

radio-methylene iodide and methane. There is some possibility that the $\text{CH}_2\text{I}\cdot$ radical decomposes before reacting with iodine. However if this occurs, this should result in a higher radiomethylene iodide yield or a quantum yield of ethylene greater than the observed value of less than 0.0002.

It will be observed that the above mechanism eliminates, except for the recombination of iodine atoms, all reactions which are second order in radicals. This is necessary since the radicals are quickly removed by reaction with the iodine and are therefore present only at very low concentration levels. This is one point of departure between our proposal for the liquid phase photolysis and that of Schultz and Taylor in studies of the vapor phase. We postulate that ethane results from a hot process (reaction 6-H) while Schultz and Taylor

prefer to regard it as being formed by the combination of methyl radicals. This latter process can be of greater importance in the vapor phase because of a relatively low concentration of iodine. Recent work on the flash photolysis of methyl iodide by Davidson and Carrington¹⁶ further indicates the importance of methyl radical combination in the vapor phase at very high light intensities.

Acknowledgment.—The authors wish to thank Professor William H. Hamill of the University of Notre Dame for numerous discussions on the subject. One of us (C. T. C.) is indebted to the Research Corporation for the grant of a fellowship.

(16) N. Davidson and T. Carrington, *THIS JOURNAL*, **74**, 6277 (1952).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CANISIUS COLLEGE]

The Radiolysis of Liquid Methyl Iodide¹

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Hydrogen, methane, ethane, ethylene and acetylene have been observed as gaseous products in the 100 kev. X-ray decomposition of liquid methyl iodide. The respective yields are found to be, relative to the yield of iodine as unity, equal to 0.067, 0.47, 0.90, 0.067 and 0.026 and are directly proportional to the total irradiation dose given the sample. The formation of trace amounts of higher hydrocarbons is indicated in the mass spectrometer analysis of the less volatile fractions. Methylene iodide and ethyl iodide are shown to be minor products of the radiolysis. In the presence of large amounts of iodine (1–20 mole per cent.) the yield of gaseous products decreases, with the effectivity of the iodine in quenching the reactions varying for the different products. The relative yields observed for decomposition produced by very low intensity Co^{60} γ -radiation are found to be identical to those given above for the more intense X-radiation. The absolute decomposition yields are in approximate agreement with the values obtained in fast-electron bombardment. The relatively high yield of ethane and iodine, together with other complications evidenced by the formation of ethylene, acetylene and higher hydrocarbons, indicates very strongly the importance of ionic processes in the over-all decomposition.

Lefort, Bonet-Maury and Frilley³ have studied iodine production in the decomposition of air saturated liquid ethyl iodide by X-radiation and by radon alpha particles. Sue and Saeland⁴ have studied the same process in various alkyl iodides using the mixed fast neutron-gamma radiation from a 300 mc. radium-beryllium source, and Schuler and Hamill⁵ have observed the fast-electron and X-radiation induced processes using a 1-2 mev. Van de Graaf generator as the source of radiation. It was evidenced in this previous work⁵ that the yield of iodine in the radiolysis of methyl iodide is much greater than anticipated from the low quantum yield for iodine production observed in the photodecomposition. The purpose of this investigation was to obtain information on the gaseous products of the radiolysis and to compare the yields to those observed in the photolysis of the same system.⁶

Experimental

Methyl Iodide.—The methyl iodide samples were from the same preparations used in the photolytic work.⁶ The

boiling point was 42.4° and the refractive index (n_D^{20}) 1.5271–1.5272.

Irradiation.—The unfiltered radiation from a line operated, industrial X-ray unit with a tungsten target was used as the major source of activation. The instrument was operated at a constant intensity characterized by a current of 5 ma. at 120 pkv., the effective wave length of the radiation being in the region of 0.2–0.4 Å. The current was maintained at a constant value electronically and was monitored on a recording milliammeter. Variations in line voltage could be compensated for by a manual adjustment of the transformer setting.

The samples (10 ml.) were contained in a 50-ml. Florence flask to which a high-vacuum stopcock and ground joint had been affixed for ease of attachment to the vacuum line. These were irradiated in the position of maximum X-ray dosage by placing the cell in the well of the tube with the radiation entering vertically through the bottom of the cell. During irradiation the sample temperature rose slightly due to heat transferred from the X-ray tube. A blower circulated air over the cell to keep this temperature rise to a minimum. No other temperature control was attempted. Utilizing this arrangement the reproducibility in positioning the sample was very good. The limiting factor in these investigations is the constancy in the intensity out-put of the X-ray tube. Our measurements indicate that this is controlled to within $\pm 2\%$.

In the case of expt. 31, the radiation from 300 millicuries of Co^{60} was used for activation. The irradiation vessel consisted of a cylindrical tube with an attached break-off seal through which the sample could be attached to the vacuum line after irradiation, and a square Pyrex absorption cell which was used for measurement of the iodine concentration during the course of irradiation.

In reporting the results, the reaction yields are given in terms of moles of reaction product per unit of irradiation at the constant intensities described above. Both experimen-

(1) From the M.S. Dissertation of R. C. Petry, Canisius College, June 1953. This work was supported, in part, under Contract AT(30-1)-1084 with the U. S. Atomic Energy Commission.

(2) Brookhaven National Laboratory, Upton, N. Y.

(3) M. Lefort, P. Bonet-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948).

(4) P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949).

(5) R. H. Schuler and W. H. Hamill, *THIS JOURNAL*, **74**, 8171 (1952).

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

tal arrangements were monitored through the radiation induced oxidation of ferrous sulfate in 0.8 *N* sulfuric acid solution.

Gas Measurement.—The methods employed in degassing the samples and in measuring the gaseous products are essentially the same as those described in the previous contribution.⁸ The hydrogen-methane fraction was taken as that volatile at liquid nitrogen temperature (-196°) and the higher hydrocarbons were degassed and distilled at ethyl bromide msh temperature ($\sim -115^{\circ}$). The higher yield of ethane relative to methane makes it possible to obtain a somewhat greater accuracy in the present measurement than is possible in the case of photolysis.

Gas Analysis.—The combustion analyses were performed essentially as previously described.⁸ A measure of the unsaturation of the fraction volatile at -115° was obtained by hydrogenation on nickel catalyst at room temperature in a tube attached to the Saunders-Taylor apparatus. The catalyst was prepared by the method of McMillan, Cole and Ritchie⁷ and activated by heating in a hydrogen atmosphere at 300° . After hydrogenation, the excess hydrogen was burned over copper oxide at 275° and the remaining sample subjected to combustion analysis. As both ethylene and acetylene are products of the radiolysis, the results are expressed in terms of the total unsaturation, *i.e.*, as extra bonds per molecule for the fraction volatile at ethyl bromide msh temperature. Preliminary tests with ethylene and ethane-ethylene mixtures indicate that the results of the hydrogenation analyses are reliable to within a few per cent. of the total sample (*e.g.*, sample 100% ethylene, observed 1.00, 0.98, 1.00 C=C/molecule; sample 17.6% ethylene, 82.4% ethane, observed 0.182 C=C/molecule).

In two cases, one in which the sample initially contained no added iodine and one in which 10 mole % iodine was dissolved before irradiation, samples of the material volatile at -115° were sealed in tubes and submitted for mass spectrometer analysis.⁸

Radiochemical Analysis for Methylene Iodide and Ethyl Iodide.—McKenney⁹ and Schuler and Hamill^{5,10} have shown that exchange between methyl iodide and iodine is induced by irradiation with X-rays and fast electrons. The former work was done under conditions similar to those used here. In the present experiments, methyl iodide was exchanged with radio-iodine,¹¹ carrier methylene iodide was added, and the active methyl iodide was washed out of the sample.¹² The formation of methyl iodide is characterized in terms of the fraction of the total activity retained in the methylene iodide.

In one experiment, ethyl iodide carrier was also added and the activity retained in the ethyl iodide after thorough washing with methyl iodide, was attributed to the formation of this as product. A 30-cm. Podbielniak column was employed in the separations required in this particular case.

Iodine Analysis.—Iodine was determined colorimetrically from observations of the optical density at 480, 500 and 520 μ . In the case of longer irradiations, where the concentrations of iodine produced were too high for accurate determinations at these wave lengths, the samples were diluted with known amounts of methyl iodide and the optical densities determined as above. The production of iodine was also determined during the initial phases of the irradiation utilizing a 1-cm. square Pyrex absorption cell sealed to the reaction vessel. A Beckman quartz spectrophotometer was used for all determinations of optical density.

Results

Gas Analysis.—Combustion analysis of the fraction volatile at liquid nitrogen temperature shows that about 13% of this is hydrogen. The gas remaining after the hydrogen is burned off is

(7) W. A. McMillan, H. A. Cole and A. J. Ritchie, *Ind. Eng. Chem., Anal. Ed.*, **8**, 105 (1936).

(8) The analytical services of Consolidated Engineering Corp., Pasadena, California, were employed.

(9) D. H. McKenney, M.S. Dissertation, Canisius College, 1951.

(10) R. H. Schuler, D. H. McKenney and W. H. Hamill, to be published.

(11) I¹³¹ obtained through the U. S. Atomic Energy Commission, Oak Ridge, Tenn.

(12) R. G. Badger, C. T. Chmiel and R. H. Schuler, *THIS JOURNAL*, **75**, 2498 (1953).

methane (*i.e.*, *nc* of this residue is 0.99–1.01 for all experiments reported in Table III). The hydrogen and methane yields are reported in Table III for the individual experiments in terms of the analysis for each particular experiment.

Measurement of the unsaturation of the fraction volatile at -115° shows the presence of about 0.1 extra bonds per molecule of gas as indicated in Table I. Combustion analysis shows the entire fraction to be mainly C₂.

TABLE I

ANALYSIS OF PRODUCT VOLATILE AT -115°

Experiment	23	24 ^a	31 ^b
Sample, moles $\times 10^8$	15.0	8.0	17.4
Pressure, mm. ^c			
Initial	75	115.5	64
Hydrogen added	147	160	99
After hydrogenation	215	259	156
After oxidation at 275°	77	117	63.5
After oxidation at 575°	150	226	125
After absorption	3	4	1
Unsaturation	0.09	0.14	0.10
<i>nc</i>	2.04	1.99	1.97
Combustion, %	96	97	98

^a Sample contained 2 mole per cent. iodine. ^b Sample irradiated with Co⁶⁰ γ -radiation. ^c All pressures are corrected to the original volume.

In Table II are reported the results obtained in the mass spectrometer analysis of the less volatile fraction together with the analysis of a similar fraction from the photolysis of methyl iodide which is included for comparison purposes. The major component is seen to be ethane. Ethylene and acetylene are produced in relatively high yields together with traces of higher hydrocarbons which are characteristically absent in the photolysis. The radiation yields of ethylene and acetylene are reported in terms of the mass spectrometer analysis for these products from experiment 27. The carbon dioxide is probably due to a residue remaining after the original degassings. The chloromethane is presumably real and probably originates as an impurity in the iodine added to the system (the amount present corresponds to 10^{-8} mole or 0.00001% of the iodine added).

TABLE II

MASS SPECTROMETER ANALYSIS OF PRODUCT VOLATILE AT -115°

Experiment	27	28 ^a	P ^b
Sample, moles $\times 10^6$	42	8.5	5.1
Product, %			
Ethane	88.6	88.6	92.4
Ethylene	6.8	0.9	2.3
Acetylene	2.6	5.2	..
Propane	0.4	0.1	..
Propylene	0.1	0.03	..
C ₄ +	0.04	0.1	..
Oxygen	0.04	0.1	0.3
Carbon dioxide	1.4	4.9	4.6
Chloromethane	..	0.1	..
Methane	0.2

^a Sample contained 10 mole per cent. iodine. ^b Sample from similar photolytic experiment.

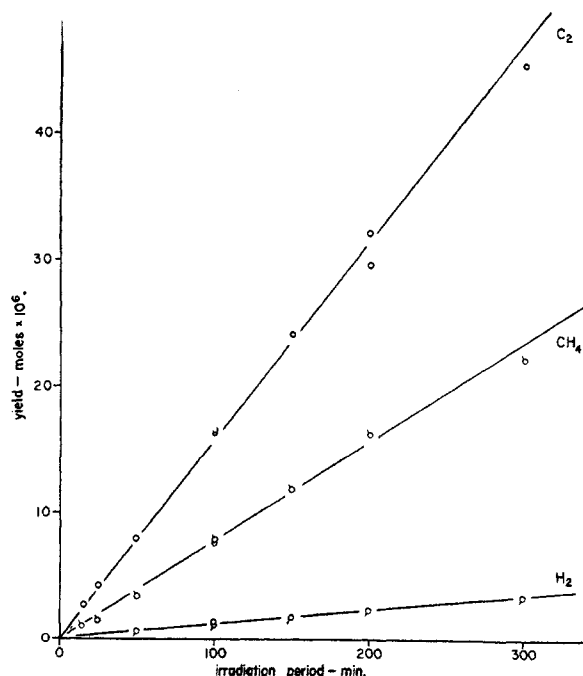


Fig. 1.—Production of C₂ hydrocarbon, methane and hydrogen in the X-ray decomposition of methyl iodide.

Gas Production.—The total yields of hydrogen, methane and ethane, are given in Fig. 1 for the radiolysis of methyl iodide samples initially containing no added iodine. In Table III are summarized the yields observed in the individual experiments. These are seen to be directly proportional to the irradiation dose with very little, if any, induction effect being observed. The presence of small amounts of iodine produced as a result of the decomposition does not apparently inhibit the formation of products to any appreciable extent. It is estimated, from the further experiments on the effect of high iodine concentrations, that at an iodine concentration of 0.004 *M* (the amount of iodine present after 250 minutes of irradiation) the gas yield is 98% of that for a sample containing only traces of iodine.

TABLE III

DECOMPOSITION YIELDS

Expt.	Period, min.	Yield, moles × 10 ⁶ /min.			
		H ₂	CH ₄	C ₂	I ₂
X-Irradiation: (Fe ⁺⁺ oxidation = 18.0 × 10 ⁻⁸ equil./min.)					
12	15	1.0	6.8	19.0	22.0
8	25	1.0	5.7	16.8	18.3
11	50	1.3	6.6	15.9	16.7
10	100	1.4	7.6	..	17.4
13	100	1.1	7.6	16.5	17.5
23	100	1.1	7.9	16.3	17.5
14	150	1.1	7.9	16.1	17.8
9	200	1.1	6.5	14.8	16.1
15	200	1.2	8.1	16.1	18.1
27	300	1.1	7.4	15.2	16.0
(Graphical mean)		1.1	7.8	16.3	17.5 ^a

γ-Irradiation: (Fe⁺⁺ oxidation = 0.24 × 10⁻⁸ equil./min.)

31 58,800 0.0019 0.0134 0.0301 0.0297

^a Irradiation #33 indicates 16.5 × 10⁻⁸ mole I₂/min.

It will be noted that, in comparison to the photolysis where the methane yield is the greater, in the radiolysis the methane yield is less than that for ethane.

Effect of Added Iodine.—In the presence of iodine added to the sample before the irradiation (all experiments are of 100 minutes duration except expt. 28 which is 300 minutes) the yields are found to decrease as shown in Fig. 2. It is seen that the iodine affects the products of the decomposition to an appreciable extent only when present at relatively high concentration (0.1–4 *M* in iodine). The effect of iodine on the various products is somewhat different, the yields being, respectively, for hydrogen, methane and ethane production 64, 36 and 24% of normal in an irradiated sample containing 10 mole % iodine. Previously⁵ a slight decrease in the iodine yield was observed at high iodine concentration.

Iodine Production.—In Fig. 3, the results are given for iodine production in the X-ray decomposition of air free and air saturated methyl iodide together with data for the decomposition of air free methyl iodide induced by radiation from the 300 mc. of Co⁶⁰. The iodine yield in ethyl iodide radiolysis is given here for comparison purposes. The data given in Fig. 3 were obtained during the course of decomposition of samples irradiated particularly for this purpose. The results listed in Table III were obtained from the individual samples after they had stood some time in the degassing operations. These are slightly (~10%) higher. In Fig. 3 the constancy of the iodine production yield over the course of the radiolysis is illustrated. The yields of iodine, on a mole basis, and of total C₂ gas are equivalent within experimental error.

Formation of Methylene Iodide and Ethyl Iodide.—The results of the radio-iodine carrier experiments are given in Table IV. It is seen that 2.8% of the active organic fraction carries with methylene iodide and 0.7% carries with ethyl iodide. The identification of the latter activity is given additional weight by the fact that, in the final distillation, the methyl iodide fraction preceding the active ethyl iodide contained little activity.

TABLE IV

FORMATION OF METHYLENE IODIDE

Expt.	Carrier iodine, moles × 10 ⁴	Exch., %	Org. activity, c./min.	Activity	
				as CH ₂ I ₂ , %	as C ₂ H ₅ I, %
29	40	61.0	4238	2.7	... ^b
30	20	71.0	2308	2.9	... ^b
32	29	73.8	2739	2.8	0.7

^a In 10 ml. of sample ^b Not observed.

If the fraction of the activity appearing in the above products is multiplied by the total exchange yield of 98 × 10⁻⁸ iodine atoms exchanged per minute,¹⁰ a radiomethylene iodide yield of 2.8 × 10⁻⁸ mole/min. is obtained together with a radioethyl iodide yield of 0.7 × 10⁻⁸ mole/min. Thus, although largely masked by the exchange process, these products do account for a significant part of the net chemical reactions.

It will be noted that there is considerable discrep-

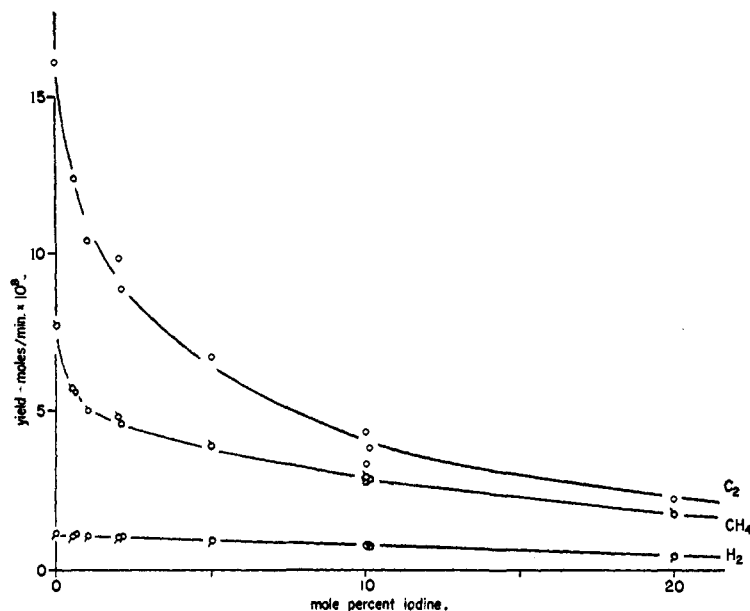


Fig. 2.—Effect of iodine on the gas production yields.

ancy between our results and the 19% of the activity reported as methylene iodide and 15% reported as ethyl iodide by Gevantman and Williams.¹³ The present results represent the lower value and are presumably less liable to error by contamination. Also, if the yield of methylene iodide is compared to that of methane, a maximum of 8% of the activity would be expected to appear in the methylene iodide. The analogous yield in the photochemical case is likewise lower than anticipated.

The present results indicate even more strongly the general conclusion of Gevantman and Williams, that in the radiation decomposition of the alkyl iodides the C-I bond is preferentially broken. Methyl iodide, which seemed to be somewhat anomalous in their pattern, is seen to be in complete agreement with this principle.

Decomposition by γ -Radiation.—Experiment 31 was undertaken utilizing γ -radiation in order to provide data for comparison to ferrous oxidation and to check any possible effects of radiation intensity and energy on the relative yields of products. Degassed methyl iodide was subjected to a five week irradiation over 300 millicuries of Co⁶⁰

at a rate of energy absorption approximately one six hundredth that used in the X-ray experiments. The relative yields of the various products (I₂: H₂: CH₄: C₂H₆: C=C: : 1:0.065:0.45:0.89:0.13) are in excellent agreement with the relative yields observed in the X-ray decomposition. Since it is not likely that any intensity controlled process should affect all the products in so similar a manner over such a large intensity range, these results indicate that the absolute yields are not intensity dependent

(13) L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

to any appreciable extent in this region.

Discussion

It is known from studies of the radiation induced exchange^{9,10} that, in the region of iodine concentration of 10⁻⁴ to 10⁻² M, the iodine is reacting with the products of the decomposition. However, in spite of the effectivity of the iodine in removing the major fraction of the radicals formed in the decomposition, the yields of the various products observed in the radiolysis of methyl iodide are not appreciably affected by the increase in the iodine concentration which occurs during the course of irradiation. Presumably the iodine serves as a sink, efficiently removing the thermal radicals formed.



As in the photolysis,^{6,14} iodine cannot be involved in the present case in processes which are rate controlling with respect to the formation of net products. Reactions other than those of normal thermal radicals must be included in the over-all mechanism in order to account

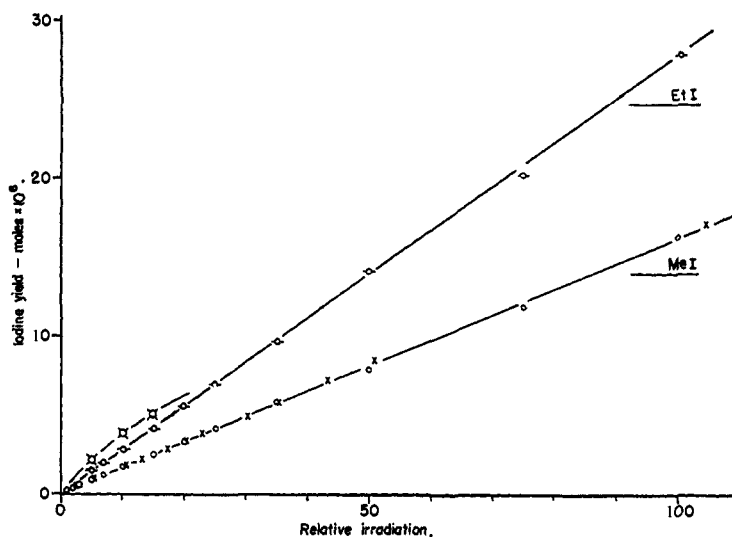


Fig. 3.—Iodine production in the X-ray decomposition of methyl iodide, O; air saturated methyl iodide, X; ethyl iodide, \circ ; and in the γ -radiation decomposition of methyl iodide, X. The relative irradiation is given in minutes for the X-ray decomposition and minutes \times 1/560 for the γ -ray decomposition.

for the observed decomposition. It has already been indicated,⁵ from the high yield of iodine production in the radiolysis of methyl iodide relative to ethyl iodide (1:1.5) as compared to the same relative yields for the photolysis (1:25), that processes involving considerably greater energies are extremely important.

In addition to the methane, ethane and iodine which are formed in the photolysis, hydrogen, ethylene, acetylene, and small amounts of propane,

(14) W. H. Hamill and R. H. Schuler, *THIS JOURNAL*, **73**, 3466 (1951).

propylene and higher hydrocarbons are observed as minor products in the radiolysis. A comparison of the yields is made in Table V based on the fractional yields for the radiolysis being calculated on the assumption that the total primary yield is equal to the sum of the iodine molecule production and the iodine atom exchange. It is assumed that in this respect the over-all processes approximate the photochemical behavior.

TABLE V
RELATIVE YIELDS

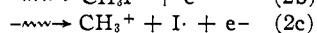
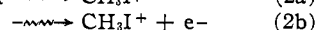
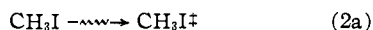
	Photolysis, ϕ	Radiolysis, G/G_0^a
H ₂	<0.0001	0.010
CH ₄	.023	.068
C ₂ H ₆	.007	.129
C ₂ H ₄	< .0002	.010
C ₂ H ₂004
I ₂	.008	.144
Exchange	~1.0	~ .85
CH ₂ I ₂ *	0.014	.024
C ₂ H ₅ I*006

^a G₁ corresponds to yield of exchange plus iodine production.

The net decomposition reactions are seen to represent the resultant products of an appreciable portion of the primary dissociation processes. The general indications are that reactions involving hot radicals, highly excited states and ionic species are extremely important in the processes that control the over-all reactions. Because of the complexities of the system it is difficult to describe a detailed mechanism for the decomposition. We shall attempt here only to suggest various processes of varying importance which may be operative in the formation of products.

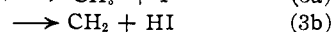
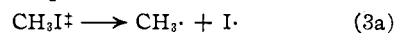
The Radiation Processes.—With the presence of large amounts of iodine in the system, the absorption of the X-radiation is almost entirely due to the photoelectric effect and results in primary electrons which have an energy distribution (due to the heterogeneity of the radiation) in the region of 30–120 kev. As the photoelectric absorption coefficient of iodine is very high at the wave lengths employed here, the radiation is almost completely absorbed in the 0.7 cm. thickness of sample. Transmission measurements show 96% of the incident energy as being absorbed by the sample. In the case of γ -radiation in the mev. region, the absorption is predominantly of the Compton type with only a fraction of the energy of each quantum being transferred to the electron. The energy distribution in this case is continuous from 0 to approximately 1 mev., with a small photoelectric contribution being also made because of the presence of the iodine.

The absorption of the radiation energy results in the formation of excited methyl iodide molecules and various ionic species



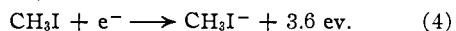
Reaction 2c will occur only if the transfer of energy in the ionization exceeds 12.4 ev.¹⁵ For ionizing

energies between 9.5 ev. (the ionizing potential of methyl iodide) and 12.4 ev. CH₃I ions should persist until discharged. The excited species formed in 2a may lose its energy or may dissociate along a number of reaction paths such as



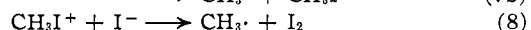
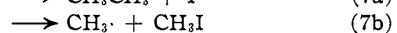
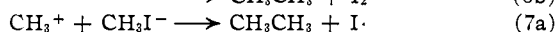
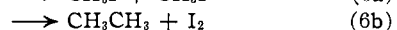
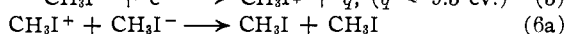
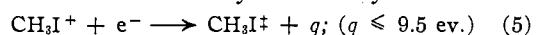
For reaction 3a, representing dissociation of the lowest excited state of methyl iodide, we have some knowledge of the chemical characteristics from studies of the photolysis at 2537 Å.⁶ Since considerable amounts of energy are available, it seems likely that the methyl radical will have a sufficiently high kinetic energy in order to be able to produce hot radical effects analogous to those postulated in the photochemical case. Reactions 3a and 3b represent possible modes of dissociation of the more highly excited states which are expected to complicate the observed results.

Negative ion formation appears to be very important in determining the course of the net reactions. The free electrons, produced in ionization, after thermalization may attach themselves to the solvent methyl iodide



This reaction is exothermic by the value of the electron affinity of methyl iodide (assumed in 4 to be approximately that of iodine), with this energy being sufficient to rupture the C–I bond. The excess energy is, however, not great (~1 ev.) and a redistribution may result in stabilization of the negative ion.¹⁶

With the reactions of both free electron and negative ions having possible importance, the charge neutralization reactions are quite numerous. Among others the following are postulated in the mechanism of the radiolysis of methyl iodide



These charge neutralization reactions are highly exothermic (~6 ev. for reaction 6a) so that the initial products may or may not be stable depending upon the distribution of the energy within the reacting species.

Hydrogen Production.—Hydrogen is produced in a small, constant yield which is affected only slightly by the addition of large amounts of iodine. The lack of effect of iodine indicates the absence of processes involving hydrogen atoms as intermediates. Hydrogen presumably is formed directly by the dissociation of the highly excited states and ionic species and possibly indirectly through the formation of hydrogen iodide as product. Hydrogen is also expected as a product of the charge neutralization reactions which ultimately produce unsaturated products.

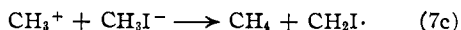
It will be noted that the hydrogen yield is only about 1/50 of that observed in hydrocarbon decomposition. The presence of a group more eas-

(15) C. A. McDowell and B. G. Cox, *J. Chem. Phys.*, **20**, 1496 (1952).

(16) J. L. Magee and M. Burton, *This Journal*, **72**, 1965 (1950); **73**, 523 (1951), have discussed some of the theoretical aspects of negative ion formation.

ily affected by the radiation reactions tends to lessen hydrogen production.

Methane and Methylene Iodide Production.—Methane and methylene iodide are produced in yields which are only slightly greater than observed in the photolysis. Since extrathermal methyl radicals are produced, at least in the dissociation of the lowest excited state and as a result of certain of the charge neutralization processes (in reactions 7b and 8 the energy of the methyl radical recoiling from the heavier molecule is of the order of 5 ev.), it seems likely that hot radical reactions are responsible for a major fraction of the methane and methylene iodide production. Reactions such as



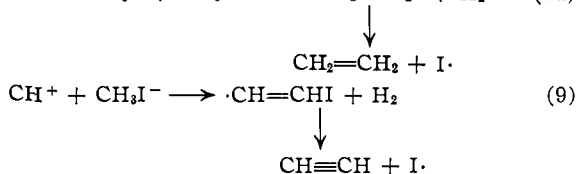
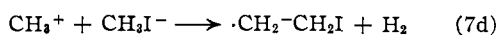
may have a minor importance here.

Ethane Production.—The high yield of ethane indicates very strongly the importance of ionic processes in its formation. Reactions 6b and 7a are postulated and appear to depend only on the stability of the ionic species.

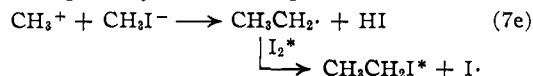
Hot radical production of ethane, as inferred from the low methane yield, probably accounts for only a small fraction of the total yield. Since in general the energy regions are not greatly different, it is not expected that the relative cross sections for methane and ethane production, in the hot radical processes, should differ very much from the photolysis to the radiolysis.

Radiochemical Exchange.—Exchange results from the quench of thermal radicals by the molecular iodine present, according to reaction 1. The results of the exchange experiments are somewhat complicated and will be reported elsewhere.¹⁰ Because of the low mole fraction of iodine in these systems, the exchange must result predominantly from radicals which have survived numerous collisions. These results show that a major fraction (~85%) of the primary decomposition results in species which are eventually thermalized and react with free iodine giving no net observed chemical yield. The reactions producing net chemical effects correspond, therefore, to only a minor, but significant, part of the primary decomposition. This part is considerably more important in the radiolysis than in the photolysis (*i.e.*, 15% as compared to 3%).

Ethylene and Acetylene Production.—Ethylene and acetylene are produced in a total yield which approximates the yield of hydrogen. The lack of formation of these products, in any appreciable extent in the photolysis, indicates that they probably do not form from radical intermediates. Since two molecules must be involved in the formation of these products, it seems unlikely that excited species will be directly involved. Ionic processes which can account for these products are represented in reactions 7d and 9



Ethyl Iodide Production.—A low, but apparently real, yield of radio-ethyl iodide is produced in the radiolysis of methyl iodide containing radio-iodine. Ethyl radicals very probably are precursors to this product. Reaction 7e represents a possible reaction path by which this product can be formed.



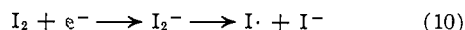
Higher Hydrocarbons.—The propane, propylene and minute traces of C₄ hydrocarbons which are observed as products apparently result from processes which occur in regions of very high ionization density.

The Effect of Added Iodine.—The presence of iodine as a large fraction of the irradiation system results in a decrease in the product yields. This decrease very probably involves changes in the reacting system which result from charge transfer reactions and electron capture by the iodine present rather than by the methyl iodide.

The empirical nature of the quenching reactions is such that the ratio of quench (the difference between the yield at low iodine concentration and the observed yield) to yield is found to be approximately a linear function of the ratio of iodine to methyl iodide concentrations

$$(G_0 - G)/G = Q(\text{I}_2)/(\text{CH}_3\text{I}) \quad (I)$$

In Equation I, *Q* has the value of 28 in the case of ethane production, 13 for methane production and approximately 6 for hydrogen production. In the region of 0.5–1.0% iodine there is an initial decrease in yield somewhat greater than indicated by the above values. An effect of the type illustrated in I would be expected if there is competition of iodine and methyl iodide for some important intermediate. Reaction 10 suggests itself as having the possibility of competing favorably with reaction 4.



Absolute Yields.—The absolute yields for the decomposition of methyl iodide by Co⁶⁰ γ -radiation can be estimated by comparison with ferrous oxidation. In making such a comparison the relative absorption of the two systems must be taken into account. If the absorption is totally due to the Compton effect and it is assumed that the cross section for absorption per electron is the same in both the case of methyl iodide and water, then the ratio of the absorption of methyl iodide and water may be taken as the relative electron densities of the two samples (1.78:1). It is estimated from absorption coefficient data¹⁷ that an additional contribution of about 15% is due to photoelectric absorption in iodine. The ratio of the absorption of methyl iodide to water (for mev. γ -radiation) is taken here to be 2.03.

Unfortunately, at the present time, the absolute yield for ferrous oxidation is somewhat in question.¹⁸ The measured yields vary from 15.5¹⁹ to 20.4²⁰ and

(17) "The Science and Engineering of Nuclear Power," Addison-Wesley Press, Inc., Cambridge, Mass., 1949, Chapter 1.

(18) N. Miller and J. Wilkinson, *Discussion Far. Soc.*, **12**, 50 (1952).

(19) C. J. Hochanadel and J. A. Ghormley, *J. Phys. Chem.*, **56**, 587 (1952); *J. Chem., Phys.*, **21**, 880 (1953).

(20) T. J. Hardwick, *Can. J. Chem.*, **30**, 17 (1952); **30**, 23 (1952).

slightly higher. Basing our calculations on the higher value which is presently given the greater emphasis, and correcting for absorption as indicated above, we obtain the following G values for the decomposition of methyl iodide induced by Co^{60} γ -radiation: (Fe oxid. = 20.4); $\text{I}_2 = 1.26$; $\text{C}_2 = 1.28$; $\text{CH}_4 = 0.57$; $\text{H}_2 = 0.08$. It is seen that the G for iodine production compares very favorably with the value ($G_{\text{I}_2} = 1.38$) obtained in electron bombardment studies where the energy input was measured directly in terms of the electron current and particle energy.⁵

The γ -radiation and fast electron yields are apparently very similar. One must, however, be careful in identifying these yields in this case, at least in principle, since effects of intensity may be present in the fast electron studies. Such effects are apparently minimized in this particular system. It is indeed surprising that for the large difference in the rates of energy absorption, 4×10^{18} ev./cc./min. in the fast electron experiments and 6×10^{14} ev./cc./min. in the γ -radiation experiments, the decomposition yields are found to be so similar.

Accurate yield calculations for the X-ray experiments are more difficult since in the region of 0.2–0.4 Å. the absorption of the water is due to both the photoelectric and Compton effects. Because of the inhomogeneity of the radiation the precise fractional absorption in the water is not known. The calculation is aided somewhat by the fact of complete absorption in methyl iodide. If an absorption of 5.5% of the incident energy is assumed for the water (corresponding to an effective wave length of 0.3 Å.) then the yield of iodine corresponds to G_{I_2} of 1.20. This latter value, which is somewhat in question because of the uncertainty in the absorption, indicates that there is no extreme dependency of the reaction yield upon energy or intensity. As mentioned previously, the constancy in the relative yields in going from the X-ray to the more energetic but less intense Co^{60} γ -radiation would indicate that the yields should be very similar in both of these cases.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Kinetics of the Simultaneous Reduction of Oxygen and Pervanadyl Ion by Iodide Ion in Acid Solution

BY M. H. BOYER AND J. B. RAMSEY

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The effect of the concentrations of each of the ions, hydrogen, pervanadyl and iodide, and of oxygen on the catalysis of the oxygen-iodide reaction, manifest during the simultaneous occurrence of the pervanadyl-iodide reaction, has been determined. The observed dependence of the induction factor on these concentrations has been shown to be satisfactorily accounted for by the assumption that diiodide ion, I_2^- , is the intermediate of the pervanadyl-iodide reaction which acts as the catalyst of the oxygen-iodide reaction. Contributory evidence, substantiating this assumption, has been presented.

Historically, interest in induced reactions arose from the fact that large errors were found when an attempt was made to determine a number of oxidizing agents by means of their reaction with known quantities of certain reducing agents (or *vice versa*) in the presence of air. It was subsequently shown that these errors were due to an accelerated rate of reduction of oxygen. According to the nomenclature adopted in the study of such phenomena,¹ in general, the reduction of oxygen was said to have been induced. The catalytic character of a number of these induced reductions of oxygen was demonstrated long ago by Lenssen and Löwenthal² in their paper, entitled "Zur Katalyse des Sauerstoffs." For example, they stressed the fact that, while a small quantity of dichromate is being reduced by stannous chloride in acid solution containing dissolved air, the quantity of stannous tin oxidized by oxygen is several times greater than that oxidized by the dichromate, and than that which would have been oxidized by the oxygen (of the air) in the absence of the dichromate-stannous reaction under otherwise the same conditions.

Although a considerable number of induced reductions of oxygen have been reported, none have been investigated in such a way as to permit the formulation of a probable mechanism of the induction. However, in their study of the induction of the oxygen-iodide reaction by the pervanadyl-iodide reaction in acid solutions, Bray and Ramsey^{3,4} varied the initial concentrations of pervanadyl ion, $\text{V}(\text{OH})_4^+$ [hereafter symbolized by $(\text{V}^{+5})_0$], keeping the concentrations of oxygen, iodide ion, and acid constant. Over the lower range of initial concentrations of pervanadyl ion, from 2.6×10^{-5} to 10.3×10^{-5} *m*, their results conform to the relation

$$\text{Induction factor} = \text{Constant}/(\text{V}^{+5})_0^{1/2}$$

In this case the induction factor (hereafter symbolized by I. F.) is defined, in conformity with its general use, by the relation

$$\text{I. F.} = \frac{\text{O}_2 \text{ reduced, equivalents per liter}}{\text{V}^{+5} \text{ reduced, equivalents per liter}}$$

They obtained values of the induction factor as

(3) W. C. Bray and J. B. Ramsey, *THIS JOURNAL*, **55**, 2279 (1933); considerable historical background included.

(4) See also I. M. Kolthoff and N. H. Furman "Volumetric Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, Chapter VII, for history and importance of induced oxidations by oxygen in volumetric analysis.

(1) Fully discussed by R. Luther and N. Schilow, *Z. physik. Chem.*, **46**, 777 (1903).

(2) E. Lenssen and J. Löwenthal, *J. prakt. Chem.*, **86**, 193 (1862).