Kinetics of the Photolysis of Methyl Iodide and the Hydrogen Halides II. Photolysis of Methyl Iodide in the Presence of Iodine and the Hydrogen Halides

Russell R. Williams Jr. and Richard A. Ogg Jr.

percent of iodine "completely inhibits" the photolysis of hydrogen iodide. On this observation they base their estimate of k_2/k_1 as greater than 100. Their experiments were conducted at extremely low gas pressures, and the secondary reactions probably occurred principally on the walls of the vessel. The value reported in this work certainly corresponds to the true homogeneous reactions.

The value of k_4/k_3 has been accurately determined by other workers[10] as 8.4 and is also independent of temperature. The value of k_6/k_5 has been estimated to be greater than 100.[11] The new values for k_2/k_1 therefore fall into a more logical sequence with the other halogens and hydrogen halides.

The value of k_1/k_3 obtained in this work was $0.54 \exp(1000/RT)$. In view of the "hot atom"

hypothesis proposed above, this representation of the data can be regarded only as tentative, until further experiments with deactivating agent present have been performed. However, the activation energy given is not in conflict with other information, such as an estimate by Morris and Pease[11] that reaction 3 has an activation energy of about 1 Kilocalorie/mole. This would give reactions 1 and 2 small and nearly equal activation energies.

Note: The ratio of rate constants k_1/k_5 obtained in this work corresponds to the form

$$0.002 \exp(7500/RT).$$

The approximate nature of this portion of the work and the extremely small ratio of frequency factors obtained leave this result open to grave doubt. Further experiments in the presence of a deactivating agent have given significantly different results, which may contribute to a better understanding of this value.

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[10] M. Bodenstein and G. Jung, Zeits. f. physik. Chemie 121, 127 (1926).
[11] J. C. Morris and R. N. Pease, J. Chem. Phys. 3, 796 (1935).

# Kinetics of the Photolysis of Methyl Iodide and the Hydrogen Halides*

II. Photolysis of Methyl Iodide in the Presence of Iodine and the Hydrogen Halides

RUSSELL R. WILLIAMS, JR.** AND RICHARD A. OGG, JR.
Department of Chemistry, Stanford University, Stanford University, California
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The photodissociation of methyl iodide by light of λ2537A has been utilized as a source of methyl radicals for a study of their subsequent reactions with iodine and the hydrogen halides. The observed rate of methane formation has been used to evaluate the ratio of rate constants for the following reactions:

$$CH_3+HX \rightarrow CH_4+X$$
$$CH_3+I_2 \rightarrow CH_3I+I$$
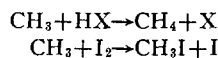
where X represents Cl, Br or I. The reaction with hydrogen chloride has been found to be complicated by the unequal yield of methane and iodine, and possible explanations of this phenomenon have been considered.

INTRODUCTION

GASEOUS methyl iodide absorbs ultra-violet radiation below λ3650A with an absorption maximum occurring at λ2632A.[1] The reactions

resulting when pure methyl iodide vapor is irradiated with light of λ2537A have been carefully studied[2] with the conclusion that the primary process of light absorption results in the formation of a methyl radical and an iodine atom. The very low quantum yield obtained with pure

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* Presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
** Present address: Department of Chemistry, University of Notre Dame.
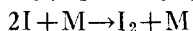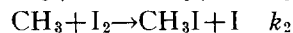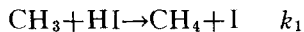[1] G. K. Rollefson and M. Burton, *Photochemistry* (Prentice-Hall, New York), 1939.

[2] W. West and L. Schlesinger, J. Am. Chem. Soc. 60, 961 (1938).

methyl iodide indicates that reactions of the type

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

are very slow. Therefore, in the fast photolysis with hydrogen halides, the important reactions will be

$$CH_3I + h\nu \rightarrow CH_3 + I \quad E_{abs.}$$
$$CH_3 + HI \rightarrow CH_4 + I \quad k_1$$
$$CH_3 + I_2 \rightarrow CH_3I + I \quad k_2$$
$$2I + M \rightarrow I_2 + M$$

neglecting, of course, atom-radical reactions. The rate of the last reaction is assumed to be such that the rate of formation of molecular iodine is substantially equal to the rate of formation of methane.

The photolysis of methyl iodide thus furnishes us with a convenient source of methyl radicals for the study of their relative rates of reaction with hydrogen halides and iodine.[3]

By application of the "steady state" treatment it is possible to derive the following differential rate expression:

$$\frac{d(CH_4)}{dt} = \frac{E_{abs.}}{1 + k_2(I_2)/k_1(HI)}. \quad (1)$$

After integrating and performing the indicated substitutions we have:

$$X + k_2/k_1 \left[(a+b) \ln \frac{a}{a-X} - X \right] = E_{abs.} \cdot t \quad (2)$$

where X = change in (CH_4) in time interval $t = \Delta(CH_4)$, $a = (HI)$ at beginning of time interval $t = (HI)_0$, and $b = (I_2)$ at beginning of time interval $t = (I_2)_0$.

The photochemical reaction of methyl iodide and hydrogen iodide has been studied[4] in a roughly quantitative fashion, using mixtures varying from fifty to zero percent hydrogen iodide. It was found that the quantum efficiency of iodine production stayed near two until concentrations of hydrogen iodide as low as ten percent of the total were reached. The work suffers somewhat in that the light source used gave a variety of wave-lengths in the absorbing region, and contrary to the opinion of the in-

vestigators, the absorption characteristics of the two vapors are somewhat dissimilar. Methyl iodide, as previously mentioned, shows an absorption maximum at $\lambda 2632A$ while the absorption of hydrogen iodide increases continuously toward shorter wave-lengths in this region.[5] The work indicates that the primary process in this reaction, as well as in the photolysis of methyl iodide, is the dissociation of the methyl iodide molecule into a methyl radical and an iodine atom.

The present work is designed to give more quantitative information about the photochemical reactions of methyl iodide and hydrogen halides, and in particular about the reaction rates of the methyl radicals produced in the course of the reaction.

The photochemical reaction of methyl iodide and hydrogen bromide has also been studied[6] to gain information about the relative rates of the following two reactions:

$$CH_3 + HBr \rightarrow CH_4 + Br \quad k_3$$
$$CH_3 + I_2 \rightarrow CH_3I + I \quad k_2$$
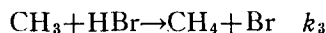
The present work was continued to check and extend this work. Also, further extension to the reaction involving hydrogen chloride seemed feasible, and was accordingly carried out. The appropriate modifications in the rate expressions will be noted in the section on Experimental Results.

The analogy of these studies to those reported in the first paper of this series[7] is clear, the difference being that in the former cases the reactant of interest is the hydrogen atom, and in the present case it is the methyl radical.

EXPERIMENTAL DETAILS

Methyl iodide was prepared according to the method outlined in *Organic Syntheses*.[8] This method consists of the addition of dimethyl sulfate to a heated solution of potassium iodide and calcium carbonate. The product distills into an ice-cold receiving flask. This product was

[3] E. W. R. Steacie and D. J. LeRoy, Chem. Reviews 31, 227 (1942).
[4] T. Iredale and D. Stephen, Trans. Faraday Soc. 33, 800 (1937).
[5] K. F. Bonhoeffer and P. Harteck, *Grundlagen der Photochemie* (Steinkopf, Dresden and Leipzig, 1933).
[6] H. C. Andersen and G. B. Kistiakowsky, J. Chem. Phys. 11, 6 (1943).
[7] R. R. Williams, Jr. and R. A. Ogg, Jr., J. Chem. Phys 15, 691 (1947).
[8] *Organic Syntheses*, Vol. 18, R. Fuson, Ed., John Wiley & Sons, New York, 1938.

TABLE I. Photolysis of methyl iodide and hydrogen iodide.

Exposure	Temp. °C	$(CH_3I)_0$* mm Hg	$(HI)_0$* mm Hg	$E_{abs.}$**	Time hrs.	$\Delta(CH_4)$* mm Hg	k_2/k_1
35a	82.5	181.60	27.70	1.19	3.00	2.35	12.3
35b	82.5			1.19	4.25	1.85	12.8
36a	82.5	190.10	7.90	1.06	7.92	2.50	11.8
39a	154.5	198.95	27.75	1.06	3.13	2.25	10.7
39b	154.5			1.06	5.92	2.50	10.5
40a	154.5	196.40	26.90	1.14	2.53	2.05	10.5
38a	192.0	196.25	27.75	1.06	3.72	3.00	5.5
38b	192.0			1.06	5.50	2.75	6.0
38c	192.0			0.00	7.5	0.20	

* Concentrations of all reactants and products measured in millimeters of mercury and corrected to 25°C.
** $E_{abs.}$ measured in millimeters of hydrogen (or methane) per hour for the system used.

washed, dried with anhydrous sodium sulfate and redistilled over a crystal of potassium iodide. The fraction distilling between 42.3° and 42.8°C was collected and kept under vacuum at 0°C where it remained waterwhite for nine months.

The apparatus used was that described in the first paper of this series.[7] All details of filling, illumination, and analysis are the same.

EXPERIMENTAL RESULTS

Methyl Iodide

A single experiment was conducted to check the low quantum efficiency of methyl iodide decomposition reported by West and Schlesinger.[2] They report a quantum efficiency of approximately 0.001, with 80 percent of the hydrocarbon products being methane. The experiment reported here consisted in exposing methyl iodide at a pressure of 186.70 mm to radiation of λ2537A in the reaction system previously described. The exposure lasted 4.00 hours at a temperature of 159.8°C, and 8.12 hours at 21°C, during which time less than one-tenth of a millimeter of non-condensible gas was formed. The $E_{abs.}$ for this system was equivalent to 1.20 mm of methane per hour. This work confirms the low quantum efficiency reported and shows that direct decomposition of methyl iodide will not interfere with the reactions involving the hydrogen halides.

Methyl Iodide and Hydrogen Iodide

The relative absorption coefficients of methyl iodide and hydrogen iodide are such that the concentration of hydrogen iodide must be less than about one-sixth the concentration of methyl iodide, if practically all of the light is to be absorbed by methyl iodide. If the hydrogen iodide concentration increases above this amount, it absorbs radiation and decomposes into hydrogen and iodine. Analyses were made, as indicated,[7] by measuring the pressure of non-condensable gas, and therefore the products hydrogen and methane are indistinguishable as far as the pressure measurements are concerned. The assumption that the products of this reaction are methane and iodine only may be justified by the following observations: Comparison of the amounts of non-condensible gas, as determined by pressure measurements, and of iodine, as determined by titration, shows that they are formed in equal amounts. This rules out of consideration any higher hydrocarbons, since they would be condensed by liquid air. The non-condensible product must then be methane or hydrogen. In early experiments liquid nitrogen was used as the condensing agent, and it was found that pressures of non-condensible gas in excess of approximately fifteen millimeters were never reached regardless of the length of exposure. This is attributed to the fact that this pressure is approximately the vapor pressure of liquid methane at the normal boiling point of liquid nitrogen (n.b.p. = −196°C).[9] Later measurements used liquid oxygen (n.b.p. = −183°C) as a cooling agent and this difficulty was not encountered. The time of diffusion of a given amount of iodine from the main bulb to the cold side-arm was three or four times as long for these experiments as in the case of the hydrogen-halide experiments,[7] where the non-condensible product is known to be hydrogen. The diffusion coefficients for bromine through hydrogen and methane at 20°C are, respectively, 0.562 and 0.1558 cm²/sec.[10] Comparison with the observed rates shows the approximate analogy. These three types of observations support the assumption of the simple mechanism given in the Introduction involving the production of methane as the principal non-condensible product.

It is apparent from the introductory discussion

[9] Landolt-Bornstein, *Physikalische-Chemische Tabellen* (Erganzungsband I), Julius Springer, Berlin, 1935), p. 730.
[10] Landolt-Bornstein, *Physikalische-Chemische Tabellen* (Erganzungsband III), (Julius Springer, Berlin, 1935) p. 240.

that the concentration of methyl iodide should not affect the rate of the reaction as long as it is present in sufficient quantity to absorb practically all of the incident radiation.

Table I gives the data for several representative experiments with methyl iodide and hydrogen iodide. The values of $E_{abs.}$ were obtained by independent actinometer runs using pure hydrogen iodide.[7] Precise control of light intensity is not as important in these experiments as in the case of hydrogen-halide mixtures, since the retardation is quite considerable. The various exposures and measurements show that the ratio of rate constants k_2/k_1 does not vary with variations in the HI pressure from 5 mm to 27 mm (Exps. 35 and 36) and in the I_2 pressure from 0 to 5 mm.

The experiments show that the value of the ratio of rate constants k_2/k_1 is slightly dependent on temperature. This dependence is barely large enough to be detectable. Figure 1 contains a plot of $\log k_2/k_1$ against $1/T$. The points corresponding to 192.0°C definitely do not fall on a straight line with those at the lower temperatures. Exposure No. 38c shows that a slow thermal reaction takes place at this higher temperature, which probably accounts for the increased rate. This thermal reaction is known from other sources.[11] No such thermal reaction was detected at the lower temperatures. The slope and intercept of the indicated line correspond to
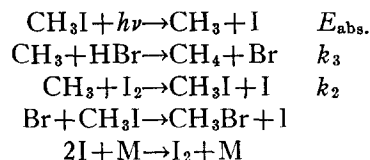
$$k_2/k_1 = 4.4 \exp(750/RT).$$

Several experiments were performed with methyl iodide and hydrogen iodide in which the reactants were illuminated simultaneously with ultraviolet and visible light. This procedure was designed to examine the possibility that the iodine atoms produced when iodine vapor absorbs green light might have an appreciable effect on the course of the reaction, namely, to combine with methyl radicals and thus lower the rate of methane production. The source of visible light was a 1000-watt tungsten filament lamp, focussed on the cell by means of a water lens. No retardation was found and, in fact, a slight acceleration was noted. This was later traced to a heating of the ultra-violet source by the tungsten lamp. As

has been previously mentioned,[7] the ultra-violet source is quite sensitive to the temperature of its environment.

Methyl Iodide and Hydrogen Bromide

When hydrogen bromide is added to methyl iodide and the mixture illuminated with light of λ2537A, a reaction analogous to that described in the previous section takes place. The low absorption coefficient of hydrogen bromide at this wave-length[5] makes possible the use of higher concentrations than is the case with hydrogen iodide. The mechanism given for methyl iodide and hydrogen iodide is modified to the following form:

$$CH_3I + h\nu \rightarrow CH_3 + I \qquad E_{abs.}$$
$$CH_3 + HBr \rightarrow CH_4 + Br \qquad k_3$$
$$CH_3 + I_2 \rightarrow CH_3I + I \qquad k_2$$
$$Br + CH_3I \rightarrow CH_3Br + I$$
$$2I + M \rightarrow I_2 + M$$

The fourth reaction is assumed to be rapid enough so that no appreciable concentration of molecular bromine is built up. As in previous cases, the last reaction is assumed to be rapid enough so that the rate of formation of molecular iodine is equal to the rate of formation of methane.

The differential and integrated rate expressions are entirely analogous to those previously given, with (HBr) substituted for (HI). If $E_{abs.}$ is

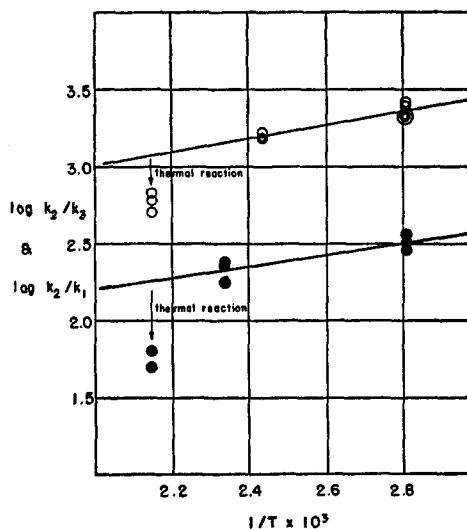FIG. 1. $\log k_2/k_3$ (upper points) and $\log k_2/k_1$ (lower points) as functions of $1/T$.

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[11] R. A. Ogg, Jr., J. Am. Chem. Soc. **56**, 526 (1934).

TABLE II. Photolysis of methyl iodide and hydrogen bromide.

| Ex-posure	Temp. °C	$(CH_3I)_0$* mm Hg	$(HBr)_0$* mm Hg	$E_{abs.}$**	Time hr.	$\Delta(CH_4)$* mm Hg	k_2/k_3
6a	82.5	186.95	35.75	1.19	4.05	2.30	28
6b	82.5			1.19	5.87	1.85	30
6c	82.5			1.19	7.42	1.60	28
7a	82.5	193.30	59.40	1.06	3.00	2.10	31
7b	82.5			1.06	6.13	2.30	28
7c	137.5			1.06	5.17	1.60	24
8a	137.5	127.50	40.70	1.19	4.65	2.90	24
8b	137.5			1.19	6.07	2.00	25
9a	192.0	192.00	60.00	1.06	3.38	2.70	15
9b	192.0			1.06	5.08	2.50	16
10a	192.0	190.40	57.10	1.14	4.08	3.20	16
10b	192.0			1.14	5.07	2.35	17
11a	192.0	189.50	55.00	1.14	3.25	2.55	17
11b	192.0			0.00	12	0.30	

* Concentrations of reactants and products were measured in millimeters of mercury and corrected to 25°C.
** $E_{abs.}$ is measured in millimeters of hydrogen (or methane) per hour for the system used.

determined by independent actinometer runs of the type described previously,[7] then the value of k_2/k_3 can be obtained by observations of the rate of the reaction such as those given in Table II.

The amounts of methane and iodine formed were compared and found to be equal, confirming the assumption that no appreciable quantities of complicated products are formed. Other workers[6] have analyzed the gaseous products of this reaction and found them to contain at least 94 percent methane.

From the values of k_2/k_3 given in Table II it
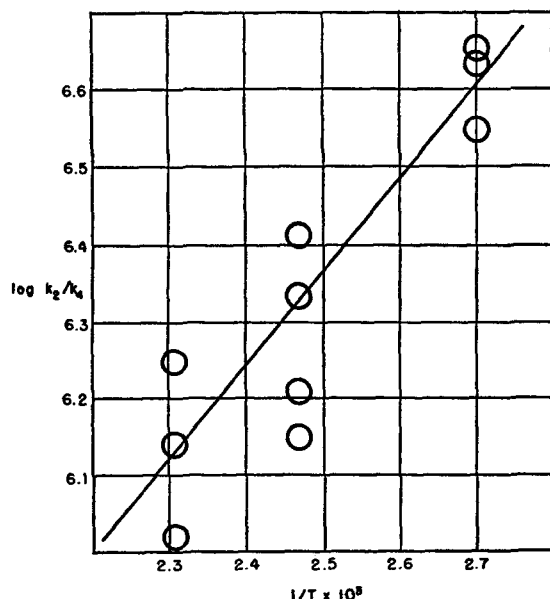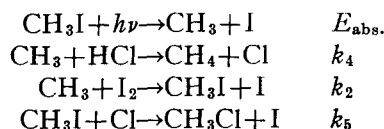

FIG. 2. Logk_2/k_4 as a function of $1/T$.

appears that this reaction is somewhat slower than the photoreaction of methyl iodide and hydrogen iodide. Also, the ratio of rate constants k_2/k_3 has a small temperature coefficient. Figure 1 contains a plot of logk_2/k_3 against $1/T$. It is obvious that the points obtained do not lie on a straight line. This can be explained by noting exposure 11b, in which $E_{abs.} = 0$. This experiment was made to test for a thermal reaction which might be contributing to the observed rate. The amount of thermal reaction noted in this experiment is approximately enough to account for the deviation of the points at 192.0°C from the straight line corresponding to the values at lower temperatures. This result is entirely analogous to that obtained with methyl iodide and hydrogen iodide.

The slope and intercept of the indicated line in Fig. 1 correspond to

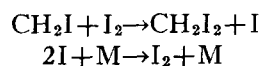$$k_2/k_3 = 7.5 \exp(950/RT).$$

Methyl Iodide and Hydrogen Chloride

The photochemical reaction between methyl iodide and hydrogen chloride is initiated in the same way as those described in the previous sections. It differs from them in two important respects, however. The reaction is much slower than those involving hydrogen iodide and hydrogen bromide, and the products, methane and iodine, are not formed in equal quantities. This second fact indicates a more complicated mechanism. One possible way in which the inequality in products may be explained is the mechanism given below. A rate expression based on these assumptions will be formulated in order to facilitate treatment of the data. The proposed reactions and their corresponding rate constants are given as follows:

$$CH_3I + h\nu \rightarrow CH_3 + I \qquad E_{abs.}$$
$$CH_3 + HCl \rightarrow CH_4 + Cl \qquad k_4$$
$$CH_3 + I_2 \rightarrow CH_3I + I \qquad k_2$$
$$CH_3I + Cl \rightarrow CH_3Cl + I \qquad k_5$$

competing with

$$CH_3I + Cl \rightarrow CH_2I + HCl \qquad k_6$$

followed by

$$CH_2I + I_2 \rightarrow CH_2I_2 + I$$
$$2I + M \rightarrow I_2 + M$$

The entrance of the complicating steps represented by the fourth through sixth equations above has the effect of accelerating the total reaction, since hydrogen chloride is regenerated, and the concentration of iodine is less than would otherwise be the case.

A rate expression similar to those used in the preceeding sections can be derived if certain approximations are made. A factor R, the ratio of methane to iodine produced in a given experiment, and assumed to be independent of time during the run, is introduced. At any time therefore:

$$(I_2) = (CH_4)/R.$$

Also, a large concentration of hydrogen chloride is necessary to obtain a reasonable rate of reaction, and since very little is consumed in a given experiment, it is taken as remaining constant. The differential rate expression proposed for the photo-reaction of methyl iodide with hydrogen chloride is therefore as follows:

$$\frac{d(CH_4)}{dt} = \frac{E_{abs.}}{1 + k_2(CH_4)/k_4R(HCl)_0}. \quad (3)$$

Integration of this relation gives the following formula for the ratio of rate constants k_2/k_4:

$$\frac{k_2}{k_4} = \frac{2Ra}{x^2}(E_{abs.} \cdot t - x) \quad (4)$$

where x = change in (CH_4) in time interval $t = \Delta(CH_4)$, and a = initial concentration of hydrogen chloride = $(HCl)_0$.

The ratio of products, R, varies with temperature, and, to a smaller and more doubtful extent, with the concentration of hydrogen chloride. Neglecting, as a first approximation, the variation with hydrogen-chloride concentration, we see that the ratio R is related to the ratio of rate constants k_6/k_5 in the following manner:

$$R - 1 = k_6/k_5. \quad (5)$$

Table III contains the data obtained for the photo-reaction of methyl iodide and hydrogen chloride. The ratio of rate constants k_2/k_4 appears to be large and temperature dependent. Figure 2 contains a plot of $\log k_2/k_4$ against $1/T$. The scattering of points is quite large, and only a
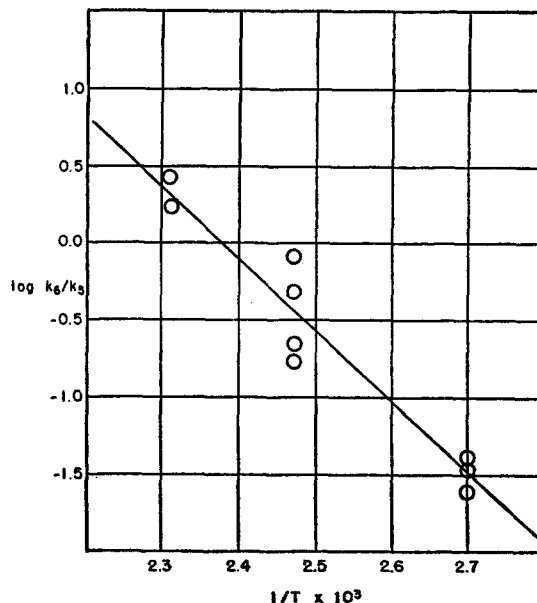

FIG. 3. $\log k_6/k_5$ as a function of $1/T$.

rough estimate of the slope of a line drawn through the points may be made. The slope and intercept of the indicated line correspond to

$$k_2/k_4 = 28.7 \exp.(2400/RT).$$

Figure 3 contains a plot of k_6/k_5, as obtained by use of Eq. (5), against $1/T$. The slope and intercept of the line correspond to:

$$k_6/k_5 = 6 \times 10^4 \exp(-9000/RT).$$

DISCUSSION

Considerable evidence supports the belief that the simple mechanisms given for the photo-reactions of methyl iodide with hydrogen iodide

TABLE III. Photolysis of methyl iodide and hydrogen chloride.

Exposure	Temp. °C	$(CH_3I)_0$* mm Hg	$(HCl)_0$* mm Hg	$E_{abs.}$**	Time hr.	$(CH_4)_f$* mm Hg	$\frac{(CH_4)}{(I_2)}$	k_2/k_4
4	97.7	126.70	279.30	1.25	14.05	3.70	1.25	700
5	97.7	70.30	406.50	1.25	8.00	3.00	1.23	780
8	97.7	118.30	406.00	1.25	8.58	3.15	1.20	760
9	131.5	121.80	391.70	1.20	8.12	3.50	1.52	610
10	131.5	183.50	275.50	1.15	14.25	4.50	1.73	560
11	131.5	61.80	390.20	1.20	12.11	4.80	1.46	470
12	131.5	126.30	280.00	1.15	26.25	7.05	1.92	500
1	159.8	191.95	74.55	1.25	10.08	2.90		410
2	159.8	128.50	273.30	1.20	17.00	6.50	2.27	460
3	159.8	128.80	200.00	1.25	7.88	3.45	2.55	520

* All pressures of reactants were measured at room temperature and corrected to 25°C.
** $E_{abs.}$ is measured in millimeters of hydrogen (or methane) per hour for the system used.

and hydrogen bromide are essentially correct. Abnormally increased rates at higher temperatures are to be expected from a knowledge of the similar thermal reactions. The value of k_2/k_3 reported here is in fair agreement with the value obtained by Andersen and Kistiakowsky[6] at 60°C. Their observation of up to six percent of hydrogen in the non-condensible gas products is probably due to the fact that they used a light source having a rather broad range of wavelengths, since the absorption coefficient of hydrogen bromide increases rapidly below $\lambda 2500A$.

The primary process in this case, as well as in the photolysis of hydrogen iodide,[7] is highly exothermic, although not as great a fraction of this energy will be given to the methyl radical as was the case with the hydrogen atom. In addition, the large amounts of methyl iodide present in the photolysis with hydrogen iodide and hydrogen bromide will serve to deactivate the "hot" methyl radicals.[12] This is confirmed by experiments which show that addition of an inert gas has little effect on the rates of these reactions.[13]
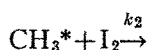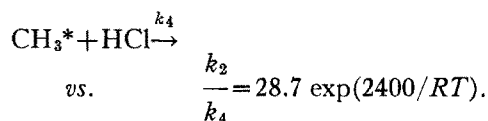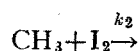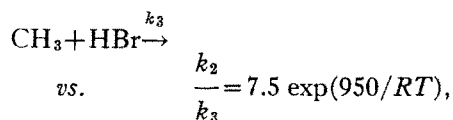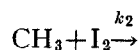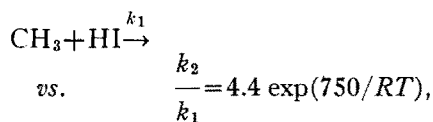
In the photolysis of methyl iodide and hydrogen chloride, the large amounts of hydrogen chloride used have made the reactions of "hot" methyl radicals important, as shown by experiments with inert gas in which the ratio k_2/k_4 increases by several hundred fold.[13] It must be assumed, therefore, that the values reported here refer to the reactions of high velocity methyl radicals. The ratio k_6/k_5, obtained from the ratio of products, showed an abnormally large fre-

quency factor, which is ordinarily observed only when a chain process is involved. A chain such as the following is conceivable:

$$CH_3I + Cl \rightarrow CH_2I + HCl$$
$$CH_2I + CH_3I \rightarrow CH_3 + CH_2I_2$$
CH$_3$ follows usual steps.
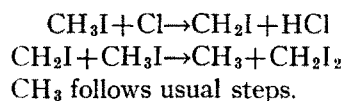
This would result in an increase of the methane yield without producing iodine, but since the amount of methane is never greater than two or three times that of the iodine, the chain cannot be very long.

The values of the ratio of rate constants for the reactions of methyl radicals with hydrogen halides and halogens are summarized below:

$$CH_3 + HI \xrightarrow{k_1}$$
$$vs. \qquad \frac{k_2}{k_1} = 4.4 \exp(750/RT),$$
$$CH_3 + I_2 \xrightarrow{k_2}$$

$$CH_3 + HBr \xrightarrow{k_3}$$
$$vs. \qquad \frac{k_2}{k_3} = 7.5 \exp(950/RT),$$
$$CH_3 + I_2 \xrightarrow{k_2}$$

$$CH_3^* + HCl \xrightarrow{k_4}$$
$$vs. \qquad \frac{k_2}{k_4} = 28.7 \exp(2400/RT).$$
$$CH_3^* + I_2 \xrightarrow{k_2}$$

[12] R. A. Ogg, Jr. and R. R. Williams, Jr., J. Chem. Phys. 13, 586 (1945).
[13] R. A. Ogg, Jr., unpublished work.

* "hot" methyl radicals.