cally quantitatively into 1,3-butadiene and ethylene by heating at about 10 mm. pressure and 800°.

2. The rate of decomposition of ethylene and 1,3-butadiene is negligible under these conditions as compared with cyclohexene.

3. A test for free radicals showed that the rate of removal of metallic mirrors by the fragments from cyclohexene is of a lower order as compared with the rate of removal by open chain compounds such as acetone.

4. We assume that the primary step consists of rupture of a C–C bond in the beta-position to the double bond, followed by decomposition into ethylene and butadiene. No radical chain mechanism occurs as in the case of open chain compounds.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Mechanism of the Photodecomposition of Methyl and Ethyl Iodides[1]

BY W. WEST AND LEO SCHLESSINGER

The investigations of the photodecompositions of the alkyl iodides hitherto reported have been concerned chiefly with the value of the quantum yield in terms of the relation between the amount of iodine produced and the number of photons absorbed. But a detailed comparison between the carbonaceous products and the iodine formed is essential to an understanding of the reaction, as, obviously, estimates of the quantum yield based solely on the iodine produced will be completely fallacious if, as is conceivable, substantial amounts of iodated hydrocarbons are also formed. Emschwiller[2] has indeed described in considerable detail the carbonaceous and other products in the photodecomposition in the liquid phase, and Spence and Wild[3] have investigated the gaseous products of the decomposition of methyl iodide. These were found to consist mostly of methane, in an amount several times more than equivalent to the iodine formed, showing the production of iodated products. In the experiments to be described, we have sought to determine quantitatively the decomposition products of the two lower alkyl iodides, both in the region of continuous absorption centered round λ 2500 Å. and in the second region of ultraviolet absorption beginning at about λ 2000 Å.

Experimental Procedure

The photolyses were carried out statically. Quartz vessels attached to the vacuum line by graded seals, were filled to the desired pressure with alkyl iodide vapor and detached, with strict precautions to eliminate traces of oxygen and mercury vapor, by the procedure previously described.[4] Illumination in the region of continuous absorption was effected by placing the vessels, 25-cc. cylinders, 1.5 cm. in diameter, as close as possible to two or four low pressure high voltage mercury arcs, emitting most of their radiation at λ 2537 and 1849 Å. The latter radiation was mostly excluded by wrapping the cell in two layers of cellophane, or, in certain experiments, in which the elimination of even traces of the short wave radiation became essential, by immersing lamps and cell in a solution of 1 *N* acetic acid. Cells with plane windows, exposed to an intense zinc spark from which the radiation at λ 2026 to 2100 Å. was isolated by differential focusing, were used in the second region of absorption.

In collecting the products, arrangements were made to avoid the passage of material through stopcocks by means of the well-known device of breaking a capillary tube by a magnetic hammer: at the same time this absence of stopcocks during illumination prevented the possibility of small air leaks. After exposure, the reaction cell was sealed to the collecting system, consisting of various traps and a Töpler pump. By appropriate cooling, the capillary separating the reaction cell from the traps having been broken by the hammer, the products volatile at −180° (hydrogen and methane) were collected and examined separately from those volatile at −80° and the residue was examined for iodine and other non-volatile products. Pressure gages on the high and low pressure sides of the Töpler allowed the removal of the gas to be followed; usually 0.5 to 1.5 cc. (at one atm.) was collected, and this represented about 95% of the total gaseous product.

The micro-analytical technique for gases developed by Leighton, Blacet and Macdonald[5] proved highly satisfactory for the examination of the gaseous products. A few operations specific to the analyses performed here should perhaps be alluded to. Small amounts of alkyl iodide vapors were removed by sintered glass beads impregnated with dimethylaniline, the absorption requiring ten to fifteen minutes at 70°. Ethane and ethylene, however, are appreciably soluble in dimethylaniline, and in order to avoid errors due to loss of these gases, the sample of gas to be analyzed was divided into two portions, one of which was used to saturate the bead, which was then transferred to the sample to be analyzed, saturated with

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(1) Presented in part at the meeting of the American Chemical Society, April, 1937, at Chapel Hill, N. C.

(2) G. Emschwiller, *Ann. chim.*, **17**, 413 (1932).

(3) R. Spence and W. Wild, *Proc. Leeds Phil. Soc.*, **3**, 141 (1936).

(4) W. West and E. Ginsburg, THIS JOURNAL, **56**, 2626 (1934).

(5) Leighton, Blacet and Macdonald, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 266 (1931); **6**, 344 (1934).

respect to ethane and ethylene from a mixture of the same composition. This method was found to remove ethyl iodide vapor from gas mixtures of known composition without introducing error in the determination of the other constituents. Ethylene was removed rapidly by fuming sulfuric acid, and proved to be ethylene, and not some higher unsaturate, by burning the gas with the saturated hydrocarbons, after these had been determined separately. Ethane, methane and hydrogen were determined by explosion in oxygen. All procedures were tested on known mixtures of pure gases.

After the collection of the gases, the trap containing material non-volatile in solid carbon dioxide was cut off from the collecting system. From this the iodine was rinsed out with hexane and its amount determined by a photoelectric colorimeter using a photronic cell, filter, and galvanometer.

Only in the case of methyl iodide was any other condensed product identified. This proved to be methylene diiodide, characterized as follows. Iodine was removed from part of the hexane extract of non-volatile material by shaking with mercury, and the residue after filtration and evaporation heated to 180° with lead oxide and 0.5 cc. of water in a sealed tube. After hydrolysis, the presence of formaldehyde was shown by the Schriver test, the formation of a red color on the addition of phenylhydrazine hydrochloride, potassium ferricyanide and hydrochloric acid. Blank tests showed the absence of formaldehyde in the product untreated with lead oxide. This procedure was standardized with known amounts of methylene diiodide in hexane, and quantitative estimates of that formed in the photoreactions made. The melting point confirmed the production of methylene diiodide.

Experimental Results

The following tables contain data on the products found in the photodissociation of methyl and ethyl iodides. The quantity of gas collected in any experiment allowed three determinations of each sample to be made, and the figures are the mean of three excellent checks. There are somewhat considerable differences in the composition of the gas obtained in different experiments under nearly identical conditions, suggesting that the exact course of the reaction depends on difficultly controllable factors, such as surface conditions, but within these limits, the general reproducibility from experiment to experiment is reasonably good.

Table I

Photodecomposition of Methyl Iodide

$\lambda = 2537$ Å. $T = 25°$ $p = 300$ mm.

No. of arcs	Time hrs.	Total gas collected cc.	CH_4, %	C_2H_4, %	C_2H_6, %	Free iodine g. atoms × 10^5	CH_2I_2 g. moles × 10^5
2	115	2.08	79.5	11.3	9.6	6.2	Qual.
2	160	1.29	78.8	9.5	11.6		Qual.
4	49.5	1.99	89.5	5.8	4.1	5.14	5.59
4	49.5	2.17	91.0	3.9	5.2	4.40	5.80
2[a]	20	0.59	27.8	18.4	54.3	0	0
2[b]	216	.54	90	Present			

[a] Experiment in presence of silver foil; rate of decomposition increased about 40-fold.

[b] Reaction vessel packed with quartz.

Table II

Expt.		CH_3I	CH_4	C_2H_4	C_2H_6	CH_2I_2	Free I_2
3	No. of moles × 10^5 dec. or produced	15.32	7.9	0.51	0.37	5.6	2.57
4		16.35	8.83	.38	.48	5.8	2.2
3	% moles CH_3I appearing as		51.7	6.6	4.8	36.5	
4			54	4.6	5.9	35.5	

In Table II the figures for the third and fourth experiments of Table I are presented so as to show the molecular distribution of the decomposed methyl iodide among the various products, on the assumption that those listed are all the products of the reaction.

Table III

Photodecomposition of Ethyl Iodide Vapor

$\lambda = 2537$ Å. $T = 25°$ $p = 100$ mm.

Time, hrs.	Total gas, cc.	H_2, %	CH_4, %	C_2H_4, %	C_2H_6, %
58	0.77	–	6.9	47.7	45.2
51	1.85	–	–	50.7	49.3
64	2.37	–	–	35.4	64.7
22	1.02	–	–	42.6	57.3
2.5[a]	1.22	–	–	54.6	44.6
		$\lambda = 2026$ Å.			
17	0.93	Trace	4.5	57.4	58.1
20	1.26	Trace	Trace	50.2	50
13	0.79	6.4	8.1	51	34.5

[a] Silver surface present.

The essential results can be summarized: the photodecomposition of methyl iodide vapor at λ 2537 Å. yields, with low quantum efficiency (not more than a few thousandths) mostly methane, and small quantities of ethylene and ethane. Rather more than a third of the iodide decomposed appears as methylene diiodide, so that the true quantum yield is about four times that estimated solely from the free iodine produced. This still keeps the yield small, and does not seriously modify conclusions based on the iodine yield. Addition of silver foil increases the rate of reaction at least fortyfold, yields all the iodine as silver iodide, and a gaseous product mostly ethane, some ethylene and much less methane than without silver. Packing the reaction tube with quartz had no appreciable effect on the products. The products of the decomposition of ethyl iodide both at 2537 and 2060 Å. are comparable amounts of ethane and ethylene, with small amounts of hydrogen and methane in the shorter region. Very small amounts of a liquid product also were observed on the sides of the reaction tube after exposure, but this represented a product in practically negligible amount.

We shall refer to certain other experiments relevant to the mechanism in the course of the discussion.

Discussion

With most recent investigators of the photochemistry of the lighter alkyl idodes, we shall postulate that the primary reaction on illuminating methyl iodide in its region of continuous absorption, *e. g.*, at λ 2537 Å., is a dissociation into the radicals CH_3 and I.[4,6] It is true that recent work of Mulliken and of Price[7] has indicated that the electron which is most readily excited by light in the alkyl halides is a non-bonding one, mostly attached to the halogen atom, but the continuous nature of the spectrum from about λ 2600 to 2300 Å. indicates such a high probability of energy transfer from this electron to those forming the C–I bond, that dissociation will follow very quickly after excitation, so that, practically, the process still may be written

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

The occurrence of the following reactions at appropriate relative rates will now account for the observed course of the reaction.

$$\begin{array}{rlr}
CH_3 + I & \longrightarrow CH_3I & (2) \\
CH_3 + CH_3I & \longrightarrow CH_4 + CH_2I & (3) \\
CH_2I + I & \longrightarrow CH_2I_2 & (4) \\
CH_2I + CH_3 & \longrightarrow C_2H_5I & (4a) \\
CH_2I + CH_3I & \longrightarrow CH_2I_2 + CH_3 & (5) \\
CH_2I_2 + h\nu & \longrightarrow CH_2 + I_2 & (6) \\
CH_2 + CH_2 & \longrightarrow C_2H_4 & (7) \\
CH_2 + CH_3I & \longrightarrow C_2H_5I & (8) \\
CH_3 + CH_3 & \longrightarrow C_2H_6 & (9) \\
I + I + X & \longrightarrow I_2 + X & (10)
\end{array}$$

The outstanding characteristic of the photodecomposition of methyl iodide in this region, the extremely low yield, will be accounted for by postulating that the recombination reaction (2) far exceeds in rate all other possibilities. A few methyls react by (3), which, with (4) and (5), accounts for the main products. The ethylene is formed from the photodecomposition of methylene diiodide and the ethane results from association of methyls which have escaped other fates. The answer to the question presented by the great probability of (2) compared with that of (3) in spite of the enormously greater concentration of methyl iodide molecules than of iodine atoms, lies in the fact that, while (2) has little or no energy of activation, (3) probably requires an activation energy of not much less than 10,000 cal.[8] An immediate consequence of this interpretation is that reaction (3) and the sequence of events springing from it, (4), (4a), etc., should take place more readily at increased temperature, the competition between (2) and (3) growing ever more favorable toward the latter, and the quantum yield for the decomposition should increase with temperature. That this is true has been shown by Ginsburg,[9] who found that while the iodine produced by some hours of exposure of ethyl iodide vapor to the mercury arc at 25° required less than 0.01 cc. of 0.005 *N* thiosulfate, the iodine produced at 200° required 1.5 cc., against a dark blank of 0.6 cc. If (3) has an energy of activation of 10,000 cal., it should proceed some twenty-five times as fast at 100° and 400 times as fast at 200° as at 25°, and the subsequent reactions involving iodine formation, which are probably only slightly temperature-sensitive, will increase in about the same proportion. Although these results have been ascertained experimentally for ethyl iodide, the photo-behavior of methyl and ethyl iodides will be shown to be sufficiently analogous to make the argument valid when applied to the behavior of methyl iodide.

There is no difficulty in understanding the high rate of the recombination (2) in comparison with the associations (9) and (10) whose occurrence tends to increase the yield. Formation of iodine by triple collisions must be rare in the gas phase, and, unless the accommodation coefficient of iodine atoms on quartz is high, need not occur very rapidly even on the wall. In contrast to (10), (2) and (9) may occur as binary collisions[10] but, in virtue of the greater number of difficultly transferable rotational degrees of freedom which must pass over to vibrations in the association of two methyls, in contrast to the association of a methyl and an iodine atom, the "transition state" theory of reaction velocities predicts a much greater collision efficiency for the formation of methyl iodide than of ethane. For instance, Bawn[11] concludes that approximately

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[6] T. Iredale, *J. Phys. Chem.*, **33**, 290 (1929); J. R. Bates and R. Spence, This Journal, **53**, 1689 (1931); W. West, *ibid.*, **57**, 1931 (1935).

[7] R. A. Mulliken, *Phys. Rev.*, **47**, 413 (1935); W. C. Price, *J. Chem. Phys.*, **4**, 539, 547 (1936).

[8] See, for instance, F. O. and K. K. Rice, "Aliphatic Free Radicals," Johns Hopkins Press, Baltimore, Md., 1935, p. 190.

[9] E. Ginsburg, Thesis, New York University, 1934, p. 30.

[10] L. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Company, Inc., New York, N. Y., 1932, p. 45.

[11] C. E. H. Bawn, *Trans. Faraday Soc.*, **31**, 1536 (1935).

every collision between CH_3 and I will be chemically effective, while the "steric factor" for the association of two methyls is of the order 10^{-4} to 10^{-5}. The increased rate of decomposition of methyl iodide in the presence of solid silver can now be interpreted immediately—iodine atoms, diffusing to the silver surface, are at once fixed as silver iodide, the only observed iodine product; the concentration of I atoms in the gas is reduced, diminishing the probability of recombination; at the same time, Paneth's experiments[12] indicate no greater tendency for methyls to associate on silver than on quartz, the concentration of gaseous methyls is increased, and since the probability of ethane formation increases as the square of the methyl concentration, and that of methane by (3) only as the first power, the ratio of ethane to methane in the products will increase, as is found experimentally to be true.

Reactions (4) to (7) follow naturally on (3), in which, according to the reasoning already employed, (4a) and (5) will be of minor importance compared with (4), although in view of the probably smaller energy of activation of (5) than of (3), this reaction will not be so disproportionally improbable compared with (4) as (3) is with (2).

The small amount of ethylene observed is attributed to photodissociation of methylene diiodine, followed by association of methylene radicals, and one must also consider the possibility of reaction (8). Finally, methyl radicals which have escaped these various fates associate to ethane.

The scheme just discussed involves the existence of several quantitative relationships between the products, which we can now proceed to test. For instance, it follows that if no methylene radicals are lost by associating with methyl iodide to form ethyl iodide, the number of moles of ethylene produced = $^1/_2$ (number of moles of methane formed − number of moles of methylene iodide formed). In experiment 3 of Table II, the predicted and observed productions of ethylene are, respectively, 1.15×10^{-5} and 0.51×10^{-5} mole, suggesting the loss of methylene radicals by reaction (8). Again, if no methylenes are lost by (8), number of moles of C_2H_4 = $^1/_4$ (number of gram atoms of iodine − 2 number of moles of C_2H_6), giving a predicted ethylene production, in experiment 3 of 1.10×10^5 moles. The deficiency in ethylene is the same in the two tests, and it may be said that the observed products are in accord with our scheme, if ethyl iodide is formed in amount equivalent to the ethylene deficiency in the above tests; this would involve the conversion of about 6% of the methyl iodide which reacted to ethyl iodide.

That no considerable quantity of product was overlooked is suggested by the approximate fulfilling of the requirements by the observed products that the ratio of total iodine to total carbon in gram atoms equal one, and that the corresponding hydrogen–carbon ratio equal three. In experiment 3 the products found show the values 1.07 and 3.04 for these two ratios: the assumption of the production of ethyl iodide as discussed leads to the somewhat better values of 0.99 and 3.03.

Decomposition of Ethyl Iodide at λ 2537 Å.—A scheme analogous to that suggested for methyl iodide will account for the observed products in the photodecomposition of ethyl iodide in the continuum.

$$\begin{array}{rcll}
C_2H_5I + h\nu & \longrightarrow & C_2H_5 + I & (1)\\
C_2H_5 + I & \longrightarrow & C_2H_5I & (2)\\
C_2H_5 + C_2H_5I & \longrightarrow & C_2H_6 + C_2H_4I & (3)\\
C_2H_4I + I & \longrightarrow & C_2H_4I_2 & (4)\\
C_2H_4I & \longrightarrow & C_2H_4 + I & (4a)\\
C_2H_4I + C_2H_5I & \longrightarrow & C_2H_4I_2 + C_2H_5 & (5)\\
C_2H_4I_2 + h\nu & \longrightarrow & C_2H_4 + I_2 & (6)\\
I + I + X & \longrightarrow & I_2 + X & (7)
\end{array}$$

Here only traces of high-boiling product were observed, and nearly all of any ethylene iodide is evidently decomposed to ethylene and iodine. Butane was specially sought for, and its absence shows the improbability of binary association of ethyls in the presence of iodine atoms or ethyl iodide. The approximate equality, in a number of the experiments of Table III, in the amounts of ethane and of ethylene, points to the conclusion that reactions (3), (4) or (4a) and (6) are the essential secondary reactions responsible for the decomposition. Even in the presence of silver, when the momentary concentration of ethyl is considerably increased, no butane was observed.

It will be observed that there is an essential difference in the nature of the products in the photodecomposition of the alkyl iodides and certain other compounds whose photolysis also involves the production of methyl and ethyl radicals. For instance, while methyl iodide gives a gaseous product, 80 to 90% of which is methane

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[12] Paneth and Lautsch, *Ber.*, **64B**, 2408 (1931).

acetone under similar conditions yields mostly ethane and carbon monoxide.[13] The ethane scarcely can be formed otherwise than by association of methyls, which reaction must then predominate over the reaction

$$CH_3 + CH_3COCH_3 = CH_4 + CH_2COCH_3$$

analogous to the methane producing reaction in the methyl iodide decomposition. The answer is to be found most probably in the low momentary concentration of methyl radicals in the presence of iodine atoms, although it is not excluded that methane formation in the acetone reaction may require a somewhat higher energy of activation than the corresponding methyl iodide reaction. Since the rate of association of radicals in the gas phase is proportional to the square of the radical concentration, and the formation of methane to the first power, the rate of association will diminish more rapidly with concentration than that of methane production. In fact, when, in the dissociation of methyl iodide, the iodine atom concentration is kept low, as by fixing the atoms as metallic iodide, the tendency to ethane formation from methyl iodide begins to approach that from acetone.

Decomposition of Ethyl Iodide in Presence of Foreign Gas.—The photodecompositions of the alkyl iodides are characterized by the great increase in yield in the liquid or dissolved state over that in the gaseous. One possible reason for this increase is the action of solvent molecules in providing third bodies for the yield-increasing radical associations, particularly the reaction $I + I = I_2$ and we have therefore investigated the photodecomposition of ethyl iodide in the presence of considerable pressures of foreign gases, at λ 2537 Å. These reactions were carried out in quartz capillary tubes, 2 mm. internal and 7 mm. external diameter, in which, along with the iodide, known amounts of purified carbon dioxide or argon were condensed at −180°. The charged tubes were placed at an equal distance from a low pressure mercury arc as a standard tube of the same material and dimensions containing ethyl iodide in hexane, and the relative rates of production of iodine compared. The iodine produced under these circumstances in ethyl iodide vapor in the same time of illumination is below our limits of determination. In such experiments with carbon dioxide care must be taken to exclude even traces of short wave ultraviolet light, as otherwise much iodine is produced, presumably by photo-oxidation by carbon dioxide.

Some results are tabulated in Table IV.

TABLE IV

RELATIVE YIELDS OF IODINE FOR ETHYL IODIDE WITH CARBON DIOXIDE AT λ 2537 Å. AND $T = 30°$

	Pressure atm.	Density g./cc.	Rel. yield
CO_2	40	0.192	0.135
CO_2	20	.0961	.086
CO_2	10	.0486	.049
Hexane			1.00

Similar results were obtained with argon, carbon dioxide being the more effective. It will be observed that at these pressures of foreign gas the rate of production of iodine is a substantial fraction of that in hexane solution and increases approximately as the density of foreign gas; and it seems to us that the best interpretation to place on them is that the foreign gas does act as third body in the homogeneous association of iodine atoms produced by the primary photoreaction.

Decomposition of Ethyl Iodide at λ 2026 Å.—The products in this region are not markedly different from those at 2537 Å., the chief difference being the appearance of small amounts of hydrogen and methane. While it is quite true that the well-defined appearance of the absorption bands in this region at low pressures strongly suggests the production of stable excited molecules, at the pressure used in these photo-experiments, the bands are overlaid by a continuum which does not seem to be a mere pressure broadening effect of the ordinary type. The possibility of a dissociation into radicals is therefore, perhaps, not entirely excluded, by some process involving the absorption of light by a molecule in the process of collision with another; nevertheless the great increase in yield in this region seems to point to a mechanism not involving free radicals as the main one. The sequence

$$C_2H_5I + h\nu \longrightarrow C_2H_5I \quad (1)$$

$$C_2H_5I + C_2H_5I \longrightarrow C_2H_6 + C_2H_4 + I_2 \quad (2)$$

yielding saturated molecules in one elementary act, would give a relatively high yield of product in about the proportions observed. The small amounts of methane and hydrogen could be produced in several ways which are scarcely worth considering without fuller information.

Quantum Yields of Iodine for *n*-Propyl and Isopropyl Iodides.—The following table con-

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[13] G. H. Damon and F. Daniels, THIS JOURNAL, 55, 2368 (1933).

tains the mean of several consistent determinations of the iodine yields of the four lower saturated iodides, made by the analytical method described in this paper and the radiometric method previously described.[4]

TABLE V

		T, °C.	p, mm.	Yield
Methyl	2026	25	140	0.002
Ethyl	2026	25	95	.10
n-Propyl	2026	25	35	.01
	2610	25	35	.01
Isopropyl	2026	25	56	.43
	2610	25	26	.17

The yields for ethyl and methyl iodides in the continuum were too small to be determined directly, though comparative experiments showed that of ethyl to exceed that of methyl iodide. The yield for *n*-propyl is small at 2610 Å., but larger than that of ethyl, but, curiously, the iodine production in the short wave region is only about a tenth of that for ethyl. A possible origin of this anomaly may be that the photoreaction at λ 2026 Å. involves the production of propyl radicals, which are well known to be unstable, decomposing to methyl and ethylene. The great tendency toward recombination of methyl and iodine atoms evidenced in the photo-behavior of methyl iodide would then account for the low iodine yield, but further speculation on the photochemistry of the propyl iodides seems unwarranted until precise knowledge on the products of their decompositions is available.

Summary

1. The gaseous products in the static photolysis of methyl iodide vapor at λ 2537 Å., 25°, and 300 mm. pressure are chiefly methane, with small amounts of ethane and ethylene. About one-third of the iodide decomposed appears as methylene diiodide. In the presence of silver foil, however, the chief product is ethane, with substantial quantities of methane and ethylene, and all the iodine appears as silver iodide. Also the rate of decomposition is increased at least fortyfold by silver.

2. Ethyl iodide similarly gives at λ 2537 Å., 25°, and 100 mm., ethane and ethylene in comparable proportions; and likewise at λ 2026 Å., in the second absorption region, with the addition of small amounts of methane and hydrogen. The presence of silver, at λ 2537 Å., increases the rate of reaction, without any great effect on the nature of the products.

3. The photolysis of ethyl iodide in the presence of pressures of inert gas up to 40 atmospheres has an iodine yield increasing approximately linearly with the density of inert gas to values approaching one-third of the yield in inert liquid solvents.

4. A scheme is proposed which seems to account for these and other observations, the essence of which is that, (a) the most rapid secondary reaction is recombination of free radicals and iodine atoms; (b) most of the net change in the alkyl iodide at low pressure is due to the reaction $R' + R''H_2I = R'H + R''HI$, this predominating over the association of R' to R'_2 and I to I_2; (c) the decomposition of iodide will increase in the presence of any agency which will remove iodine atoms, *e. g.*, silver, which fixes iodine atoms as metal iodide, or high pressures of inert gas, which promotes the triple-bodied association of the atoms to molecules.

5. The iodine quantum yield of *n*-propyl iodide vapor at λ 2026 Å. is considerably lower than that of ethyl iodide, and the corresponding yields for isopropyl iodide are 0.17 and 0.43 at 2610 and 2026 Å., respectively.

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