure of iodine rather than to a temperature coefficient of the rates of reaction.

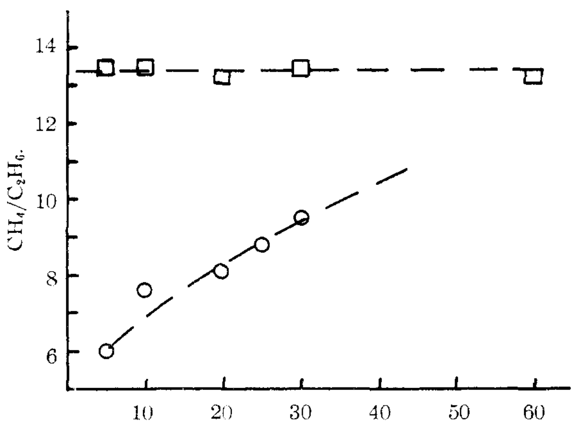

Fig. 2.—Methane—ethane ratio: ○, pure methyl iodide; □, iodine added initially.

The effect of added moderators on the rates of production of methane and ethane in the presence of iodine is shown in Fig. 3. Within the precision of the measurements all of the moderators have the same effect on methane production, but some distinctions are visible in the case of ethane. The unit rate in each case is the rate of production of methane or ethane in the absence of moderator, but in the presence of added iodine.

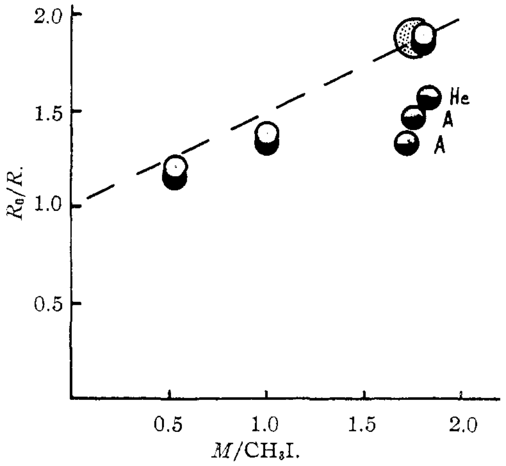

Fig. 3.—Moderation by inert gases: ○, moderation of methane production by neon; ●, moderation of ethane production by neon; ◒, moderation of ethane production by other gases. Points for moderation of ethane production by N_2 and methane production by N_2, He, A lie in the larger shaded circle.

Several samples were photolyzed with deuterium, hydrogen and methane-d_4 added initially. The yields of methane, methane-d_1 and ethane were measured and compared to the normal yields of methane under identical conditions of irradiation. The results of these experiments are given in Table I.

Table I

Photolysis of Methyl Iodide in the Presence of Various Substrates

20 min. irradiation, 58 mm. CH_3I

Substrate	Mole fraction	Temp., °C.	I_2 initial	Relative yield of products CH_4	C_2H_6	CH_3D
None	0.000	Various	Satd.	1.00	0.075	...
D_2	.644	27.5	0	0.64	.17	0.048
D_2	.644	3.5	0	.71	.26	.048
D_2	.645	27.5	Satd.	.51	.060	.048
D_2	.645	3.5	Satd.	.58	.060	.044
H_2	.644	28	Satd.	.58	.060	...
H_2	.644	28	Satd.	.64	.056	...
CD_4	.646	50	Satd.	.36	.050	.28
CD_4	.646	50	Satd.	.37	.043	.28

The quantum yields of the various products in the photolysis of methyl iodide have been determined by comparison with the rate of decomposition of gaseous hydrogen iodide in the same reaction cell under identical conditions of irradiation. The gaseous products of the two reactions were collected and measured in the same calibrated volume, then analyzed mass spectrometrically. Hydrogen iodide at increasing pressures was irradiated for 3 minutes and it was found that the rate of hydrogen production reached a limiting value of 6.78×10^{-6} mole/min. at pressures above *ca.* 300 mm. This corresponds to an absorbed light intensity of 40.9×10^{17} quanta/min. Samples of methyl iodide irradiated under the same conditions yielded $3.25 \pm 0.32 \times 10^{-8}$ mole/min. of methane corresponding to $\Phi_{CH_4} = 0.0048 \pm 0.0005$.

An isotope effect in the rate of production of methane was sought without success. Methane obtained by four different methods was subjected to mass spectrometric analysis and the ratio of the mass 17 to mass 16 peaks measured. The results of this investigation are reported in Table II, where the precision estimates given are standard deviations from the mean. The four sources of methane were: (1) Matheson tank methane; (2) thermal reaction of methyl iodide with hydrogen iodide at 270 and 370°; (3) photochemical decomposition of methyl iodide at 50° for times ranging from 5 min. to 4 hr.; (4) photochemical decomposition of methyl iodide with added iodine for times ranging from 5 to 60 min. and temperatures from 0 to 100°.

TABLE II

ISOTOPE RATIO IN METHANE

Source	No. detns.	% C^{13}
Tank methane	2	1.12, 1.12
Thermal reaction	2	1.11, 1.09
Photolysis	13	1.09 ± 0.04
Photolysis with I_2	22	1.07 ± 0.03

The data in Table II indicate no isotope discrimination in excess of the precision measure.

In the course of this work we have also confirmed the observation of Harris and Willard[5] that a photochemical reaction of iodine with methane is induced by 1849 Å. radiation. A mixture of iodine and methane irradiated in a quartz cell showed measurable quantities of hydrogen iodide, as determined by titration with base. A blank experiment in which the irradiation was carried out in Vycor yielded no such product.

Discussion

The data presented above demonstrate that the rate of methane production is independent of iodine concentration whether iodine was initially present or not. The observed rate compared with a hydrogen iodide actinometer leads to $\Phi_{CH_4} = 0.0048 \pm 0.0005$, which is in conflict with the value of 0.0028 reported by Harris and Willard.[5] The reason for this discrepancy is not evident.

The rates of production of ethane and iodine are at all times equal and decrease during the early stages of photolysis. Initial addition of iodine decreases the ethane rate to a limiting value 0.075 times the methane rate. This limiting rate is independent of further changes in iodine concentration and therefore cannot be a wall reaction. We attribute this production of ethane to the hot radical reaction 3 and the quantum yield for this process is 3.6×10^{-4}. Since no other hydrocarbon products were detected the stoichiometric requirements for the production of iodine are met and

$$\Phi_{I_2} = \Phi_{C_2H_6} = 3.6 \times 10^{-4} \text{ (presence of } I_2\text{)}$$
$$\Phi_{CH_3I} = 2\Phi_{CH_4} + 2\Phi_{C_2H_6} = 0.010 \pm 0.001$$

Production of ethane and iodine at low concentrations of iodine is enhanced by combination of thermal radicals (reaction 5). By subtracting the constant rate of reaction 3 from the observed rate in short photolyses it has been possible to estimate the amount of thermal ethane produced. The computed values are indicated in Fig. 1. Since the rate of reaction 6 is approximately equal to the absorbed light intensity, I_{abs}, variation of thermal ethane with time, t, yields

$$\frac{k_5}{k_6^2} = \frac{(C_2H_6)^3}{3 \times I_{abs.}^2 \times t} = 5.3 \times 10^{-17} \text{ mole l.}^{-1} \text{ sec.}$$

which agrees with the value obtained by Davidson and Carrington.[7] The success of this analysis lends support to the hot radical mechanism for ethane production.

The effect of moderators incapable of chemical reaction with the hot methyl radicals is always to decrease the yield of methane and ethane, although not always to the same degree. In the case of methane all moderators appear to have the same efficiency, confirming previous observations.[3] By steady-state treatment of (CH_3) and simplification by noting that $k_2 + k_3 << k_4$ the following expression relating the rate of methane production in the presence of (R) and in the absence (R_0) of moderator, M, may be obtained.

$$\frac{R_0}{R} = 1 + \frac{k_4\,(M)}{k_4\,(CH_3I)} \qquad (9)$$

This relation has been used to test the moderation effects of inert gases as shown in Fig. 3. Within the precision of measurement the points for neon fall on a straight line whose slope yields $k_{4a}/k_4 = 0.5$. Since all other moderators show experimentally identical effects on the methane production, the corresponding values of k_{4a}/k_4 would be the same.

Moderation of ethane production, on the other hand, appears to depend on the nature of the moderator, although the differences are barely greater than the uncertainty. With neon, application of equation 9 yields a value of $k_{4a}/k_4 = 0.5$ and the curve shown in Fig. 3. Application of equation 9 to data for other moderators yields for nitrogen, $k_{4a}/k_4 = 0.5$; for argon $k_{4a}/k_4 = 0.3$, 0.2; for helium $k_{4a}/k_4 = 0.3$. The qualitative conclusion may be drawn that for ethane production, neon and nitrogen are better moderators than argon or helium.

The effect of moderators on the rate of ethane production is "normal" in the sense that the moderating effect, k_{4a}/k_4, is greatest when the mass of the moderator is most nearly equal to the mass of the hot radical, as has been found for hot H and D atoms.[8] On the other hand, moderation of methane

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[7] N. Davidson and T. Carrington, THIS JOURNAL, **74**, 6628 (1952).

[8] H. A. Schwarz, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **74**, 6007 (1952); R. J. Carter, W. H. Hamill and R. R. Williams, Jr., *ibid.*, **77**, 6457 (1955).

production is "abnormal" in that no such mass effect is evident. This contrast suggests that ethane production is the result of excess translational energy in the methyl radical while methane production may be the result of excess internal energy. However, this proposal cannot be regarded seriously until further evidence is available.

When a hydrogenous substance is present during the photolysis of methyl iodide, that substance may act as a moderator and also give rise to methane through a hot radical reaction. By use of deuterium, this product may be distinguished from that arising from reaction 2. From the yields given in Table I for systems containing deuterium, equation 9 yields $k_{4a}/k_4 = 0.35$ for methane production and 0.15 for ethane production. For systems containing methane-d_4, equation 9 yields $k_{4a}/k_4 = 1$ for methane production and $k_{4a}/k_4 = 0.33$ for ethane production. It is evident that methane-d_4 is by far the best moderator of methane production, but not unusual in moderation of ethane production.

The production of methane-d in the presence of deuterium or methane-d_4 is clearly a hot radical reaction, since it occurs with relatively good efficiency even in the presence of iodine. The production of methane-d is especially efficient from methane-d_4.

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NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Surface Tension of Ammonia and of Solutions of Alkali Halides in Ammonia

BY R. A. STAIRS AND M. J. SIENKO

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The surface tension of liquid ammonia from −75 to −40° and of solutions in ammonia of sodium chloride and bromide and potassium bromide and iodide at −40° were measured by the method of maximum bubble pressure and checked by a few measurements by the capillary rise method. The surface tension of ammonia may be represented by the equation $\gamma = 23.41 - 0.3371t - 0.000943t^2$ with a standard error of 0.15 dyne/cm. from −75 to −40°. The results obtained with the salt solutions may be expressed in the form $\Delta\gamma = Ac + Bc^2$ where c is the concentration in moles per liter. The A coefficients decrease regularly with increase in the polarizabilities of the ions, as they do in aqueous solutions. An argument is presented relating the B coefficients to the Bjerrum theory of ionic association.

The theories of the surface tension of salt solutions due to Oka[1] and Onsager and Samaras[2] are in agreement in predicting the approximate magnitude of the effect of KCl on the surface tension of water. They also agree in predicting an inverse dependence of the magnitude of the effect on the dielectric constant. The measurements of Kosakevich[3] on solutions of several salts in a number of solvents appear not to demonstrate the expected relationship. Kosakevich noted that the order of the effects of different salts in a given solvent was usually different from that found in water.

As was pointed out by Onsager and Samaras, neither of these theories takes account of higher order electrostatic forces between the ions and the surface that would be expected to arise from the polarizability of the ions. That different salts of a given charge type do not have the same effect on the surface tension of water is well known. For example, for LiCl (where the sum of the ionic polarizabilities[4] is equal to 3.01 Å.^{3}) the surface tension increment over that of the pure solvent in one molar solution in water[5] is approximately twice that of KI ($\Sigma\alpha = 7.44$ Å.^{3}). Onsager and Samaras showed that an effect of this magnitude would not be expected to result from differences in size alone, so the observed effect presumably arises from the polarizability differences. Though the amount of scatter is considerable, there seems to be a linear relationship between the surface tension increment and the sum of the ionic polarizabilities.

The experiments to be described were designed to find out whether a similar relationship between the surface tension increment and the polarizability exists in liquid ammonia, and to examine further the dependence of the surface tension increment on the dielectric constant. It proved necessary also to make some measurements of the surface tension of pure liquid ammonia, as existing data were few.

Experimental

The method chosen was Sugden's modification of the maximum bubble pressure method.[6] As a check, however, a few measurements were also made by capillary rise. Since the diameters of the precision-bore capillary were measured only at both ends and the heights of the liquid in the capillaries were measured through the walls of a clear Dewar flask, the highest accuracy attainable by the capillary rise method was not achieved.

The maximum bubble pressure method has the advantage of being virtually independent of contact angle and it is less sensitive to small amounts of dirt than other methods by virtue of the continual formation of new surface. Long and Nutting[7] demonstrated that, at least with ionic solutions, it appears to yield the true "static" value of the surface tension at reasonable bubbling rates. The apparatus was calibrated using benzene as a standard liquid, and the bubble pressures were measured with a manometer containing m-xylene. Both liquids were Baker and Adamson Reagent grade, refluxed in the presence of sodium, and distilled through a short column in all-glass apparatus. The hydrogen used to blow the bubbles was Matheson electrolytic grade, further purified over hot copper and dried with

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