dicate an over-all heterogeneity. In some cases it is not possible to determine whether the data should be interpreted on the basis of a few rates or a spectrum of rates. This difficulty arises from the fact that it is sometimes possible to describe curves, such as those obtained in these runs, by a sum of a few exponentials even though a large number of rates are involved.

The conclusion that only a few rates are involved is based on the fact that there are examples where the medium rate is much faster than the slow rate. When $R_2 \gg R_3$ (the initial fast rate for which there are no data being R_1) curves are obtained which may be plotted to appear as a series of relatively straight portions with most of the curvature concentrated in sharp knees.[16] Although there may be differences within the R_2 portion these differences are small compared to the differences between the portions.

The data in Figs. 4 and 5 indicate that the surface of the catalyst may be described on the basis of a relatively few portions which differ from each other but are homogeneous within themselves. The term homogeneous should be interpreted to include the possibility of exchange occurring only at a few sites with rapid surface migration within each portion.

The cause of the over-all heterogeneity has not been determined. There is a temptation to identify each of the homogeneous portions as exposed crystal faces. However, difficulties inherent in powder samples such as adsorbed gases, traces of oxide and concentration of impurities on the surface make it impossible to come to a definite conclusion. Neither an increase in the severity of the reduction conditions nor the deliberate addition of oxygen has a marked effect on the general characteristics of the exchange.

Isotopic Effect.—The study of the chemisorption–exchange is simplified if there is no appreciable difference in the chemical properties of C*O and CO. In order to determine whether the isotopic factor was appreciable, radioactive measurements were made on the excess C*O over the catalyst during the chemisorption period. If either the $C^{14}O$ or CO were preferentially adsorbed from the C*O, the calibration activity of the C*O would change.

No differences greater than the limit of experimental accuracy of 1% could be detected after 20 hours contact with the iron. These results indicate that the isotopic factor can be neglected in the chemisorption–exchange experiments.

Acknowledgment.—The author is grateful to Supervisor L. C. Roess and the members of the Physical Research Department for their interest and suggestions and to A. K. Blom and E. J. Bane for their help with the experimental work.

BEACON, N. Y.

[16] R. P. Eischens, *J. Chem. Phys.*, **19**, 377 (1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Fast Electron and X-Ray Decomposition of the Alkyl Halides[1,2]

BY ROBERT H. SCHULER[3] AND WILLIAM H. HAMILL

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The liquid phase decomposition of a number of alkyl halides upon exposure to fast electrons and energetic X-radiation has been investigated in the region of 0.5 to 2.0 million volts. Alkyl iodides decompose in high yield to free iodine and exhibit considerable radiation-induced exchange with radioiodine present in the system during irradiation. Decomposition of the alkyl bromides yields mainly hydrogen bromide and small amounts of free bromine and is in general complicated by secondary effects. These reactions are sensitive to small amounts of additives present in the reaction. Processes which are peculiar to the radiation chemistry of the system are illustrated, particularly in the decomposition of methyl iodide.

There are evident similarities between radiation chemistry and photochemistry but there is little information permitting direct comparison of the relative effects of both types of irradiation for the same system.[4] The alkyl halides have been chosen for the present survey because of the possibility of conveniently and arbitrarily restricting observations to the displaced halogens[5] and because of the information available from photochemical studies of the alkyl halides, in particular a parallel investigation of the alkyl iodides.[6] Prior to initiation of this work there was little information available on the radiation chemistry of the alkyl halides[7a]; more recently observations on the radiation decomposition of the alkyl iodides have been reported by Williams[5] and others.[7b]

Experimental

The source of radiation used in these investigations was an electrostatic accelerator (Van de Graaff Generator) operated by the Department of Physics of the University of Notre Dame. This instrument supplies a high energy monochromatic beam of electrons in the 1–2 Mev. region. The energy of the beam, previously calibrated by the Physics group, is known to better than 1%. The current in the elec-

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[1] Presented at the 115th Meeting of the American Chemical Society in San Francisco, March, 1949. From the doctoral dissertation of Robert M. Schuler, University of Notre Dame, 1949.

[2] This work was supported in part under contract N6 ori 165, T.O. II with the Office of Naval Research.

[3] Peter C. Reilly Fellow.

[4] A very recent example of such a comparative study is provided by the work of R. R. Hentz and M. Burton, THIS JOURNAL, **73**, 532 (1951).

[5] This limitation is particularly well justified for the iodides because it can be expected that interaction with ionizing radiations will be largely confined to iodine, due to its large atomic number. Energy absorption therefore becomes rather specific in effect, for the C–I bond, as in the photochemical case. Confirmation of this view is supplied by the work of L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56**, 569 (1952).

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

[7] (a) A. Kailan, *Monatsh.*, **38**, 537 (1918); P. Gunther, *Z. angew. Chem.*, **41**, 1357 (1928); (b) P. Sue and E. Saeland, *Bull. soc. chim. France*, 437 (1949); M. Lefort, P. Bonet-Maury and M. Frilley, *Compt. rend.*, **226**, 1904 (1948).

tron beam was recorded by placing a low impedance Brown potentiometer, used as a recording microammeter, between the electron target and ground. The total exposure of a sample was determined from the integrated area under the recorded curve. This measurement agreed with a rough calorimetric determination of radiation dosage. In the X-radiation experiments this dosage is reproducible to 1%. In the fast electron experiments the reproducibility is *ca.* 5%; at very small currents it is poorer. The difficulty arises from current leakage due to extensive ionization of air near the cell; much larger systematic errors may be expected.

Electron Irradiation.—In the electron irradiation experiments the target substance was placed in a cell, which has a window approximating 60 mg./cm.^{2}, of the type illustrated in Fig. 1. Electrical connection to the microammeter was made through the tungsten lead. The cell was placed behind a brass diaphragm which served to limit the electron beam to the central, thin window and also acted as an electrostatic shield. In all experiments except those with carbon tetrachloride and chloroform, when arcing within the sample was observed, the ionization within the sample was sufficient to provide good electrical contact to ground. Cold water was circulated around the cell to dissipate heat but no other attempt was made to control temperature in these experiments.

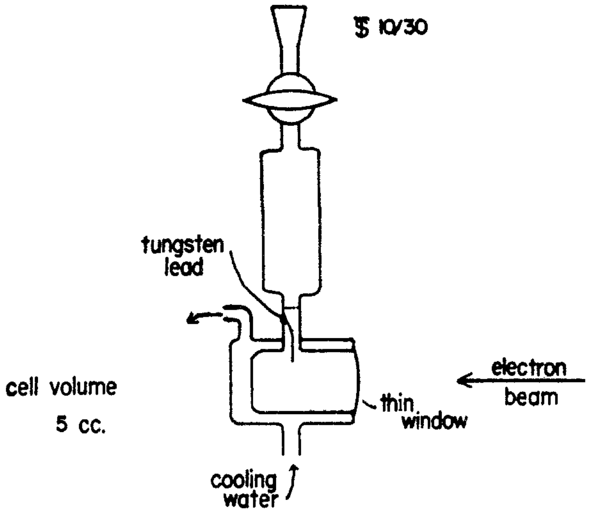

Fig. 1.—Fast electron irradiation cell.

X-Irradiation.—X-Rays were produced by stopping high energy electrons with a gold target. At the high potentials used here the energy is radiated principally in the forward direction.[8] The sample container, a cylinder 7.5 cm. long and 4.0 cm. in diameter, was placed against the target and coaxial with the electron beam. Since the rate of energy dissipation in the sample was low these irradiations were performed at room temperature.

Materials and Analysis.—All organic halides used were purified by distillation. Radioactive iodine (I^{128}) was prepared by the Szilard–Chalmers enrichment of ethyl iodide which had been bombarded by the total flux of a 300-mg. radium–beryllium neutron source. Dissolved air was removed, where noted, by repeated freezing and pumping of the sample and sealing under vacuum.

Hydrogen halide was removed from irradiated samples by extraction with water and weighed as the silver halide. When interference from free halogen was possible the aqueous extract was repeatedly extracted with carbon tetrachloride. Free iodine was measured spectrophotometrically in the irradiated sample or, more usually, titrated with standard thiosulfate solution. Free bromine was allowed to react with potassium iodide, then titrated similarly.

Fast Electron Experiments

Iodides.—Methyl, ethyl, *n*-propyl and methylene iodides were subjected to fast electron bombardment at energies between 0.60 and 1.76 Mev. Within experimental error the yield of iodine (expressed as G, the number of atoms of free iodine formed per 100 ev. of energy absorbed by the sample) did not depend upon the electron energy, the electron current or the total exposure of the sample. That is, the radiation yield depended only upon the energy absorbed by the sample. These results are summarized in Table IV.

There was no appreciable effect of dissolved oxygen for methyl and ethyl iodides (Table IV). Although some oxidation undoubtedly occurs, this is apparently overwhelmed by the relatively high extent of decomposition. The effect of oxidation reactions might become significant at small total decompositions per unit volume of sample.

Several irradiations were performed on samples containing added iodine at initial concentrations as high as 0.24 M. Iodine production was somewhat diminished by the added iodine but retardation, if real, was not pronounced.

To test the extent of back reaction (1) radioactive iodine

$$R\cdot + I_2 \longrightarrow RI + I\cdot \qquad (1)$$

(I^{128}, 25 min.) was added to some samples before irradiation. The yields for exchange were approximately $G = 6.0$ atoms per 100 ev. for methyl iodide and $G = 5.5$ for ethyl iodide. It is evident that radiation-induced exchange contributes appreciably to the over-all reaction. Because of the high degree of inhomogeneity within the sample during electron bombardment it was difficult to obtain reliable values for exchange and the values reported here indicate only that considerable back reaction occurs even at low iodine concentrations ($\sim 0.01\ M$). Further study of exchange reactions induced by X-radiation is in progress.

Solutions of ethyl iodide in *n*-heptane were also subjected to fast electron irradiation. At 25–100 weight per cent. of ethyl iodide the yield of iodine, calculated on the basis of the fraction of the energy absorbed by the ethyl iodide, is approximately the same as for pure ethyl iodide. In dilute solutions (0–25%) the yield decreases rapidly with decreasing concentration of ethyl iodide. This effect is presumably due to absorption of free iodine by radicals produced in the decomposition of the hydrocarbon substrate. This view is confirmed by the electron irradiation of *n*-heptane 0.0024 and 0.0086 M in iodine. Complete and partial absorption of the iodine, respectively, were observed for these samples, the yield in the latter case being $G = 7.3$ for the absorption of $^1/_2\ I_2$.

Bromides.—In the radiolysis of ethyl bromide, both hydrogen bromide and free bromine were produced in low yields (Table I) which imply considerable back reaction. There is some evidence for dependence of the yield on beam intensity. To obtain a better measure of total primary decomposition triphenylmethane was added before irradiation (Fig. 2). Any triphenylmethyl bromide which may form as a result of reaction with free bromine hydrolyzes readily and is included in the total analysis. With this additive the yield increased to about $G = 6.5$.

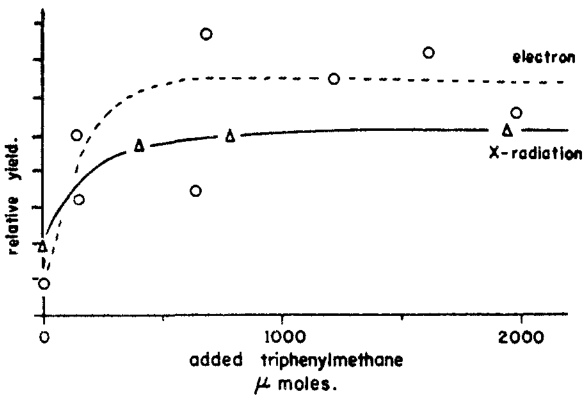

Fig. 2.—Radiation decomposition of ethyl bromide with added triphenylmethane. Sample volumes were 5 ml. for electrons and 76 ml. for X-rays.

The principal product from the radiolysis of ethylene bromide was free bromine (Table I). There is an apparent dependence upon beam intensity at constant energy input and evidence of retardation by the radiation product. The yields again are very low. Direct evidence of retardation

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[8] A. A. Petrauskas, L. C. Van Atta and F. E. Myers, *Phys. Rev.*, **63**, 389 (1943).

due to back reaction of radicals with bromine was obtained by qualitative observation of considerable radiation-induced exchange between bromobenzene and free radioactive bromine.

Chlorides.—After several preliminary experiments with air-saturated chloroform and carbon tetrachloride further work was discontinued because arcing occurred within the samples.

TABLE I

ELECTRON IRRADIATION OF ALKYL BROMIDES

Expt. no.	Electron energy, Mv.	Current, μa.	Integrated current, coulombs $\times 10^6$	Bromine liberated, g. atoms $\times 10^6$	Reaction yield, G
		Ethyl bromide[a]			
62	1.50	0.8	270	36	0.9
59	1.69	1.8	257	48	1.2
68	1.76	1.9	329	63	1.2
65	1.50	4.0	550	43	0.6
71	1.76	4.3	700	104	.9
60	1.69	6.0	397	38	.6
67	1.50	7.6	783	59	.5
61	1.69	10.2	322	30	.6
66	1.50	10.2	1086	75	.5
102	1.76	3.0	645	22[b]	.2[b]
		Ethylene bromide[b]			
118	1.65	1.8	849	85	0.65
117	1.65	3.4	918	77	.54
121	1.65	4.5	469	38	.52
116	1.65	6.0	924	70	.48
119	1.65	8.8	1123	63	.46
120	1.65	4.1	4400	168	.25

[a] As HBr; Br_2 formed but not measured. [b] As $^1/_2Br_2$; HBr not measured.

X-Ray Irradiations

Iodides.—Methyl and ethyl iodides liberated free iodine but little or no hydrogen iodide upon exposure to X-rays in the region of 1 Mv. (Fig. 3, Table II). Dissolved atmospheric oxygen resulted in some radiation-induced oxidation, corresponding to the production of several milligrams of free iodine.

TABLE II

X-RAY DECOMPOSITION OF THE ALKYL HALIDES

Expt. no.	Electron energy, Mv.	Current, μa.	Decomposition, g. atoms $\times 10^4$	Specific[a] reaction, g. atoms/coul. $\times 10^3$
		Ethyl iodide		
43	1.67	75	49	2.99[e]
93	1.65	55	75	1.99[b,e]
96	1.65	35	59	2.09[b,e]
		Methyl iodide		
55	1.50	50	57	2.70[e]
123	1.65	110	103	1.88[b,e]
		Ethyl bromide		
85	1.66	100	70	0.76[b,d]
124	1.65	100	21	.40[b,c,d]
			21	.41[b,c,e]
		Ethylene bromide		
29	1.62	110	1100	9.5[d]
90	1.65	15	160	11.2[d]
91	1.65	40	410	10.3[d]
92	1.65	60	490	9.9[d]
		Ethylene chloride		
47	1.50	100	19	1.2[d]
35	2.00	110	31	2.5[d]
38	2.20	80	30	3.5[d]

[a] Particular to the geometrical arrangement used. [b] Sample deaerated before irradiation. [c] Sample cooled to Dry Ice–acetone temperature before irradiation. [d] As HX. [e] As $^1/_2X_2$.

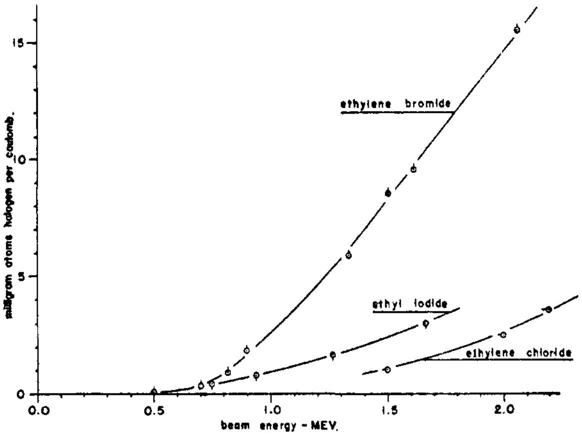

Fig. 3.—X-Ray decomposition of the alkyl halides.

Bromides.—Ethyl bromide, subjected to X-ray bombardment, was found to decompose to hydrogen bromide, and, at low temperature, free bromine (Table II). The yields were low although somewhat higher than for electron bombardment. Addition of triphenylmethane to the target substance again enhanced the yield of recoverable bromide ion (Fig. 2), although less than for electrons.

Ethylene bromide gave a considerable yield of hydrogen bromide but no free bromine. When small amounts of cyclohexene were added to the ethylene bromide before irradiation, the extractable bromide ion was reduced by a factor of approximately four (Table III). Larger concentrations of cyclohexene did not cause any further effect.

TABLE III

X-RAY DECOMPOSITION OF ETHYLENE BROMIDE CONTAINING ADDED CYCLOHEXENE

C_6H_{10}, mole/liter	0	0.01	0.05	0.20
HBr produced, moles/coulomb $\times 10^3$	15.5	4.7	3.9	3.6

TABLE IV

SUMMARY OF RADIATION YIELDS (G)

	Product	Electron decomposition	X-Ray[a] decomposition
Ethyl iodide	$^1/_2 I_2$	4.1	(4.1)[a]
Air saturated	$^1/_2 I_2$	...	5.9[b]
0.24 M in iodine	$^1/_2 I_2$	3.5	...
10% in *n*-heptane	$^1/_2 I_2$	0.07	...
Cont. radioiodine	Exchange	5.5	...
Methyl iodide	$^1/_2 I_2$	2.7	3.3
Air saturated	$^1/_2 I_2$	...	5.7
Cont. radioiodine	Exchange	6.1	...
Methylene iodide	$^1/_2 I_2$	2.5	...
n-Propyl iodide	$^1/_2 I_2$	3.5	...
Ethyl bromide	HBr	0.6–0.9	2.0
Triphenylmethane added	HBr	6.5	5.1
Ethylene bromide	$^1/_2 Br_2$	0.5	0.0
	HBr	...	17.8
Cyclohexene added	HBr	...	4.3
Bromobenzene	HBr	...	2.0
Radiobromine added	Exchange	...	...
Ethylene chloride	HCl	...	4.1

[a] X-Ray yields relative to an assumed G of 4.1 for the ethyl iodide decomposition. [b] Lefort, Bonet-Maury and Frilley, ref. 7b, report a G of 5.7 for soft X-radiation and 2.4 for α-radiation for the decomposition of air-saturated ethyl iodide.

Chlorides.—Ethylene chloride decomposed to form hydrogen chloride with a yield similar to that for the above reactions.

A summary of all results appears in Table IV.

Discussion

Accurate calculation of the energy input for the X-irradiations is difficult since it requires a knowledge of the absolute intensity of the X-ray beam and of the absorption of the radiation by the sample. This latter consideration is simplified somewhat by the fact that, at high energies, the X-ray absorption is largely of the Compton type, the coefficient of which is proportional to the electron density of the sample. At the energies involved here a small contribution of photoelectric absorption is made by iodine and a still smaller one by bromine. An attempt has been made to estimate the energy absorbed by ethyl iodide in experiment 93, Table II, taking into account the efficiency of X-ray production (~6%), the geometry (~30%), and the absorption by the sample (~20%). The three factors together give 0.0035 as the fraction of the original electron energy appearing in the sample and $G = 3.6$ for the reaction. Correspondingly, an approximate calorimetric measurement gives $G = 4$. In Table IV the relative yields for the X-ray decompositions are summarized upon the basis of an assumed yield of 4.1 for ethyl iodide. The absorption of radiation is taken to be proportional to the relative electron density of the sample.

The yields from electron bombardment, Tables I, IV, are proportional to the energy absorbed by the sample over a wide range. The yields from X-ray bombardment may also be presumed to depend only on the energy absorbed. The curvature of the yield–energy curves in Fig. 3 reflects only the increased efficiency of X-ray production as the electron energy increases.

The over-all decomposition processes induced in the alkyl iodides by electron and X-ray bombardment resemble superficially the decomposition reactions initiated by light at 2537 Å.[6] in that the liberation of iodine is dependent on the total energy absorbed by the sample and is independent of iodine concentration, of particle energy, and of intensity. The observed radiation yield of iodine corresponds to only a part of the primary reaction if one considers that the primary yield includes the separate effects of exchange and of net production of iodine.

There is a striking difference between the relative decomposition yields for methyl and ethyl iodides by radiolysis and photolysis (2537 Å.) where

$$\frac{G_{\mathrm{MeI}}}{G_{\mathrm{EtI}}} = \frac{2.7}{4.1} \text{ and } \frac{(\phi_{\mathrm{MeI}})}{(\phi_{\mathrm{EtI}})} = \frac{0.016^{6}}{0.40}$$

The corresponding energy requirements per $^1/_2I_2$ from methyl iodide are 300 ev. by photolysis and 37 ev. by radiolysis. It is evident that, for either mode of decomposition, net liberation of iodine must be compensated by equivalent C–C bond formation, *e.g.*, ethane from methyl iodide.[9] That such processes do not result from the combination of methyl radicals following diffusion can be inferred, in both cases, from the substantial independence of the yield of iodine upon its concentration and upon the intensity of radiation. The simplest explanation for the radiolytic process, consistent with the facts just mentioned and also that of radiation-induced exchange of iodine, is that charge neutralization occurs between CH_3I^+ and CH_3I^-, and that either ethane or methyl radicals can be formed. In view of the very exothermic nature of charge neutralization a multiplicity of products[9] may well be expected.

The yield from electrons in ethyl bromide is small, *viz.*, $G_{\mathrm{HBr}} = 0.7$, but it increases tenfold with the addition of triphenylmethane. Since small amounts of this reagent are fully effective (Fig. 2) it must be involved in reactions with particles which have diffused some distance from the scene of the primary process. It appears likely that the following reactions may occur and the question

$$(C_6H_5)_3CH + Br\cdot \longrightarrow (C_6H_5)_3C\cdot + HBr$$
$$(C_6H_5)_3CH + C_2H_5\cdot \longrightarrow (C_6H_5)_3C\cdot + C_2H_6$$

arises concerning the back reaction which apparently involves 90% of the bromine atoms (or hydrogen bromide) originally produced, and also why back reaction is much less important in ethyl iodide. The most obvious difference between these systems is that bromine atoms tend to form hydrogen bromide whereas iodine atoms tend to form iodine. Further, if carbon-to-carbon bond formation occurs *via* disproportionation of ethyl radicals, the other facts can be accounted for. Hydrogen bromide adds efficiently to ethylene by a chain mechanism[10] and the addition would therefore be inhibited by triphenylmethane. Since vicinal diiodides are unstable the back reaction here, as indicated by isotopic exchange, would be limited to reaction of ethyl radicals with molecular iodine. This interpretation is supported by the replacement of hydrogen bromide by bromine at low temperature (Table II) and the greatly decreased yield of hydrogen bromide from ethylene bromide upon addition of cyclohexene (Table III).

Acknowledgment.—The authors are indebted to Prof. Bernard Waldman for permission to use the equipment of the nuclear physics laboratories and to Drs. Donald Gideon and Eligius Wolicki for their aid in operating the equipment.

NOTRE DAME, INDIANA

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[9] It has been shown by R. H. Schuler and C. T. Chmiel, abstracts of papers, 121st meeting of the Am. Chem. Soc., Buffalo, 1952, that during the photolysis of methyl iodide, ethane is liberated in amount equivalent to iodine, together with methane. It had been claimed by G. Emschwiller, *Compt. rend.*, **192**, 799 (1931), that pure methane resulted. Very recently R. H. Schuler and N. C. Petry have also obtained the following unpublished results for the radiolysis of liquid methyl iodide: C_2H_6, 90; CH_4, 45; H_2, 5; C_2H_4, 5 relative to I_2 as 100 on a molar basis.

[10] W. E. Vaughan, F. F. Rust and T. W. Evans, *J. Org. Chem.*, **7**, 477 (1942).