in terms of the mechanism. The values $b = 0.09$, $k_2^*/k_{13} = 9.4$ from the biacetyl data inserted in 15 gave

$$\frac{2R_EP_E + R_MP_M}{R(P_0 - P_1)} = 1.09 + 0.91\,(1 + 0.11P_1)^{-1} \quad (16)$$

The solid line drawn in Fig. 3 was based entirely on the right-hand side of equation 16. The points fitted this line within experimental error, except runs 33, 35 and 37.

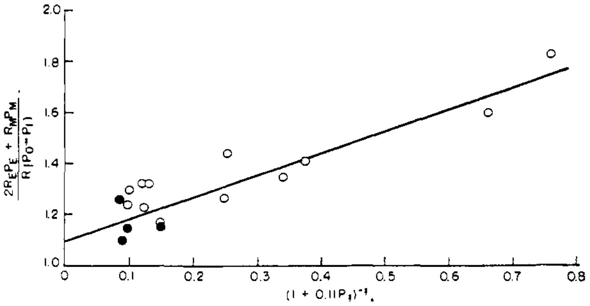

Fig. 3.—Relative ethane–methane yield.

Discussion

In this work as in the classical results of Herr and Noyes it was postulated that a fraction b of the acetone molecules absorbing radiation, spontaneously dissociate into methyl and acetyl radicals. The value of b for heterochromatic light found from this work fell within the range of the more precise values given by Herr and Noyes.

The fraction $(1 - b)$ of the acetone molecules which have absorbed light decomposed into methyl radicals and acetyl radicals, the latter in some excited energy state. In order to explain the increased biacetyl yield at higher pressure a collision reaction between excited acetyl radicals and acetone, equation 4 was proposed. The energy transferred in the deactivation collision either was distributed among the many vibrational modes of the acetone molecule or was dissipated possibly by acetone fluorescence. Follow dissociation processes from reaction 4 forming methyl radical and carbon monoxide appear to be ruled out, for the formation of such intermediates would call for considerable different kinetic interpretation than was consistent with these data.

It is easily shown that the modifications of mechanism proposed in this work introduced no effect which could be detected in the high pressure studies of Herr and Noyes or of Howland and Noyes. However, our experimentally determined quantum yields for acetone decomposition did not depend on the light absorbed whereas the calculated results of Howland and Noyes showed dependence. The reasons for this were not certain. However, possible traces of methane in the samples of carbon monoxide analyzed by Howland and Noyes could account for part of the variation of their calculated acetone quantum yield.

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COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

Photochemical Reactions in the System Methyl Iodide–Iodine–Methane; The Reaction $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$

BY G. M. HARRIS[1] AND J. E. WILLARD

RECEIVED JANUARY 11, 1954

The work reported includes studies of: (1) exchange of iodine between CH_3I and I_2, using I^{131} as tracer; (2) photolysis of CH_3I to produce CH_4, CH_2I_2, CHI_3 and I_2; (3) reaction of $C^{14}H_3$ radicals with CH_4 to form $C^{14}H_4 + CH_3$; and (4) formation of CH_3I and HI as the result of absorption of 1849 Å. light by I_2 in CH_4–I_2 mixtures. It has been found that: (1) Gaseous CH_3I and I_2 undergo a slow surface catalyzed exchange reaction in Pyrex in the dark at 25°, and that exchange is also induced by light from a tungsten filament lamp transmitted by Pyrex and absorbed by CH_3I. (2) The quantum yield for the gas phase exchange between CH_3I and I_2 in 2537 Å. light absorbed by CH_3I is unity. (3) "Hot" methyl radicals formed by the dissociation of gaseous CH_3I by 2537 Å. light undergo the reaction $CH_3 + CH_3I \rightarrow CH_4 + CH_2I$ with a quantum yield of about 0.0027, in agreement with the earlier result of Schultz and Taylor. For radicals formed by 1849 Å. light the yield is twelve-fold higher. (4) For hot radicals formed by 2537 Å. light the relative probability per collision that they will abstract hydrogen from CH_3I, CH_2I_2 and CH_4 is $1 : \geqq 16 : 0.3$. (5) The rate of the photolysis of CH_3I to form CH_4 and CH_2I_2 is independent of temperature up to at least 300°. It is inhibited by the presence of A or CH_4. (6) Secondary products from the photolysis of gaseous CH_3I include CHI_3, C_2H_4 and probably C_2H_2 but not H_2. (7) By coupling spectrophotometric and mass spectra analyses a satisfactory material balance for I, C and H in the products of the photolysis of CH_3I has been obtained. (8) 1849 Å. is absorbed by I_2 to produce excited molecules which react with CH_4 to produce CH_3I and HI with a quantum yield of 0.1. (9) Thermal $C^{14}H_3$ radicals from the photolysis of $C^{14}H_3I$ undergo the reaction $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$ with an activation energy which is about 6.5 kcal./mole higher and a frequency factor about 3×10^{-4} lower than the $C^{14}H_3 + I_2 \rightarrow C^{14}H_3I + I$ reaction.

Introduction

The purpose of this research was to investigate the feasibility of using the photodissociation of $C^{14}H_3I$ as a means of producing labeled methyl radicals for use in studying their reactions.

The first step in the photolysis of CH_3I is its dissociation by the reaction $CH_3I \xrightarrow{h\nu} CH_3 + I$. This conclusion is supported by the presence of a continuum in its absorption spectrum,[2] by the fact that

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[1] Department of Chemistry, University of Buffalo, Buffalo, New York.

[2] (a) G. Herzberg and G. Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930); (b) C. F. Goodeve and D. Porret, *Proc. Roy. Soc.* (*London*), **A166**, 31 (1938).

the exchange reaction with radioiodine in solution has a quantum yield of approximately unity,[3] by the fact that the normally low quantum yield of C_2H_6 formation is increased by conditions which favor the reaction $CH_3 + CH_3 \rightarrow C_2H_6$ relative to the reaction $CH_3 + I_2 \rightarrow CH_3I + I$ (*i.e.*, by the presence of silver[4,5a] in the reaction vessel or by high intensity flash photolysis[6]), and by the fact that the quantum yield for the production of $^1/_2I_2$ is unity in the presence of an excess of oxygen[7] or nitric oxide.[8] Both for the gas phase[4,5] and the liquid photolyses[3,9] the reported products include methane, ethane, iodine, methylene iodide and ethylene. Except when silver is present or high intensity flash techniques are used all of these are formed with quantum yields of less than 0.1, the methane having the highest yield. Since the yield of methane is independent of temperature,[5] is not lowered by the presence of iodine to the extent that would be expected if thermal methyl radicals were responsible,[5a,9] and is decreased by added inert gas,[5] it must result from a "hot radical" process. This is plausible because the photons of 2537 Å. commonly used have sufficient energy to break the C–I bond giving an iodine atom in the $^2P_{1/2}$ state and leaving the methyl radical with 32 kcal./mole.

Experimental

Reagents.—Eastman Kodak Co. white label methyl iodide was purified by passage through a 30-cm. column of fresh anhydrous silica gel and by fractional distillation in a 1 meter glass-helix-packed vacuum-jacketed column, at 42.2° at atmospheric pressure. The middle third was distilled from anhydrous sodium sulfate and clean copper wire *in vacuo* and stored in an evacuated Pyrex bulb closed by a stopcock greased with fluorocarbon grease. No coloration appeared in the liquid during a year of exposure to the light of the laboratory while in this container. Infrared spectra indicated that the silica gel column removed oxygenated impurities from the commercial material. The spectra of samples which received only silica gel treatment and those which had also been distilled were identical.

Methyl iodide having a C^{14} specific activity of about 1 mc./millimole was obtained from Tracerlab, Inc. Samples for the experiments were vaporized from iodine and other heavy impurities at −40° or lower. The condensed vapor was pumped on at liquid air temperature to remove any methane or ethane.

Mallinckrodt analytical reagent iodine was purified[10] by grinding with potassium iodide and ignited lime, and subliming. To prepare radioiodine of the desired specific activity a weighed amount of the purified inactive iodine was added to carrier-free NaI^{131} solution,[11] and the mixture was distilled through P_2O_5 on the vacuum system and condensed in a liquid air trap. Exchange between the aqueous iodide and the excess molecular iodine achieved almost complete transfer of the radioactivity to the latter.

Phillips Research Grade methane, stated to be 99.9% pure, and Ohio Chemical Co. argon, stated to be 99.6% pure, were used without further purification.

Reaction Cells, Addition of Reagents and Thermostating.—Two sizes of cylindrical quartz reaction cells with flat end windows, one with a 50-ml. volume and 5-cm. light path, the other with a 40-ml. volume and 10-cm. light path, were used. Prior to filling they were degassed by flaming and evacuation. Introduction of the desired quantity of methyl iodide or iodine vapor to the cell or a metering flask from the storage reservoir (through stopcocks lubricated with fluorocarbon grease) was achieved by adjusting the temperature of the reservoir to give the necessary vapor pressure. Methane was allowed to enter to any desired pressure, measured on a mercury manometer, separated from the rest of the system by means of a stopcock and trap cooled with Dry Ice and alcohol. A check on the quantity of the methyl iodide and iodine in the cell was afforded by spectrophotometric measurements. Following filling, the cell could be sealed from the system for spectrophotometric analyses or left attached through a stopcock for use in the $C^{14}H_4$ analyses.

During illumination the cylindrical reaction cells were positioned reproducibly in a trough-shaped holder in an air thermostat which could be maintained at any average temperature desired between that of the room and about 300°, with fluctuations of not more than ±4°. The light beam entered from one side of the furnace, passed through the cell, and then out of the furnace through a quartz window, and onto a photocell.

Photochemical Methods.—The light source for most of this work was a Hanovia quartz SC2537 low pressure mercury vapor lamp which was operated without cooling at a temperature of about 100° at 100 ma. and 300 volts supplied by a 500 v., 110 ma. Jefferson luminous tube transformer. It consisted of a 30 cm. long, 1.5 cm. i.d. quartz tube with a flat window on one end and two side tubes for electrodes. The light from the window was partially collimated by a brass tube 6.5 cm. long and 1.5 cm. i.d. which projected through the wall of the air furnace to the face of the reaction cell. The total energy was measured with a multiple junction quartz window thermopile having a receiving surface larger than the cross sectional area of the light beam. Readings were taken with the aid of a Leeds and Northrup microvolt amplifier. The thermopile was calibrated against a Bureau of Standards standard lamp. The relative energy distribution between the several lines emitted by the mercury arc in the region from 2000 to 4000 Å. was determined with the aid of a grating spectrograph. Selective filtration of different parts of the spectrum with Corning filters, the transmissions of which were quantitatively determined with a Beckman spectrophotometer, further aided in evaluating the distribution of the total energy output. A 9863 filter served to transmit wave lengths from 2000 to 4000 Å. while cutting out those above and below this range. Pyrex served to cut off at about 2900. A 791 filter cut off below 2537. Corrections were made for the transmission of the cell and thermopile windows. Under the conditions of these tests, the arc delivered to the outer surface of the thermopile window 0.80×10^4 ergs/sec. at wave lengths between 2200 and 4078 Å., distributed as follows: at 2537 Å., 0.67×10^4 ergs./sec.; 2600–4078 Å., 0.13×10^4 ergs./sec. The amount of light delivered at 1849 Å. could not be determined by this procedure. By the method described in footnote *b* of Table III, it was found that the quantum intensity available at less than 2537 Å. (predominantly 1849 Å.) and transmitted by the window of the 50-ml. cell used was *ca.* 0.45 as great as at 2537 Å.

For routine monitoring of the constancy of the light intensity of the mercury arc a Westinghouse WL-775 tantalum cathode phototube, sensitive to 2537 Å. and below but not sensitive above 3000 Å., was used in conjunction with a Leeds and Northrup microvolt amplifier. It indicated that there was negligible change in the intensity of the light from the arc over a period of several months of continuous operation.

In the few experiments where it was desired to observe relative transmissions of 1849 Å. light by methane, methyl iodide and iodine, a Westinghouse WL-789 platinum

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[3] W. H. Hamill and R. H. Schuler, This Journal, **73**, 3466 (1951).

[4] W. West and L. Schlessinger, *ibid.*, **60**, 961 (1938).

[5] (a) R. D. Schultz and H. A. Taylor, *J. Chem. Phys.*, **18**, 194 (1950); (b) F. P. Hudson, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **21**, 1894 (1953).

[6] N. Davidson and T. Carrington, This Journal, **74**, 6277 (1952).

[7] (a) S. Hacobian and T. Iredale, *Nature*, **166**, 156 (1950); (b) W. J. Blaedel, R. A. Ogg, Jr., and P. A. Leighton, This Journal, **64**, 2500 (1942).

[8] T. Iredale and E. R. McCartney, *ibid.*, **68**, 144 (1946).

[9] R. H. Schuler and C. T. Chmiel, *ibid.*, **75**, 3792 (1953).

[10] W. C. Pierce and E. L. Haenisch, "Quantitative Analysis," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 241.

[11] Item 53-F, U. S. Atomic Energy Commission Isotopes Catalogue and Price List No. 4, March, 1951.

cathode phototube which is insensitive to wave lengths greater than about 2100 Å.[12] was used.[13]

Radiochemical Analyses.—In studies of the exchange of radioiodine with methyl iodide the progress of the reaction was determined periodically by measuring the counting rate of the mixed vapors, of the background, and of the methyl iodide alone, without opening the reaction vessel. A mica-window Geiger tube was mounted directly below the vessel. When it was desired to count the background, liquid air was applied to a small lead-shielded side tube of the vessel. Warming to −50° with a cold alcohol bath allowed the methyl iodide to vaporize and be counted while retaining the iodine in the solid state. The use of a 100 mg./cm.^{2} lead foil between the cell and the Geiger tube window doubled the counting efficiency by increasing the number of secondary electrons ejected into the tube as a result of absorption of the I^{131} γ-rays.

In the experiments where methyl iodide or methane labeled with C^{14} was to be counted the gas was transferred on the vacuum system from the reaction cell to a 50-ml. chamber with a thin mica window (an old Geiger tube). This was mounted almost in contact with the mica window of a Geiger tube which served to count the C^{14} β-particles originating from the gas. The counting efficiency was about 0.6%. Frequent flexing of the mica window of the gas chamber was avoided by consistently maintaining the pressure below atmospheric, and only one breakage was experienced in many assays.

The experiments were designed so that the counting rate of the $C^{14}H_4$ would be at least 400 c./min. for each per cent. of $C^{14}H_3I$ converted to $C^{14}H_4$. This allowed the quantitative measurement of very slow reaction rates without requiring excessive times of reaction. In order to allow accurate counting of the very much higher activity in the methyl iodide fraction a 12 mg./cm.^{2} absorber was placed between the mica window of the gas chamber and that of the counter tube. The proportion of the C^{14} β-radiation cut out by this absorber when used in this counting arrangement was determined.

In order to separate methane from its reaction mixture with methyl iodide a U-tube connecting the reaction vessel to a stopcock was immersed in liquid air and the stopcock opened to a trap at −210° (cooled with pumped-down liquid air). The methyl iodide was retained in the U-tube while the methane condensed in the colder trap. Transfer to the counting chamber was accomplished by use of a cold finger on the latter. This achieved 95% transfer of the methane even though it has an appreciable vapor pressure at the liquid air temperature used.

Spectrophotometric Analyses.—The cylindrical reaction cells could be placed in a Beckman DU or Cary recording spectrophotometer and the volatile compounds CH_3I, CH_2I_2 and I_2 determined spectrophotometrically at intervals during the course of an experiment. CHI_3, having a very low vapor pressure, was determined in heptane solution at the end of the experiment.

Iodine was estimated by its absorption at 5200 Å., at which wave length all the other substances are completely transparent. The three iodides all absorb strongly in the ultraviolet, and differ sufficiently in spectra to be readily distinguishable in all the mixtures met with in this work. Table I records the values for the molar extinction coefficients used in the calculations. Those for CH_3I, CH_2I_2, CHI_3 and I_2 were obtained in the present study by determinations on measured amounts of the pure materials. A reasonable estimate of the accuracy of these values is ±5%. The values for HI were obtained by averaging the data given in two previous publications.[14,15]

Mass Spectrum Analyses.—Samples were prepared by irradiation of methyl iodide vapor in the 700-ml. annulus of a vessel shaped like a dewar flask. The major portion of the 4 cm. diam. inner tube was quartz, which was joined to the outer Pyrex portion by a graded seal. A U-shaped quartz mercury-vapor-argon lamp was made to fit inside the inner tube. This was replaced by a 4-watt Westinghouse Sterilite when it was desired to eliminate essentially all 1849 Å. radiation. Following irradiation *t*-butyl chloride ice (−120°) was placed in the inner tube. The gases not retained at this temperature were pumped off, measured and transferred to a mass spectrometer sample tube by means of a Toepler pump–gas buret combination similar to that described by LeRoy.[16]

TABLE I

MOLAR EXTINCTION COEFFICIENTS[a]

	2200 Å.	2600 Å.	2900 Å.	5200 Å.
		A. Gaseous		
HI	175[b]	40[b]	[c]	[c]
CH_3I	20	350	22	[c]
CH_2I_2	[d]	380	1100	[c]
I_2	[c]	[c]	[c]	780
	2600 Å.	2900 Å.	3600 Å.	5200 Å.
		B. Heptane Solution		
CH_3I	400	30	[c]	[c]
CH_2I_2	440	1200	40	[c]
CHI_3	900	1020	1580	[c]
I_2	160	90	10	930

[a] $\epsilon = (1/lc) \log (I_0/I_t)$ for l in cm. and c in moles/l. [b] Average of values from references 14 and 15. [c] Optical density negligible under conditions of experiments of this paper. [d] Not determined.

The Exchange Reaction between Methyl Iodide and Iodine

Dark Exchange and Photochemical Exchange in Pyrex.—When 7 mm. (*ca.* 1 × 10^{-4} mole) of CH_3I and 0.2 mm. of I_2 labeled with I^{131} were allowed to stand in a Pyrex flask in the dark, exchange of iodine occurred at a rate[17] of about 5 × 10^{-9} mole/hr. at room temperature and 2 × 10^{-7} mole/hr. at 140°. A similar reaction mixture exchanged 14 × 10^{-9} mole/hr. during a 15-day period at 25°, 3 × 10^{-6} mole/hr. during a subsequent 3-hour period at 120° and 5 × 10^{-9} mole/hr. when returned to 25°.

The rate of exchange was not increased by exposure to a 1000-watt tungsten filament lamp or sunlight through a Corning 3385 filter with a low wave length cutoff of *ca.* 4500 Å. but was increased by light passed by a 5562 filter with a cutoff at about 3000 Å. Since the maximum absorption coefficient of iodine and also the maximum intensity of the tungsten lamp occur at wave lengths higher than 4500 Å. the results suggested that the photochemical reaction was induced by light absorbed by methyl iodide in the region of 3000 Å. where the long wave length tail-off of its absorption coefficient

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[12] V. K. Zworykin and E. G. Ramberg, "Photoelectriciy and Its Application," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 118.

[13] Loan of this non-production type tube by the Westinghouse Corp., through the courtesy of V. J. Rydberg and D. E. Henry, is gratefully acknowledged.

[14] C. F. Goodeve and A. W. C. Taylor, *Proc. Roy. Soc.* (*London*), **154A**, 181 (1936).

[15] J. Romand and B. Vodar, *Compt. rend.*, **226**, 890 (1948).

[16] D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

[17] The rate of the reaction in moles of CH_3I exchanged per hour in the volume of the reaction vessel is given by $R = 2.3 \log (1 - f)/t (2[CH_3I][I_2]/([CH_3I] + 2[I_2]))$, where the brackets indicate the moles of each reactant in the vessel. Partial exchange of radioactivity had already occurred preceding each interval of measurement except the first but it was desired to obtain R for each interval, independent of the others. The value of f used is therefore based on the difference between the distribution of radioactivity which had occurred prior to the period of measurement and the expected distribution at infinite time. It is given by

$$f = \frac{(A_{2\mathrm{CH_3I}} - A_{1\mathrm{CH_3I}})(1 + 2[I_2]/[CH_3I])}{A_{1\mathrm{I_2}} - 2A_{1\mathrm{CH_3I}}[I_2]/[CH_3I]}$$

where $A_{1\mathrm{CH_3I}}$ and $A_{1\mathrm{I_2}}$ indicate the counting rates of the reactants at the start of the measurement interval and $A_{2\mathrm{CH_3I}}$ that at the end of the interval and the brackets signify concentrations.

overlaps the low wave length tail-off of the transmission of Pyrex and the 5562 filter. This conclusion was verified by the data of Table II which show that the rate of photochemical exchange increased with an increase in methyl iodide concentration but was not significantly affected by the iodine concentration. The results of Table II were obtained by filling the 300-ml. Pyrex flask with the reaction mixture (A), determining the rate of the exchange in the dark and in the light several times, and then (by means of a break seal) introducing added iodine to the concentration shown in line (B) and repeating the determinations. With the aid of a second break seal the methyl iodide concentration was then increased (line C) and further rate determinations were made. During illumination the flask was maintained at approximately room temperature by running water.

Column 4 of Table II shows that the dark reaction is sensitive to change in concentration of iodine but not of methyl iodide. The fact that the rate is independent of the pressure of one of the reactants and the fact that it has been found to vary from one vessel to another are consistent with the conclusion that it is surface catalyzed.[18] At the pressures used the surface is apparently saturated with respect to methyl iodide but not with respect to iodine.

TABLE II

EFFECT OF REACTANT CONCENTRATION ON ($CH_3I + II^{131} \rightarrow CH_3I^{131} + I_2$) REACTION IN PYREX BULB

	Amount of reactant, moles			
	CH_3I $\times 10^4$	I_2 $\times 10^6$	*R* in light, moles/hr. $\times 10^8$	*R* in dark, moles/hr. $\times 10^9$
(A)	1.4	1.5	8.7	3.9
(B)	1.4	3.2	9.0	7.5
(C)	2.8	3.2	15.6	7.2

The rate of the dark reaction is not influenced by the levels of β-radiation from the radioiodine used in this work. A reaction mixture similar to those cited above, and containing 0.2 mc. of I^{131} (8 day half-life), gave the same exchange rate at the end of a 15-day decay period as at the start.

Quantum Yield of the Exchange Reaction at 2537 Å.; Intensity of 1849 Å. Light.—The data of Table III show that the quantum yield of the gas phase exchange of iodine between CH_3I and I_2 is unity. It undoubtedly occurs by the mechanism

$$CH_3I \xrightarrow{h\nu} CH_3 + I^{2-7};\ CH_3 + I_2 \longrightarrow CH_3I + I$$

Table III also gives the data used to estimate the quanta of 1849 Å. light absorbed by methyl iodide at known pressure in our experimental set-up in the absence of the 791 filter sometimes used to exclude this light. The determination was made by observing the increase in exchange rate when the 791 filter was removed and correcting for the absorption of 2537 Å. by the filter. These data allowed a computation of the quantum yield of methyl iodide photolysis at 1849 Å. in later experiments.

TABLE III

QUANTUM YIELD OF ($CH_3I + II^{131} \rightarrow CH_3I^{131} + I_2$) REACTION AT 2537 Å.; INTENSITY OF 1849 Å. LIGHT

	Amount of reactant,[a] moles		*R*, molecules/min.		Quanta absorbed/min. at 2537 Å.			
	CH_3I $\times 10^5$	I_2 $\times 10^7$	With 791 filter $\times 10^{-16}$	Without filter $\times 10^{-16}$	With 791 filter $\times 10^{-16}$	Without filter $\times 10^{-16}$	Quantum yield at 2537 Å.	Quanta absorbed/min. by CH_3I at 1849 Å.[b] without filter $\times 10^{-16}$
(A)	2.5	7.2	2.5	4.2	2.5	3.5	1.0	0.7
(B)	1.03	5.5	1.6	2.6	1.6	2.3	1.0	.3

[a] In 50-ml. cylindrical quartz reaction cell with 5 cm. light path. [b] Based on the assumption that the quantum yield of exchange at 1849 Å., like that at 2537 Å., is unity and that light absorbed by I_2 is ineffective in causing exchange. If the molar absorption coefficients for CH_3I and I_2 at 1849 Å. are 170 and 1.1 × 10^4, respectively (as determined in work reported later in this paper), it may then be estimated from exp. A that the light reaching the inside face of the cell window when no filter was used contained 4.0 × 10^{16} photons/min. of 2537 Å. light and 2.1 × 10^{16} photons/min. of 1849 Å. light. Exp. B gives 4.0 × 10^{16} and 1.6 × 10^{16} photons/min. for the two wave lengths. The assumption that light absorbed by I_2 at 1849 Å. is not effective in causing exchange is supported by the fact that the rate of exchange initiated by 1849 Å. (last column of table) changed from 0.7 × 10^{16} to 0.3 × 10^{16} in going from exp. A to B while the fraction of the incident light absorbed by I_2 remained nearly constant (61 and 65%) and that absorbed by CH_3I dropped from *ca.* 33 to 19%.

The Photolysis of Methyl Iodide

Reaction Products; Secondary Reactions; Material Balance.—Figure 1 shows the results of a typical experiment on the photolysis of CH_3I in which the concentrations of CH_3I, CH_2I_2 and I_2 in a reaction cell were determined following successive intervals of illumination with the quartz mercury

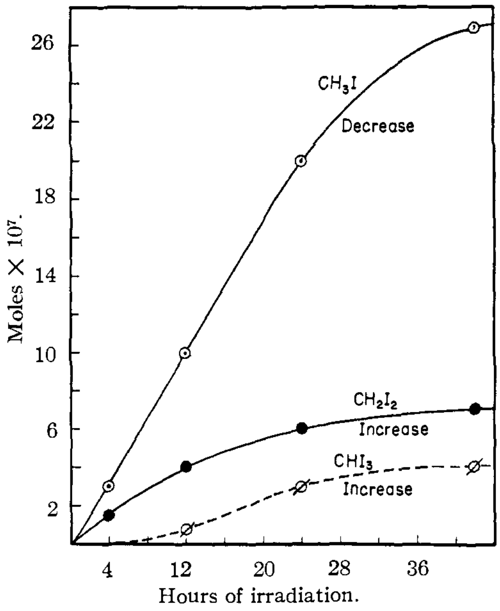

Fig. 1.—Growth of CH_2I_2 and CHI_3 as CH_3I is photolyzed. Experiment done at room temperature with unfiltered light of the arc using 40-ml. quartz reaction cell with 10-cm. light path. Initial reaction mixture 120 × 10^{-7} mole CH_3I; 4 × 10^{-7} mole I_2. Points at 12 and 24 hr. on CHI_3 curve calculated on assumption $3[CHI_3] = ([CH_3I]\ \text{decrease} - 2[CH_2I_2])$.

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[18] Following completion of this work we have learned from A. F. Trotman-Dickenson, D. Clark and H. O. Pritchard, that they have observed the catalytic effect of Pyrex on the $CH_3I + I_2$ exchange in the dark by packing the reaction vessel with Pyrex tubes.

TABLE IV

PRODUCTS OF METHYL IODIDE PHOTOLYSIS AS A FUNCTION OF EXTENT OF DECOMPOSITION AND OF WAVE LENGTH[a]

Experiment		36	37	39	40
Light source		Quartz U	Quartz U	4 Watt Sterilite[c]	Quartz U
Initial CH_3I, moles × 10^6		*ca.* 300	[d]	*ca.* 160	*ca.* 350
CH_3I reacted, %		*ca.* 30	[d]	*ca.* 6	*ca.* 4
Hydrocarbons formed, moles × 10^6	CH_4	*ca.* 50[b]	47	5.0	6.1
	C_2H_6	[e]	2	0.4	0.5
	C_2H_4	[e]	6	.1	.1
	C_2H_2	[e]	1	0	0
	H_2	[e]	0	.1	.2
Iodides formed, moles × 10^6	CH_2I_2	16	[d]	4.0	6.4
	CHI_3	6	[d]	0.3	0.6
	I_2	19	[d]	0.5	0.5
No. of moles in products × 10^6	C	[e]	87	10.3	14.3
	H	[e]	264	31.1[f]	41.2[f]
	I	88	[d]	9.9	15.6
Mole ratio of products	C_2H_6/CH_4	[e]	0.04	0.08	0.08
	C_2H_4/CH_4	[e]	.13	.02	.02
	I_2/CH_4	[e]	.38	.1	.1

[a] Photolysis made in 700-ml. dewar-reactor. Mass spectrometer analyses for hydrocarbons and hydrogen from experiments 37, 39 and 40 made by Consolidated Engineering Co. [b] Approximate measurement using isotope-ratio mass spectrometer, C_2 fraction not determined. The coöperation of Prof. R. H. Burris, who made these assays, is gratefully acknowledged. [c] Negligible amount of 1849 Å. light. [d] Not determined, but would be about same as in exp. 36 since this experiment was done in identical manner. [e] Not determined but would be about same as in exp. 37 since this experiment was done in identical manner. [f] Ignoring H from H_2. Hydrogen was not found as a product in experiment 37, where a much larger gas sample was obtained (1.20 ml. as compared to 0.15 and 0.19 in exps. 39 and 40). It is assumed that the trace found in the latter experiments is not a result of CH_3I photolysis.

arc. The amount of CHI_3 formed was determined at the end. The data indicate that a primary photolysis product is CH_2I_2, one molecule of this compound being produced for each two of CH_3I, used up at the start of the reaction. As the CH_2I_2 concentration builds up this compound undergoes reaction which results in the formation of CHI_3. Three times the CHI_3 plus twice the CH_2I_2 is essentially equal to the CH_3I consumed. This material balance is consistent with the stoichiometry of the mechanism which will be discussed later. No indication of HI was found from the iodine material balance of this or other runs, and the mass spectrum analyses (Table IV) showed negligible amounts of hydrogen. Hydrogen would be formed as a decomposition product if HI were produced.

Table IV shows the relative yields of both the hydrocarbon and iodide products of the photolysis, for experiments where the decomposition was carried only 5% to completion and also for experiments where 30% of the methyl iodide was used up. Convincing evidence that all of the major products have been included is given by the stoichiometric relation of carbon, hydrogen and iodine in the products. In terms of moles of atoms this should be the same as in CH_3I, *i.e.*, 1:3:1 and it is found to be so within experimental error in each run, even though the ratio of products to each other is much different in exp. 37 than in 39 and 40.

The fact that the C_2H_4/CH_4 ratio increases from 0.02 to 0.13 in going from 5 to 30% decomposition of the CH_3I (Table IV) indicates that the ethylene is formed by a reaction involving one of the products which accumulates as the reaction proceeds.

For each mole of ethane, ethylene and acetylene formed there must be formed one, two and three moles, respectively, of iodine, thus accounting for the high I_2/CH_4 ratio in exp. 37 as compared to exps. 39 and 40.

The C_2H_6/CH_4 ratio is smaller in exp. 37 which went 30% to completion than in exps. 39 and 40 which were much less complete. This is undoubtedly due to the fact that as the concentration of I_2 increases in the system due to ethane formation by the $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ reaction, the latter process essentially ceases as a result of the competitive reaction $CH_3 + I_2 \rightarrow CH_3I + I$. It is not possible from our results to say whether there is a relatively slow continuing production of ethane by a hot reaction of the type $CH_3 + CH_3I \rightarrow C_2H_6 + I$, such as has been suggested on the basis of studies in the liquid phase.[9]

Evidence That Ratio of Products Is Independent of Wave Length.—It will be shown in a later section that the quantum yield for the methyl iodide photolysis is about 12 times higher at 1849 Å. than at 2537 Å. Presumably this is due to the higher energy of the methyl radicals at their time of formation. The similarity of the ratios of products obtained for exps. 39 and 40 in Table IV shows that this increased energy does not affect significantly the qualitative nature of the reactions which occur.

Evidence That the Photolysis Is Due to a Hot Radical Reaction: Effect of Temperature, Wave Length and Added Gases.—Other workers have demonstrated[5] that the quantum yield of photolysis of gaseous methyl iodide is independent of temperature from 25 to 100°, and is decreased by the presence of CO_2, He and Ne. They logically conclude that the formation of CH_4 results from the reaction of hot methyl radicals by the step $\underline{CH_3} + CH_3I \rightarrow CH_4 + CH_2I$ followed by $CH_2I + I_2 \rightarrow$

CH_2I_2 + I. Our results, given in Tables V through IX, show that: (1) the rate of photolysis at constant absorbed light intensity is independent of temperature over the range from 53 to 315° (Table V); (2) the rate is decreased by added methane (Tables VI and VIII), and by argon (Table VI); (3) iodine is much more effective in reducing the rate in the full light of the mercury arc than is either argon or methane (Table VII), but this effectiveness can be ascribed entirely to the fact that the very high absorption coefficient of I_2 at 1849 Å. allows it to act as an internal filter which reduces the light available for absorption by the CH_3I; (4) methane is more effective as a moderator when activation is by 2537 Å. light alone than when 1849 Å. light is also present (Table VIII as compared to Table VI); (5) the quantum yield of CH_3I decomposition is about 12 times higher at 1849 Å. than at 2537 Å. (Table IX). We believe these last two conclusions to be correct but since they are based on single experiments they should have further verification.

TABLE V

RATE OF PHOTOLYSIS OF METHYL IODIDE AS A FUNCTION OF TEMPERATURE[a]

Initial amts., moles × 10^7 CH_3I	I_2[c]	T, °C.	CH_2I_2 formed, moles × 10^7
163	6	53	7.5
156	6	102	7.5
170	6	202	7
173[b]	6	330	0
161[b]	12	315	7.5
172	6	50	8

[a] Using 50-ml. cells with 5-cm. light path; full light of SC2537 lamp. 160 × 10^{-7} molar is equivalent to 6 mm. pressure in this cell at 25°. 24-hr. illumination was used in each experiment except that noted in footnote [b]. [b] Prior to illumination this reaction mixture stood for 54 hr. at 330°. It was then illuminated for 24 hr. During the dark period 12 × 10^{-7} mole of CH_3I decomposed and 6 × 10^{-7} mole of I_2 was formed. No CH_2I_2 was formed. The formation of I_2 presumably was due to a reaction of the type $2CH_3I \rightarrow C_2H_6 + I_2$. [c] No detectable change in iodine concentration (*i.e.*, less than 1 × 10^{-7} mole) occurred in any of these experiments except during the high temperature dark period noted in footnote [b].

TABLE VI

EFFECT OF ADDED METHANE AND ARGON ON RATE OF PHOTOLYSIS OF METHYL IODIDE[a]

T, °C.	Added gas, mm.	Initial amts., moles × 10^7 CH_3I	I_2	I_2 consumed, moles × 10^7	Rate of decomp. of CH_3I, moles × 10^7/day Uncor.	Cor.[b]
22	0	120	4	0	20	20
22	A, 740	127	5	0	14	14
25	CH_4, 850	129	5	3	4	7–10
52	CH_4, 1200	140	4	2	5	7–9

[a] Using 40-ml. cells with 10-cm. light path; full light of SC2537 lamp. 130 × 10^{-7} mole is equivalent to 6 mm. pressure in this cell at 25°. [b] Correction made on the assumption that the iodine consumed produced methyl iodide by the reaction $CH_4 + I_2 \rightarrow CH_3I + HI$ due to 1849 Å. light absorbed by the I_2, as indicated by results described in a later section. The moles of methyl iodide produced would be equal to the moles of iodine consumed if the HI is not decomposed to H_2 and I_2, or double this if it is decomposed. Experiments in which HI was measured indicate that it was probably partially decomposed in this case.

TABLE VII

INTERNAL FILTER EFFECT OF IODINE ON THE PHOTOLYSIS OF METHYL IODIDE WITH FULL LIGHT OF SC2537 LAMP[a]

Av. pressures of reactants, mm. CH_3I	I_2	Rate of CH_3I decomposition, moles × 10^{-7}/day Obsd. total	Due to 1849 Å.[c]	Due to 2537 Å.[d]
5.5	*ca.* 0.07	30	23	7
6.1	0.2	23	15	8
6.8	2.5[b]	10	2	8

[a] Using 40-ml. cells, 10-cm. light path, T, *ca.* 50°. [b] Saturated vapor pressure of I_2 at 50°. [c] Calculated on the assumption that the ratio of 2537 to 1849 input is as indicated in footnote to Table III, that the molar absorption coefficients of I_2 and CH_3I at 1849 Å. are 1.1 × 10^4 and 170, respectively, that $\Phi_{1849}/\Phi_{2537} = 12$ (Table IX) for CH_3I decomposition by light absorbed by CH_3I, and that absorption by iodine causes no decomposition of CH_3I. [d] By difference. (The expected value, calculated on the basis of the data of Table VIII and the known transmission of the $NiSO_4$ filters, is 7.5 × 10^{-7} mole/day, with the CH_3I pressure 6 mm.)

TABLE VIII

EFFECT OF 1849 Å. LIGHT FROM SC2537 LAMP ON RATE OF PHOTOLYSIS OF METHYL IODIDE; MODERATING EFFECT OF METHANE AT 2537 Å.[a]

Initial amts., moles × 10^7 CH_3I	I_2	Rate of dec. of CH_3I, moles × 10^7/day	Other conditions
131	4	5	$NiSO_4$ filter[c]
126	4	17	Full light of arc
141	4	14	Empty quartz cell as filter[d]
127	4	6	$NiSO_4$ filter[e]
120	0	5	$NiSO_4$ filter[c]
144	0	<0.4[b]	$NiSO_4$ filter[c] 700 mm. CH_4 in reaction mixture

[a] Using 40-ml. cells with 10-cm. light path; exp. 32 at 102°, others at 51°. [b] Less than 2 × 10^{-7} mole decomposed in 5 days irradiation. [c] 1 cm. aqueous $NiSO_4 \cdot 6H_2O$, 500 g./l., in quartz cell; low wave length cut off at 2200 Å., 74% transmission at 2537 Å. [d] 80% transmission at 2537 Å. [e] Same as *c* except 2-cm. filter cell with 65% transmission at 2537 Å.

TABLE IX

QUANTUM YIELDS OF PHOTOLYSIS OF METHYL IODIDE AT 2537 AND 1849 Å.[a]

	A (791 filter)	B (791 filter)	C (No filter)
Irradiation, hr.	48	48	24.4
Initial CH_3I, moles × 10^7	195	189	183
Initial I_2, moles × 10^7	0	*ca.* 0.5	0.5
CH_3I dec., moles × 10^7	6	6	15[c]
Quanta absorbed/min. by CH_3I at 2537 Å. (× 10^{-16})	2.3	2.2	3.2
Quanta absorbed/min. by CH_3I at 1849 Å. (× 10^{-16})	0	0	0.8[d]
Over-all quantum yield, molecules CH_3I dec./quantum	0.0054	0.0056	0.15
Apparent quantum yield for 1849 Å. light	....	...	0.62
Quantum yield of CH_4 formation[b]	0.0027	0.0028	.0075

[a] Using 50-ml. cell with 5-cm. light path; T, 25°. The 791 filter has a low wave length cut-off of 2200 Å. and transmits 71% of the 2537 Å. light. [b] Assuming large proportion of CH_3I decomposed goes to CH_2I_2 and CH_4. [c] A check on this figure is provided by the experiments listed in Table V, where the light path in the cell was the same and the CH_3I pressure was similar. Two moles of CH_3I is decomposed for each mole of CH_2I_2 formed. [d] Calculated from the data of Table III and the known absorption of 1849 Å. light by CH_3I and I_2. The I_2 concentration increased from 0.5 to 1.5 × 10^{-7} mole in this run. The average was taken as 1 × 10^{-7} mole.

Mechanism and Kinetics.—The detailed material balances of Table IV, supported by the growth curves of Fig. 1, show that the initial photolysis products are almost solely CH_4 and CH_2I_2 and these in almost equal amounts. The only reasonable mechanism to explain this stoichiometry is

$$CH_3I + h\nu \longrightarrow \underline{CH_3} + I \qquad (1)$$

$$\underline{CH_3} + CH_3I \longrightarrow CH_4 + CH_2I \qquad (2)$$

$$CH_3 + I_2 \longrightarrow CH_3I + I \qquad (3)$$

$$CH_2I + I_2 \longrightarrow CH_2I_2 + I \qquad (4)$$

$$I + I + M \longrightarrow I_2 + M \qquad (5)$$

Reaction 2 is only possible for "hot" methyl radicals (indicated by the underlining). About 2.7×10^{-3} of the methyl radicals produced by 2537 Å. light and 3×10^{-2} of those produced by 1849 Å. light in pure CH_3I undergo this type of reaction. The remainder dissipate their excess energy in non-reactive collisions or generate a less energetic radical by an exchange reaction of the type $CH_3 + CH_3I \rightarrow CH_3I + CH_3$. The thermalized methyl radicals then regenerate CH_3I by reaction 3 which is known[3,6,19] to have a high rate constant at room temperature.

Iodoform, iodine and C_2 hydrocarbons are found in appreciable quantities only after the fraction of CH_3I decomposed becomes considerable. It is plausible that iodoform should be produced from CH_2I_2, by steps analogous to 2 and 4

$$\underline{CH_3} + CH_2I_2 \longrightarrow CH_4 + CHI_2 \qquad (6)$$

$$CHI_2 + I_2 \longrightarrow CHI_3 + I \qquad (7)$$

Referring to Fig. 1, it is seen that CHI_3 production is negligible until the ratio CH_2I_2/CH_3I exceeds *ca.* 0.03. By the time this ratio has become *ca.* 0.06, the net rates of CH_2I_2 and CHI_3 formation are about equal. This suggests that the probability that a methyl radical from the photolysis of CH_3I at 2537 which collides with a CH_2I_2 molecule will react by 6 is 16 times as great as the probability that reaction 2 will occur when the radical strikes a CH_3I molecule. For hot radicals of this type the energy depends on the number of moderating collisions experienced since formation. Hence when there is a large excess of CHI_3 the average energy of the methyl radicals when they undergo their first collision with CH_2I_2 is lower than when the CH_3I/CH_2I_2 ratio is low. Therefore the relative probability of reaction per collision may depend on this ratio; this possibility should be tested experimentally.

The results seem to indicate that iodoform production from CH_2I_2 is initiated by reaction 6 rather than by direct photolysis of CH_2I_2. If the reaction $CH_2I_2 \xrightarrow{h\nu} CHI + HI$, followed by $CHI + I_2 \rightarrow CHI_3$, occurred HI or H_2 would have been observed among the products.

Since hydrogen was not found among the products in exp. 37, Table IV, the most probable stoichiometry for the formation of ethylene and acetylene is: $4CH_3I = C_2H_4 + 2CH_4 + 2I_2$ and $6CH_3I = C_2H_2 + 4CH_4 + 3I_2$. Ethylene is only a minor product initially, so it is likely that the mechanism requires the intermediate formation of CH_2I_2 and CHI_3, followed by photolysis of these compounds.

The fact that the hydrogen abstraction reaction 2, and presumably also 6, takes place at room temperature only with "hot" radicals is consistent with the fact that similar reactions involving radicals in thermal equilibrium with their systems have been shown to have appreciable activation energies and low frequency factors.[20,21] It might be expected that at elevated temperatures the CH_3 radicals from the photolysis which failed to react while "hot" would react by thermal activation. Judging from the data of Table V the rate of this thermal reaction up to at least 315° must be negligible compared to the rate of the "hot" reaction. In this connection it is interesting to note that the measured rate of the thermal $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$ reaction at 250° (Table X) proves to be appreciably lower than the rate of the hot $\underline{C^{14}H_3} + CH_3I \rightarrow C^{14}H_4 + CH_2I$ reaction (Table V) when estimated for similar light absorption. The rate of the hot $\underline{C^{14}H_3} + CH_4 \rightarrow C^{14}H_4 + CH_3$ reaction is several fold slower than the 250° thermal reaction.

A surprising feature of the methane and argon inhibition (Table VI) in experiments with light containing 1849 Å. is that it is not more nearly complete. Hudson, Williams and Hamill[5b] observed a similar effect in comparing the inhibition by CO_2 for experiments where 1849 Å. light was used with those where only 2537 Å. light was present. If the hot radicals produced by 1849 Å. carry their 65 kcal./mole excess energy simply as kinetic energy, a momentum transfer calculation shows that, on the average, this excess will have been reduced to 1 kcal./mole after 12 collisions with methane or 16 with argon.[22] As both these gases were in more than a hundred-fold excess, it appears that a simple kinetic energy transfer concept is inadequate. However, if the hot methyls carry their excitation as vibrational quanta, collisional deactivation may be an exceedingly inefficient process.[23,24]

The data of Table IX suggest a 12-fold higher quantum yield of photolysis at 1849 Å. than at 2537 Å. In view of the observations noted in the last paragraph it seems that this higher yield may be due to added vibrational excitation of the methyl radicals rather than to increased kinetic energy. It is of interest that our figure of 0.0055 for the quantum yield of CH_3I decomposition at 2537 Å. agrees well with Schultz and Taylor's[5] value. They state 0.003 for methane formation which is equivalent to 0.006 molecules of methyl iodide decomposed per photon. Higher quantum yields have been reported for the liquid phase photolysis.[3]

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

[20] A. F. Trotman-Dickenson, *Quart. Rev.*, **VII**, No. 2, 198 (1953).

[21] F. A. Raal and E. W. R. Steacie, *J. Chem. Phys.*, **20**, 578 (1952). These authors using methyl radicals produced by acetone photolysis have obtained values of $E_A = 10.1$ and 8.7 kcal./mole for hydrogen abstraction from CH_3Br and CH_2Br_2, respectively.

[22] The average fraction of its energy transferred per billiard-ball-type of collision of a particle of mass m_A with a stationary particle of mass m_B is: $\Delta E/E = 2m_Am_B/(m_A + m_B)$.

[23] Studies outlined by L. Bergmann ("Ultrasonics and Their Scientific and Technical Applications," John Wiley and Sons, Inc., New York, N. Y., 1938, Ch. III) based on sound dispersion measurements suggest that conversion of a vibrational quantum to translational energy occurs on the order of once in thousands of collisions for many gases. Even smaller factors have been proposed by Zener.[24]

[24] C. Zener, *Phys. Rev.*, **37**, 556 (1931).

Photosynthesis of Methyl Iodide from Methane and Iodine by Light of 1849 Å.

When quartz cells containing methane and iodine were irradiated with the full light of the quartz mercury arc, iodine was consumed and CH_3I and HI formed. No reaction occurred when water filters were placed between the arc and the cell, proving that the actinic light was the 1849 Å. mercury line.

Approximate measurements of the absorption of 1849 light by the reactants were made with the aid of a WL-789 phototube.[12,13] A pressure of 685 mm. of CH_4 in the 10-cm. cell absorbed less than 10%, indicating an absorption coefficient of less than 0.1, while 0.08 mm. of I_2 absorbed 50% indicating an absorption coefficient of *ca.* 11,000.

Since no reaction occurs between methane and iodine atoms produced by 2537 Å. light or visible light, it seemed more probable, at first consideration, that the reaction forming methyl iodide was initiated by light absorbed by the methane rather than by light absorbed by the iodine. However this conclusion is ruled out by comparing the initial rate of CH_3I formation in the experiments of Figs. 2 and 3 ($\geqq 2 \times 10^{-7}$ mole/hr.) with the rate of light absorption by the CH_4. For experiment E of Fig. 3 the fraction of the 1849 Å. light absorbed by methane was certainly less than 0.002, and the intensity of the light (Table III, footnote *b*) was 1.85×10^{-6} einstein/hr. Thus the rate of absorption was $\leqq 3.7 \times 10^{-9}$ einstein/hr., which is 50-fold lower than the rate of reaction. Since there is no plausible mechanism for a quantum yield higher than unity,[25] we are led to the conclusion that the observed reaction is due to activation of the iodine by 1849 Å. light. Consequently it must result either from a step of the type $CH_4 + I \rightarrow CH_3 + HI$, made possible by unusual excitation of the iodine atom, or by a reaction such as $CH_4 + I_2 \rightarrow CH_3I + HI$, involving an excited iodine molecule. The iodine atom has as its first two excited electronic levels $^2P_{1/2}$ at 7600 cm.$^{-1}$ and $^4P_{5/2}$ at 54600 cm.$^{-1}$ [26] above the ground state, respectively. 1849 Å. light (54,200 cm.$^{-1}$) is incapable of dissociating the iodine molecule (35 kcal./mole, 12,300 cm.$^{-1}$) and raising one of the atoms to the $^4P_{5/2}$. The $^2P_{1/2}$ state of I does not have enough energy to lead to reaction with CH_4. If an 1849 Å. photon absorbed by an I_2 molecule were to produce one atom in the ground state and one $^2P_{1/2}$ with the residual energy appearing as kinetic energy equally divided between the two atoms each would have 66 kcal./mole. This is greater than the heat of the reaction $I + CH_4 \rightarrow CH_3I + H$ but cannot be used for it because if momentum is to be conserved in the formation of the activated complex a maximum of 0.11 (*i.e.*, $M_{CH_4}/(M_I + M_{CH_4})$) of this energy can go into internal energy of the activated complex and so be available for causing bond rupture.

Furthermore, the spectrum of iodine indicates that visible light dissociates it into a $^2P_{1/2}$ and a normal atom. Since its absorption coefficient falls to nearly zero in the near ultraviolet and then rises sharply below 2000 Å., absorption in the latter region must be due to a different process.

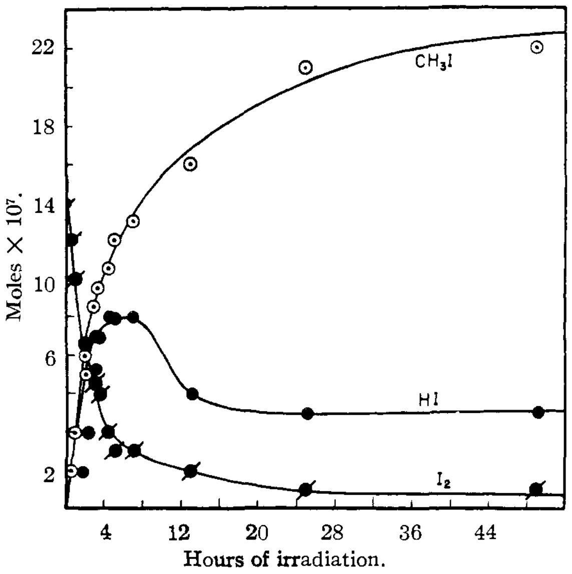

Fig. 2.—Relative change in amounts of CH_3I, HI and I_2 during irradiations of CH_4–I_2 mixture with 1849 Å. light; 50-ml. cell with 5-cm. light path; initial pressures: CH_4, 1010 mm. (2×10^{-3} mole); I_2, 0.2 mm. (4×10^{-7} mole). Solid iodine was present to make a total of 15×10^{-7} mole. Points on the I_2 curve greater than 4×10^{-7} mole were calculated on the assumption that in this region the over-all reaction was only $CH_4 + I_2 \rightarrow CH_3I + HI$.

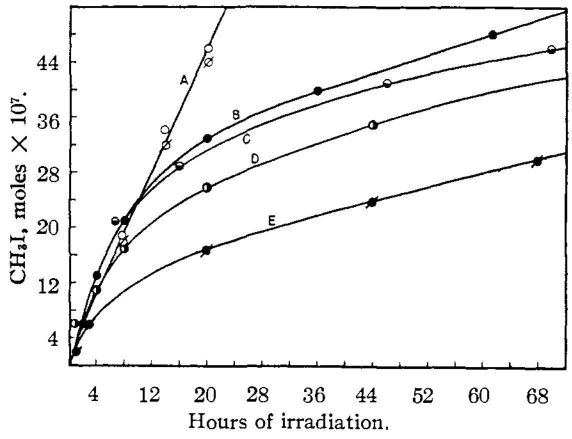

Fig. 3.—Photosynthesis of CH_3I and HI from CH_4 and I_2 with 1849 Å. light. Each curve is for a separate reaction mixture in a 40-ml. quartz reaction cell, 10-cm. path length; 1 mm. of gas in this cell at 25° is equivalent to 22×10^{-7} mole. The amounts of reactants, initial pressures (corrected to 25° for purposes of comparison), and temperatures of reaction were as follows,

	A	B	C	D	E
CH_4, mm. (25°)	108	103	98	120	12
CH_4, moles × 10^7	2300	2200	2100	2600	260
I_2, mm. (25°)	*ca.* 50	1.6	1.6	0.2	0.2
I_2, moles × 10^7	>1000	36	36	26	27
T, ° C.	102	102	52	25	25

In A, D and E part of the iodine was initially in the solid state and thus the saturated vapor was maintained throughout the first part of the run.

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(25) If reaction occurred as a result of absorption by CH_4 it would presumably go by the mechanism $CH_4 \xrightarrow{h\nu} CH_3 + H$; $CH_3 + I_2 \rightarrow CH_3I + I$; $H + I_2 \rightarrow HI + I$.

(26) Landolt-Börnstein, 6-I-I, p. 176.

The existence of a metastable state of iodine molecules excited by 1849 Å. light is suggested by the observations of fluorescence following excitation in this region,[27] and also by the sharp rise in absorption coefficient from essentially 0 at 2000 Å. to 11,000 at 1849 Å.

Figures 2 and 3 show some of the data obtained on the rate of product formation as a function of time of irradiation of different CH_4–I_2 mixtures with 1849 Å. light. Figure 2 shows that the initial rates of formation of CH_3I and HI are equal. As the iodine concentration decreases and the HI concentration increases, however, HI begins to be consumed faster than it is formed, while the rate of CH_3I production falls off markedly. Curve A of Fig. 3 shows that in the presence of a relatively high pressure (50 mm.) of I_2 in the gas the rate of CH_3I production remains constant over a large change in its concentration, while curves B, C, D and E illustrate a decreasing rate similar to that shown in Fig. 2. The nearly identical slopes of curves B and C seem to indicate that the rate controlling reactions at the concentrations of these curves are temperature independent. The initial slopes of all the curves of Fig. 3 are nearly the same. The variations in the later slopes and the shapes of the curves of Figs. 2 and 3 must be due to the interrelated effects of absorption of light by CH_3I and HI, and a variety of competing reactions such as $CH_3I + H \rightarrow CH_3 + HI$; $CH_3 + HI \rightarrow CH_4 + I$; $CH_3 + I_2 \rightarrow CH_3I + I$; $H + I_2 \rightarrow HI + I$.

The quantum yield of CH_3I formation, based on the light absorbed by I_2, is about 0.1.

The Abstraction of Hydrogen from Methane by Methyl Radicals

The results of the two series of runs carried out in this investigation are shown in Table X. The probable competing thermal reactions here are 3 and 8[28]

$$CH_3 + CH_4 \longrightarrow CH_4 + CH_3 \qquad (8)$$

The total rates of CH_4 formation given in the table are calculated from the known specific activity of the labeled methyl iodide (counted in the usual methane atmosphere). The latter remains effectively constant, since the total number of moles of $C^{14}H_4$ formation is small compared to the amount of $C^{14}H_3I$ available.[29] R_8, the net thermal rate of 8 at the various elevated temperatures, was obtained by subtracting the rate of the room temperature reaction, regarded as entirely a temperature-independent "hot radical" process. R_3, the moles per day of CH_3 radicals undergoing 3, can be taken as constant

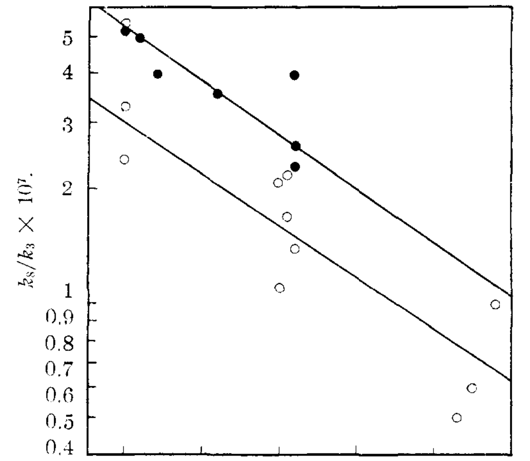

Fig. 4.—Effect of temperature on the ratio of the rate of the $C^{14}H_3 + CH_4 \rightarrow C^{14}H_4 + CH_3$ reaction to the rate of the $C^{14}H_3 + I_2 \rightarrow C^{14}H_3I + I$ reaction. Data taken from Table X: solid circles for Series A runs; open circles for Series B runs.

Table X

Rate of the $CH_3 + CH_4 \rightarrow CH_4 + CH_3$ Reaction as a Function of Temperature[a]

			Reaction rate				
T, °C.	P_{CH_4},[b] cm.	Duration, hr.	CH_4, c./min.	C.p.m./day	Moles/day[c] × 10^8	R_8,[d] net rate, moles/day × 10^8	k_8/k_3[e] × 10^7
			Series A				
198	37	23	710	740	13.7	9.1	4.0
30	51	47	470	240	4.4		
198	39	23	537	554	10.2	5.6	2.3
223	39	23	679	709	13.1	8.5	3.6
248	38	23	840	875	16.2	11.6	5.0
198	39	23	562	586	10.8	6.2	2.6
30	41	66.5	718	259	4.8		
243	38	23	724	756	14.0	9.4	4.0
252	37	22	813	887	16.4	11.8	5.2
			Series B				
200	37	19	742	938	12.8	7.8	2.2
30	38	45.3	698	370	5.0		
147	38	23	602	628	8.6	3.6	1.0
252	36	22	1617	1763	24.0	19.0	5.4
202	38	23.3	788	814	11.1	6.1	1.7
252	37	25.8	1330	1240	16.9	11.9	3.3
252	37	22	910	993	13.5	8.5	2.4
204	39	23.2	660	684	9.3	4.3	1.1
152	38	22.1	493	536	7.3	2.3	0.6
198	38	23.2	724	750	10.2	5.2	1.4
30	37	46.1	698	364	5.0		
156	37	22.5	454	484	6.6	1.6	0.5
203	37	22.5	858	915	12.4	7.4	2.1

[a] All runs made in 40-ml. cells with 10-cm. light path, using 791 glass as a filter to cut out light from the mercury arc at wave lengths below 2537 Å. [b] P_{I_2} in series A was 9×10^{-3} cm.; in B, 7×10^{-3} cm. P_{CH_3I} in Series A was 0.25 cm.; in B, 0.40 cm. [c] Specific activity of CH_3I in series A was 5400 c.p.m./micromole, in series B, 7350 c.p.m./micromole. [d] Obtained by subtracting average rate of the room temperature hot reaction in each series from the total rate. [e] R_3 (*i.e.*, rate of $CH_3 + I_2 \rightarrow CH_3I + I$) in series A = 5.5×10^{-5} mole/day; 6.8×10^{-5} mole/day in series B; and $k_8/k_3 = R_8/R_3([I_2]/[CH_4])$.

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(27) (a) J. C. McLennan, *Proc. Roy. Soc.* (*London*), **A91**, 23 (1914); (b) O. Oldenberg, *Z. physik*, **18**, 1 (1923); (c) F. W. Loomis and A. J. Allen, *Phys. Rev.*, **33**, 639 (1929); (d) P. Hirschlaff, *Z. physik*, **75**, 325 (1932); (e) H. Cordes, *ibid.*, **97**, 603 (1935).

(28) The thermal reaction $CH_3 + CH_3I \rightarrow CH_4 + CH_2I$ can be ignored since the data of Table V indicate that it does not occur even in pure CH_3I. The CH_4/CH_3I ratio in the experiments of this section was always >100

(29) Isotope effects in the reaction involving $C^{14}H_3$ radicals are assumed negligible. The maximum increase in activation energy over the reaction of $C^{12}H_3$ would be of the order of the difference in zero-point energy between $C^{14}H_3$ and $C^{12}H_3$.[30] This cannot be greater than about 200 calories, well within the estimated error in the activation energy determination of this work.

(30) J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

throughout, and numerically equal to the einsteins per day of light absorbed by the CH_3I. The ratio k_8/k_3 is thus readily calculable, since $k_8/k_3 = R_8[I_2]/R_3[CH_4]$. The activation energy difference, $E_8 - E_3$, was determined from the plot of log k_8/k_3 *vs.* $1/T$ shown in Fig. 4. The best visually determined value for series A was 7 kcal./mole; for series B, 6 kcal./mole; the estimated error is about ±2 kcal./mole. (A great deal of scatter occurred in these early determinations, as is seen in the table. It is hoped that experimental refinements will make possible a more precise figure.)

E_3 has not been directly determined experimentally, though an estimate of 0.5 ± 0.5 kcal./mole has found some support.[6,19] The following line of reasoning leads, we believe, to a more reliable figure. Electronic impact dissociation studies are in general agreement on a value of 101 ± 1 kcal./mole for $D(CH_3–H)$.[31] The activation energy for the reaction

$$\mathrm{Br} + \mathrm{CH_4} \underset{(10)}{\overset{(9)}{\rightleftarrows}} \mathrm{CH_3} + \mathrm{HBr} \qquad (9), (10)$$

has been carefully determined to be 17.8 kcal./mole.[32] The difference between the activation energy for the reverse of 9, which we label 10, and that for 3 is 0.8 ± 0.3 kcal./mole.[19] Combined with the known value of D(H–Br) (86.5 kcal./mole),[33] we have $E_3 = E_9 - D(CH_3\text{–}H) + D(H\text{–}Br) - (E_{10} - E_3) = 2.5 \pm 1$ kcal./mole. Thus $E_8 = 9 \pm 2$ kcal./mole.

The only experimental work with which comparison can be made is that on the reaction $CD_3 + CH_4 \rightarrow CD_3H + CH_3$.[20] The authors estimate an activation energy for this process of about 13 kcal./mole on the basis of a single experiment and an assumed frequency factor. From this, one would predict $E_8 \sim 12$ kcal./mole.[34] Another approach suggests that this estimate is probably too high. Berlie and LeRoy[36] find almost identical energies of activation for the closely related hydrogen abstractions $H + CH_4 \rightarrow H_2 + CH_3$ and $H + C_2H_6 \rightarrow H_2 + C_2H_5$. $E = 10.4$ kcal./mole for the reaction $CD_3 + C_2H_6 \rightarrow CD_3H + C_2H_5$,[37] and one might expect an almost identical result for $CD_3 + CH_4 \rightarrow CD_3H + CH_3$. Whence, correcting for isotope effect as above, E_8 should be about 9 kcal./mole.

Taking the collision diameters for CH_3, CH_4 and I_2 to be 3,5, 3.5 and 8 Å., respectively, it follows that P_8/P_3 is *ca.* 3×10^{-4}. It is clear that reaction 3 must have a frequency factor of the order of unity, if it is accepted that reactions of the type of 8 have factors of the order of 10^{-4}.[37,38]

It is of interest to note that the quantum yield of the "hot" reaction $\underline{CH}_3 + CH_4 \rightarrow CH_4 + CH_3$ is about 8×10^{-4},[39] as compared to 2.7×10^{-3} for $\underline{CH}_3 + CH_3I \rightarrow CH_4 + CH_2I$ found above.

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[34] The 1 kcal./mole lowering for protium methyl is assumed by comparison with the reactions of CH_3 and CD_3 with H_2.[35]

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[39] Obtained by dividing the rate of the hydrogen abstraction reaction at room temperature by the rate of CH_3 radical production (R_3).

MADISON, WISCONSIN

[CONTRIBUTION FROM CHEMISTRY DIVISION, OAK RIDGE NATIONAL LABORATORY, OAK RIDGE]

Yields of Hydrogen Peroxide in the Decomposition of Water by Cobalt γ-Radiation. I. Effect of Bromide Ion

BY THOMAS J. SWORSKI

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When air-saturated KBr solutions are subjected to cobalt γ-radiation, the initial yield of H_2O_2 is dependent upon the concentration of KBr. It is proposed that the initial yield of H_2O_2 in KBr solutions containing O_2 is equal to "$F + 2E$" when KBr is present in concentrations greater than 10^{-5} molar. The "molecular" yield of H_2O_2 (formed by the combination of OH radicals in regions of high ionization density) is 0.75 molecule per 100 e.v. in sulfuric acid solutions at a *p*H of 2 and 0.78 molecule per 100 e.v. in 0.8 *N* sulfuric acid. A mechanism is presented in which KBr (even at concentrations as low as 10^{-5} molar) decreases the "molecular" yield of H_2O_2 by reaction of bromide ion with OH radical in regions of high ionization density.

Introduction

Water, when subjected to ionizing radiation, has been considered to behave as though two reactions are occurring simultaneously[1]

$$2H_2O \longrightarrow H_2 + H_2O_2 \qquad (F)$$
$$H_2O \longrightarrow H + OH \qquad (R)$$

In reaction (F), H_2 and H_2O_2 result from the combination of many of the H atoms and OH radicals in the regions of high ionization density before these radicals have time to separate by diffusion. Dainton and Sutton[2,3] have recently presented experimental evidence showing that H_2O_2 is formed in excess of H_2 in reaction (F) in dilute ferrous sulfate

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