to the HI and I_2 throughout an experiment. It is possible that electron attachment or charge transfer processes which can lead to the net removal of HI or increased return of I_2 to organic combination become more important as the I_2 and HI concentrations increase.

Temperature and Phase Effects.—The fact that samples of the same solid alkyl iodide at the same temperature give different G values for I_2 production when they are in the glassy state than when they are in the crystalline state seems to indicate that the orientation of the molecules with respect to each other at the time energy is absorbed is an important factor in determining the chemical consequences of the energy absorption. In the ordered arrangement of a crystal hot C_2H_5 radicals formed from C_2H_5I may preferentially attack certain parts of adjacent C_2H_5I molecules, while in the random arrangement of a glass there can be no such specificity. Such preferential attack or various other sterically sensitive hot reactions may account for the difference in the G_{I_2} values in the different states.

For reactions activated by radiative neutron capture[12-14] the "organic yield" has been observed to increase, decrease or remain essentially unchanged with change of phase, depending on the compound, but with no obvious correlation with the molecular structure or the density.[12-14] In view of the contrast between the iodine yields for the glass and the crystalline phases in the present work, it seems plausible that the primary factor in determining the effect of freezing on the organic yields of activation by nuclear processes may be the orientation of the molecules in the crystal lattice.

The absence of a temperature effect in the radiolysis of liquid C_2H_5I from −78 to 108° suggests that the pattern of radical recombination reactions which occurs is not governed by the ease of diffusion of the radicals. This behavior is in contrast to that of CCl_3Br where G_{Br_2} is temperature sensitive, the apparent activation energy being about 3 kcal./mole.[15]

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MADISON, WISCONSIN

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[13] M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

[14] S. Goldhaber, R. S. H. Chiang and J. E. Willard, THIS JOURNAL, **73**, 2271 (1951).

[15] R. F. Firestone and J. E. Willard, Absts. of 127th meeting of the Am. Chem. Soc., Cincinnati, Ohio, April 1955, p. 23Q.

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

Quantitative Treatment of the Elementary Processes in the Radiolysis of Alkyl Iodides by γ-Rays

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The mechanism of radiolysis of alkyl iodides with Co^{60} γ-rays includes the production of HI, I_2, alkyl radicals and hydrocarbons within the "hot spots" of the radiation tracks, and reaction of the thermalized radicals outside the tracks with HI and I_2 to abstract H and I, respectively. From the effects of added HI and I_2 on the rates of I_2 production and radioiodine exchange, it is possible to deduce the rates of the elementary reactions. For ethyl iodide, integrated rate equations which predict the rates of I_2 and HI production and of exchange have been obtained. The predicted rates are in agreement with the experimental results.

Introduction

The yield of iodine per unit of energy absorbed in the radiolysis of degassed ethyl iodide[1] is independent of the concentration of iodine built up during the radiolysis[1,2] and is independent of the temperature from −78 to 108°.[2] It has been thought that the iodine yield is independent of initially added iodine[3,4] although the data presented might be interpreted to indicate a small decrease for such addition.[3] These facts have led to the assumption that iodine production does not occur by any reaction involving the thermalized radicals, *i.e.*, occurs only by hot processes.

In the present work a careful re-examination of the effect of I_2 added prior to radiolysis has shown that it reduces the initial rate of iodine production by nearly 50%. This, together with the observation that HI is a product of the radiolysis,[2] has indicated that an important part of the mechanism is a reaction in which thermal alkyl radicals abstract hydrogen from HI, as it is in the photolysis of ethyl iodide reported by Bunbury, Williams and Hamill.[5] A quantitative study has therefore been made of the role played by HI and I_2 in competing for thermalized radicals.

Experimental

The methods of purification and irradiation of alkyl iodides were similar to those described in the preceding paper.[2] Mallinckrodt reagent grade iodine was used without further purification. All reaction mixtures were degassed by vacuum line techniques.

Dry HI was prepared from a 55% aqueous solution of HI (Merck) from which the free iodine was removed with red phosphorus. The water was removed by covering the frozen solution with P_2O_5, and allowing it to melt after evacuation. The HI gas was then passed through more

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[1] A review and bibliography of the subject is given in the preceding paper.[2]

[2] E. O. Hornig and J. E. Willard, THIS JOURNAL, **79**, 2429 (1957).

[3] R. H. Schuler and W. H. Hamill, *ibid.*, **74**, 6171 (1952).

[4] R. H. Schuler and R. C. Petry, *ibid.*, **78**, 3954 (1956).

[5] (a) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, abstracts of 128th meeting of the Am. Chem. Soc., Minneapolis, Minn., Sept. 1955, p. 36R; (b) D. L. Bunbury, R. R. Williams, Jr., and W. H. Hamill, THIS JOURNAL, **78**, 6228 (1956).

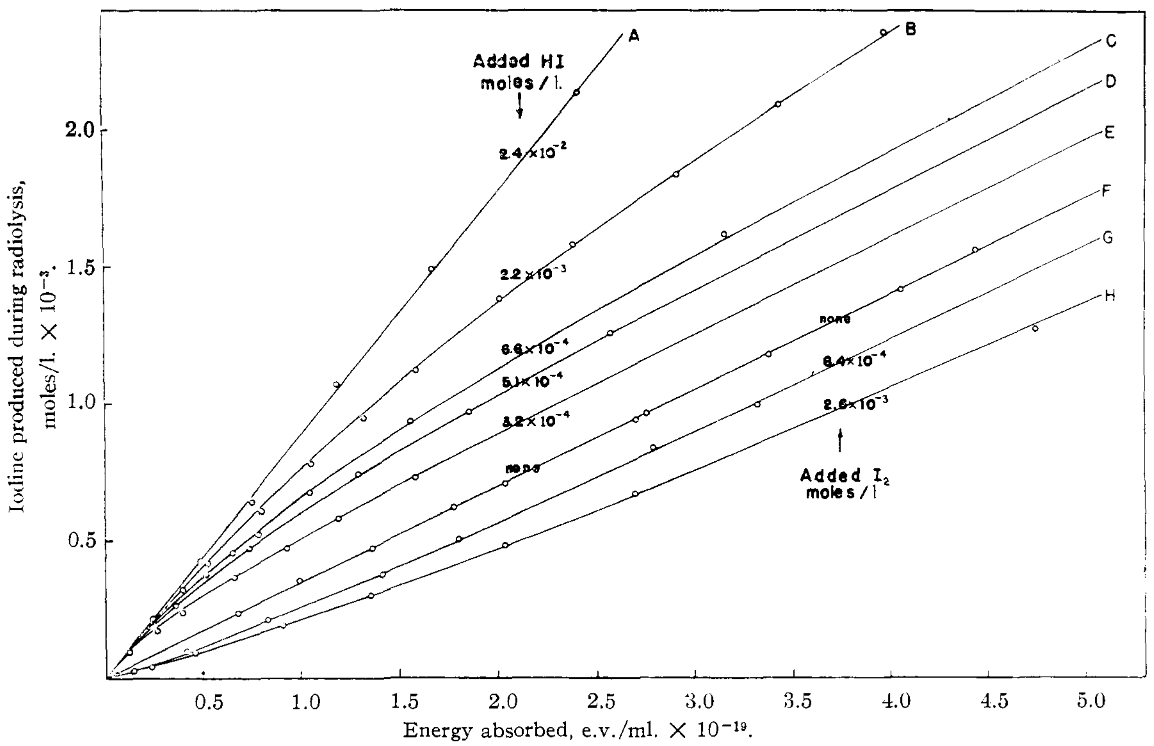

Fig. 1.—Effect of added HI and I_2 on the γ-radiolysis of ethyl iodide. Points are from experimental data[22]; curves are calculated by equation 27.

P_2O_5, supported on glass wool, on the vacuum line. Its pressure was measured with a mercury manometer, which reacted with it only slightly. Fluorocarbon grease was used on the stopcocks; silicone grease appeared to react to give volatile products. To tag the HI, carrier free I^{131} as aqueous iodide was added to the aqueous HI before the P_2O_5. To tag I_2 a similar iodide solution was added to I_2 and the latter distilled through P_2O_5.

Iodine concentrations were determined with a Beckman D.U. spectrophotometer provided with a photomultiplier tube as the detector to increase the sensitivity, and a Baird interference filter to cut out stray light coming through the monochromator. With this equipment it was possible to determine optical densities accurately up to a value of nearly 5 by taking readings against a set of standard solutions having optical densities of 1, 2 and 3. All readings were taken at 4780 Å. (visible absorption maximum; molar extinction coefficient 1280 l./mole cm.). Since the absorption spectrum of iodine in alkyl iodides is temperature sensitive,[6] rough thermostating was provided during later runs by controlling the room temperature at 24 ± 1°.

When it was desired to analyze for radioiodine in the forms of HI, I_2 and organic combination, the reaction cell was broken open while the contents were frozen at liquid air temperature and the reaction mixture was dissolved in CCl_4 and extracted with water to remove HI, and with aqueous sulfite to remove I_2. The water, sulfite and organic solutions were counted, and density corrections were applied when necessary. Solutions treated in this way which had not been irradiated showed about 1% exchange between organic and inorganic forms when opened the same day and 5% exchange when opened after two weeks. All samples were stored in the dark at all times.

Results and Discussion

Evidence for Competitive Reaction Steps.—Three lines of evidence establish the fact that organic radicals born during the radiolysis of degassed ethyl iodide do not all react with I_2 but may undergo a competing reaction which produces rather than consumes inorganic iodine. These are the decrease in iodine yield (G_{I_2}) caused by added iodine, the increase in G_{I_2} caused by added hydrogen iodide, and the increase in exchange yield ($G_{\text{exch.}}$) caused by added iodine.

Effect of Added I_2 on G_{I_2}.—The effect of added iodine on the initial rate[7] of iodine production in the radiolysis of ethyl iodide was determined in 14 experiments with initial iodine concentrations ranging from 2.6×10^{-3} to 4.3×10^{-4} M. In all cases the initial rate was, within experimental error, 54% of the rate in the absence of added iodine and increased toward the normal rate as the run continued. This is illustrated by typical results plotted as curves G and H of Fig. 1.

Effect of Added HI on G_{I_2}.—When HI is added to ethyl iodide prior to radiolysis, the effect on the rate of I_2 production is opposite to that produced by added I_2. This is illustrated by the curves above the straight line of Fig. 1. All the curves approach the same maximum rate at zero time and fall off toward the rate for ethyl iodide without additives at longer irradiation times, the falling off being slower the higher the concentration of HI. The initial rate with added HI was 2.55 times the rate without additive and 4.73 times the initial rate with added I_2. Solubility determinations for ethyl iodide solutions showed that about 95% of the HI present in a standard irradiation vessel was always in the liquid phase.

Effect of Added I_2 on Exchange Reaction.—It is known from previous work[1,2] that radioiodine

[6] D. E. Schuler and R. H. Schuler, THIS JOURNAL, **76**, 3092 (1954).

[7] Evaluated by plotting the average rate from time zero to time t *vs.* time of irradiation t and extrapolating to zero t. "Rate" as used in this paper is directly proportional to "G value," *i.e.*, number of molecules which react per 100 e.v. absorbed. For ethyl iodide a rate of 0.0312 μ equivalent per min. per 5-ml. sample equals a G value of 1.

added to ethyl iodide undergoing radiolysis enters organic combination at a measurable rate. The compound formed is about 90% ethyl iodide.[4,8] If in this exchange the only complication of normal exchange kinetics were the dilution by the inorganic iodine produced in the radiolysis, then the rate of exchange of radioiodine could be treated as

$$-d[\mathrm{I}^*]/dt = K([\mathrm{I}^*]/([\mathrm{I}_0] + [\mathrm{I}]\ \text{produced})) = \\ = K([\mathrm{I}^*]/([\mathrm{I}_0] + Rt)) \quad (1)$$

$$\log([\mathrm{I}^*]/[\mathrm{I}_0^*]) = K/R \log([\mathrm{I}_0]/([\mathrm{I}_0] + Rt)) \quad (2)$$

where $[\mathrm{I}^*]$ is the concentration of radioiodine in the inorganic phase (directly proportional to the counting rate), K is the total exchange rate in equivalents of iodine per minute (assumed constant), $[\mathrm{I}_0]$ is the initial concentration of inorganic iodine in equivalents, R is the net rate of production of inorganic iodine in equivalents per minute, which is also assumed constant, and t is the time.[9] The data of Table I for eight experiments with approximately equal initial added iodine concentrations show that the rate of iodine exchange calculated from equation 2 decreases with time of irradiation.

In a further examination of exchange during radiolysis, it was found that if radioiodine is added as HI with no I_2 initially present exchange occurs much more slowly, consistent with the conclusion that the exchange results from reaction of radicals with I_2 but not with HI. As I_2 is formed the radioiodine would be expected to equilibrate with it rapidly by HI–I_2 exchange.

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Time of irrad., min.	Initial $[I_2]$, equiv. × 10^6	$\frac{\mathrm{I^*\ not\ exchd.}}{\mathrm{I^*_{total}}}$	Exchange rate, equiv./min.[b] From eq. 2	Exchange rate, equiv./min.[b] From Fig. 2 curve B
4.93[a]	9.46	0.915	0.176	0.148
9.66	8.25	.834	.166	.146
11.2	7.73	.803	.171	.145
22.3[a]	8.04	.712	.144	.140
38.7	8.92	.614	.142	.136
58.0	9.37	.522	.153	.133
74.4	8.45	.455	.141	.131
88.3	8.66	.411	.141	.130

[a] Based on two runs; all others based on one run. [b] Rates given in equivalents × 10^6 per min. per 5-ml. sample volume, at an energy absorption rate of 3.77 × 10^{17} e.v./ml. min.

Absence of Effect by Added C_2H_4 and $C_2H_4I_2$.—Ethyl iodide containing 0.07 mole/l. of ethylene gave essentially the same G_{I_2} value as ethyl iodide with no additives and showed no back reaction with products to alter the HI/I_2 ratio during two days of standing after irradiation.

Ethylene iodide[10] at a concentration of about 10^{-3} M in ethyl iodide did not affect the rate of I_2 production in the radiolysis. In unirradiated samples of this type, slow decomposition of the $C_2H_4I_2$ occurred over a period of two months, producing iodine. No such build-up ever occurred in irradiated samples of pure C_2H_5I.

Qualitative Interpretation of HI and I_2 Effects.—The effects of added HI and I_2 on the rate of iodine production and on the rate of exchange with radioiodine indicate that these species compete with each other for thermal alkyl radicals produced in the radiolysis. In the presence of a large excess of HI over I_2, all of these radicals react by abstracting hydrogen from HI and liberating $^1/_2$ I_2, thus increasing the rate of iodine production and preventing the exchange reaction from occurring. In the presence of a large excess of I_2 every radical reacts with it to return $^1/_2$ I_2 to organic combination, a step which, together with the original formation of the radical, constitutes the exchange reaction. The fact that I_2 production continues even when there is a large excess of I_2 over HI indicates there is a reaction which produces iodine in the "hot spots" of the radiation tracks which is not affected by additives at the concentrations used in this work.[11] The fact that the rate of iodine production from pure ethyl iodide without additives is linear with energy input (*i.e.*, independent of the buildup of products) must mean that HI and I_2 are produced in a constant ratio and hence the fraction of the radicals produced which reacts with each is unchanged during continued irradiation. Radicals which become thermalized and escape reaction in the spurs diffuse into the body of the solution where they must react with HI or I_2 rather than with other radicals. The concentrations of I_2 and HI produced by even very short irradiations of pure ethyl iodide are far greater than the steady-state radical concentration in the bulk of the solution.[16]

A set of reaction steps adequate to explain the observations discussed above is given below. Underlined formulas indicate excited molecules or radicals. It is assumed that the initial excitation and ionization produced by the high energy electrons resulting from the γ-ray absorption lead to

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

(9) A similar equation is given by W. H. Hamill and R. H. Schuler, THIS JOURNAL, **73**, 3466 (1951).

(10) Prepared by the method of Semonoff, "Jahresbericht über die Fortschritte der Chemie," 1864, p. 483.

(11) The main mechanism of energy dissipation by Co^{60} γ-rays (1.1 and 1.3 mev.) is the ejection of Compton electrons (average energy *ca.* 440 kev.) which in turn eject electrons of low energies (*ca.* 100 e.v.) which loose their energy in small regions called "hot spots" or "spurs." These spurs are of the order of 1000 Å. apart. With scavenger concentrations of less than about 10^{-3} mole fraction, the only reactions which occur in the spurs are reactions of excited molecules or radicals or ions with the solvent, or reactions between radicals immediately after thermalization and before diffusion. At concentrations of the order of 10^{-3} mole fraction or somewhat higher, the probability of an additive molecule being in the solvent cage with an excited molecule or radical begins to be great enough so that alterations in hot processes may be observed. This has been illustrated by the effects of halogen scavengers on the organic yields of reactions activated by radiative neutron capture,[12,13] the probability for the case of two particle recombinations processes has been discussed and evaluated,[14,15] and observations of such effects have been made in the photolysis of liquid ethyl iodide.[5b]

(12) S. Goldhaber and J. E. Willard, THIS JOURNAL, **74**, 318 (1952).

(13) G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

(14) (a) R. M. Noyes, *ibid.*, **77**, 2042 (1955); (b) **78**, 5486 (1956).

(15) J. C. Roy, R. R. Williams, Jr., and W. H. Hamill, *ibid.*, **76**, 3274 (1954).

(16) The fact that the initial increase in rate of I_2 production caused by added HI is independent of the concentration of added HI and that the initial decrease in rate of I_2 production caused by added I_2 is independent of the concentration of added I_2 over the range tested (Fig. 1) indicates that, within the sensitivity of the experiments, each of these additives affects the rate only by competition with the other for free radicals and not by interfering with some independent process such as the combination of radicals with other radicals or atoms. The latter type of scavenger effect, which is a sensitive function of scavenger concentration, has been observed in other systems.[12,13]

excited ethyl iodide molecules (step 3) which may decompose by step 4 to produce HI or by step 5 to produce hot ethyl radicals which either react by 6 to liberate $^1/_2$ I_2 or are thermalized by 7. Ionic or ion–molecule reactions which led to a constant rate of production of HI, $^1/_2$ I_2 and thermal ethyl radicals could account equally well for the data on the thermal radical reactions investigated in the present work. The reactions listed do not include C–C bond cleavage or elimination of H_2, both of which are minor processes.[4] If C–H bond cleavage occurs, the H atoms probably react with C_2H_5I to form HI, since the activation energy is small[17a] and they must undergo 10^3 or 10^4 collisions with solvent before meeting an HI or I_2 molecule. The recombination of ethyl radicals with iodine atoms in the spurs is not included, since it is not experimentally observable by the techniques used in this work.

Reactions in spurs

$$C_2H_5I \rightsquigarrow \underline{C_2H_5I} \qquad (3)$$

$$\underline{C_2H_5I} \longrightarrow C_2H_4 + HI \qquad (4)$$

$$\underline{C_2H_5I} \longrightarrow \underline{C_2H_5\cdot} + I\cdot \qquad (5)$$

$$\underline{C_2H_5\cdot} + C_2H_5I \longrightarrow C_2H_4 + C_2H_6 + I\cdot \qquad (6)$$

$$\underline{C_2H_5\cdot} + M \longrightarrow C_2H_5\cdot + M \qquad (7)$$

Thermal radical reactions

$$I\cdot + I\cdot \longrightarrow I_2 \qquad (8)$$

$$C_2H_5\cdot + I_2 \xrightarrow{k_{I_2}} C_2H_5I + I\cdot \qquad (9)$$

$$C_2H_5\cdot + HI \xrightarrow{k_{HI}} C_2H_6 + I\cdot \qquad (10)$$

Quantitative Interpretation of HI and I_2 Effects.—On the basis of the above data and reaction scheme, it is possible to derive equations which allow the prediction of the rates of I_2 production, HI production and exchange for any concentration of added HI or I_2. For this purpose we shall let A = rate of production of thermal alkyl radicals which escape from the spurs; B = total[18] rate of production of I_2 by hot processes (reactions 5 and 6); and C = the rate of HI production *via* reaction 4. A, B and C are constants if the energy absorbed per cc. per sec. is constant. Then setting the rate of thermal radical production equal to the rate of removal by reactions 9 and 10

$$A = k_{I_2}[I_2][C_2H_5] + k_{HI}[HI][C_2H_5] = [C_2H_5](k_{I_2}[I_2] + k_{HI}[HI]) \qquad (11)$$

and

$$[C_2H_5] = A/(k_{I_2}[I_2] + k_{HI}[HI]) \qquad (12)$$

The C_2H_5 radicals do not become homogeneously distributed through the solution but in general react with HI or I_2 before they have proceeded far from the radiation tracks.[13] Therefore, the $[C_2H_5]$ term does not represent a homogeneous steady-state concentration in the usual sense but nevertheless does represent the number of radicals per unit volume, when volumes large compared to the distance between the tracks are considered. The treatment is valid because the fate of a radical depends solely on the $[HI]/[I_2]$ ratio and not on the radical concentration, because radical–radical reactions are not involved.[13] The rate of iodine production may then be expressed as

$$d[I_2]/dt = B - (k_{I_2}/2)([I_2][C_2H_5]) + (k_{HI}/2)([HI][C_2H_5]) \qquad (13)$$

The factor of $^1/_2$ is introduced by the use of molar concentrations. After substituting the expression for $[C_2H_5]$ and rearranging this becomes

$$d[I_2]/dt = B + (A/2) - A[[I_2]/([I_2] + (k_{HI}/k_{I_2})[HI])] \qquad (14)$$

Similarly the expressions for the production of HI and the rate of return of iodine to the organic phase (exchange) are

$$d[HI]/dt = C - A + A[[I_2]/([I_2] + (k_{HI}/k_{I_2})[HI])] \qquad (15)$$

$$d[C_2H_5I]_{exch}/dt = A[I_2]/([I_2] + (k_{HI}/k_{I_2})[HI]) \qquad (16)$$

It is a necessary consequence of the stoichiometry of the system, according to our mechanism, that the sum of the moles of HI and I_2 increases at a constant rate regardless of the values of the rate constants k_{HI} and k_{I_2}. Thus, on adding equations 14 and 15 one obtains

$$d([HI] + [I_2])/dt = C + B - A/2 \qquad (17)$$

or

$$([HI] + [I_2]) - ([HI] + [I_2])_0 = (C + B - A/2)t \qquad (18)$$

The experimental data on the initial rates of I_2 production with added I_2 (minimum rate),[19] with added HI (maximum rate), and without additives may be used to evaluate A and B. These rates expressed as microequivalents of product per 5-ml. sample per min., at an energy absorption rate of 3.77×10^{17} e.v./ml. min., are: without additives, 0.0654; maximum, 0.1670; minimum, 0.0353. From equation 14 it may be seen that when HI is in large excess

$$d[I_2]/dt = B + {}^1/_2A = 0.1670 \qquad (19)$$

and when I_2 is in large excess

$$d[I_2]/dt = B - {}^1/_2A = 0.0353 \qquad (20)$$

These equations yield A = 0.1317 μequivalent/min. as the rate of thermal radical production and B = 0.1012 μequivalent/min. as the total rate of iodine production by hot processes, including that which normally back-reacts *via* reaction 9.

The constant C (*i.e.*, the total rate of HI formation including that which back reacts) can be evaluated if it is assumed that the rate constants

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[17] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954, (a) p. 733; (b) pp. 742–743.

[18] The *total* rate of I_2 production by hot processes is the rate of reaction 5 and any hot processes such as (6) which ensue. It includes the rate of production of I_2 which subsequently returns to organic combination by reaction with thermalized ethyl or other radicals. It does not include the formation of I_2 *via* reaction 10. The *net* rate of I_2 production by hot processes is the "total" rate minus that which back reacts with thermal radicals in the presence of excess I_2 scavenger.

[19] If the only possible steps in the radiolysis were those represented by equations 3 through 10, the minimum rate of iodine production observed with added I_2 would be the rate of the sequence of hot reactions 5, 6 since the sequence 5, 7, 9 does not affect I_2 concentration. If, however, any ethyl iodide molecules are dissociated by steps such as $C_2H_5I \rightarrow CH_3 + CH_2I$ or $C_2H_5I \rightarrow C_2H_4I + H$, rather by rupture of a C–I bond, and the fragments then react with I_2, the sequence will consume I_2. The minimum rate is therefore the rate of the sequence 5, 6 minus the rates of any sequences of the latter type. Such sequences do not alter the quantitative treatment presented unless the assumption made below that $k_{I_2} = k_{HI}$ is not valid for them; at most the effect will be small since about 90% of the radicals produced are ethyl radicals.[4,8]

for reactions 9 and 10 (*i.e.*, k_{I_2} and k_{HI}) are equal. This assumption is not unreasonable since the activation energy for each of these processes is near zero[17b] and there are many collisions per encounter in the liquid phase,[20] so that both HI and I_2 may react with ethyl radicals on nearly every encounter. Using this assumption, the following relation, derived from equations 14, 19 and 20, may be evaluated

$$\left(\frac{[HI]}{[I_2]}\right)_{\text{Normal}} = \frac{k_{I_2}(\text{norm. rate} - \text{min. rate})}{k_{HI}(\text{max. rate} - \text{min. rate})} = 0.296 \qquad (21)$$

where the ratio applies to the radiolysis of initially pure ethyl iodide, and the normal, maximum, and minimum rates refer to the radiolysis with no additives, with excess HI, and with excess I_2, respectively. Multiplying this ratio by the iodine production rate for ethyl iodide with no additives gives

$$d[HI]/dt = ([HI]/[I_2])d[I_2]/dt = 0.296 \times 0.0654 = 0.0193\ \mu\text{mole/min.} \qquad (22)$$

Substitution of the value for the HI production rate into equation 15 together with the value of the ratio $[I_2]/([I_2] + [HI])$ for a run with no additives yields the value of C as 0.0493 µmole/minute.

The differential equations for the various rates can now be written

$$d[I_2]/dt = 0.1671 + 0.1317\ [I_2]/([I_2] + [HI]) \qquad (23)$$

$$d[HI]/dt = -0.0824 + 0.1317[I_2]/([I_2] + [HI]) \qquad (24)$$

$$d[HI + I_2]/dt = 0.0847 \qquad (25)$$

$$d[C_2H_5I]_{\text{exch}}/dt = 0.1317\ [I_2]/([I_2] + [HI]) \qquad (26)$$

The approximation $k_{I_2}/k_{HI} = 1$ has been assumed in all the above equations except (25). The equations can be integrated only when this assumption is made; the resulting equations are[21]

$$[I_2] = 0.0654t + 0.772([HI]_0 + [I_2]_0) + (0.228[I_2]_0 - 0.772[HI]_0)\left(1 + \frac{0.0847t}{[HI]_0 + [I_2]_0}\right)^{-1.55} \qquad (27)$$

$$[HI] = 0.0193t + 0.228([HI]_0 + [I_2]_0) + (0.772[HI]_0 - 0.228[I_2]_0)\left(1 + \frac{0.0847t}{[HI]_0 + [I_2]_0}\right)^{-1.55} \qquad (28)$$

$$[HI] + [I_2] = 0.0847t + [HI]_0 + [I_2]_0 \qquad (29)$$

$$[C_2H_5I]_{\text{exch}} = 0.1017t + (0.228[I_2]_0 - 0.772[HI]_0)\left(1 + \frac{0.0847t}{[HI]_0 + [I_2]_0}\right)^{-1.55} \qquad (30)$$

The last equation refers to the quantity of ethyl iodide re-formed by the back reaction, a process which can be observed only when radioiodine is present.

Comparison of Predicted Rates of I_2 and HI Production with Experimental Results.—From Fig. 1 it can be seen that values for the iodine concentration as a function of time of irradiation calculated from equation 27 agree well with the experimentally determined values for all initial concentrations of HI and I_2 tested.[22]

The rate of production of HI during radiolysis is a good test of the assumptions in deriving equations 27–30 since experimental data on HI production were not used in the derivation. In two experiments on ethyl iodide without additives, the $[HI]/[I_2]$ ratio was determined after irradiation by adding radioiodine prior to extraction in the manner described above for the exchange experiments. The values obtained for the HI production rate were 0.018 and 0.019 µmole/min. which can be compared with the predicted value of 0.0193 µmole/min.

These experimental results can be used to solve equation 21 for k_{I_2}/k_{HI}; the values obtained are 0.94 and 0.99. The difference between these values and 0.34 recently reported by Bunbury, Williams and Hamill[5b] for the same radical reactions in the photolysis of C_2H_5I is probably greater than our experimental error. The agreement of the iodine production and exchange rates predicted by equation 27–30 with the experimental results also supports the validity of the conclusion that $k_{I_2}/k_{HI} \cong 1$.

Analysis for HI during the exchange experiments shown in Table I indicated an average HI production rate of 0.037 ± 0.009 µmole/min. Under the same conditions the predicted values range from 0.046 µmole/min. at 5 min. to 0.031 µmole/min. at 60 min., giving an average value of about 0.038. The experimental data do not show any clear trend, since the trend expected is of the same order of magnitude as the experimental error. The reliability of these latter experiments is not good enough to consider the results as proof of the assumption that $k_{I_2} = k_{HI}$, but the results are consistent with this conclusion.

Comparison of Predicted Rate of Exchange with Experimental Results.—The rate of transfer of initially added radioiodine from inorganic to organic form may be expressed as $-d[I^*]/dt = (d[C_2H_5I]_{\text{exch}}/dt)([I^*]/([HI] + 2[I_2]))$ where $d[I^*]/dt$ is the rate at which equivalents of radioiodine are removed from the inorganic phase, $[I^*]/([HI] + 2[I_2])$ is the ratio of equivalents of ratioiodine to total iodine in the inorganic phase (the probability that a given iodine atom encountered by an alkyl radical is radioactive) and $d[C_2H_5I]_{\text{exch}}/dt$ is the total rate of reaction of thermalized ethyl radicals with I_2 from the bulk of the medium. Since $[I^*]$ occurs on both sides of the equation the conversion factor from concentration to counting rate cancels, and $[I^*]$ may be taken as the counting rate of the inorganic phase. It is possible to substitute for these quantities using equation 26 for the total rate of re-formation of ethyl iodide and the integrated equations 27 and

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(20) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1932).

(21) Integrate eq. 25 first and substitute in 23 and 24 giving equations in the variables $[I_2]$ and t only; integrate 23 and 24. Substitute the expressions for $[I_2]$ and $[I_2] + [HI]$ from 23 and 25, respectively, into 26 and integrate.

(22) The values for the initial I_2 concentration used in the calculation of curves G and H of Fig. 1 were those determined by spectrophotometric measurement. The value of the HI concentration used for curve D was accurately determined by using radioiodine of known specific activity. In the experiment shown by curve A, there was a sufficient excess of HI over I_2 to give the maximum rate for the entire experiment, hence knowledge of the exact concentration is not critical. The experimental values of HI added for runs B, C and E were less accurately known because they depended on measuring the *PV* product of about 10^{-5} mole of HI and transferring it quantitatively through the vacuum line. For these cases the values for the initial HI concentration used with equation 27 for the calculations were 10 to 30% different from the experimental values, a choice being made which gave a fit with the data for iodine production. As a result curves B, C and E are only a semi-quantitative verification of the mechanism.

TABLE II

G-VALUES FOR THE RADIOLYSIS OF ALKYL IODIDES WITH AND WITHOUT ADDED HI AND I_2

Iodide	No. of β-H atoms	G_I[a] for I atom production			½(max. − min.),[d] *G* for thermal free radical production	½(max. + min.), *G* for C–I bond cleavage[e]	Predicted ratio of [HI]/[I_2][f]	G_I for thermal contr. to normal rate[g]
		Normal[b]	Max. (HI added)	Min.[c] (I_2 added)				
Methyl	0	2.54	11.74	2.16	4.79	6.96	0.041	0.38
Ethyl	3	4.19	10.68	2.25	4.22	6.46	.296	1.94
n-Propyl	2	3.22	9.82	1.72	4.05	5.76	.227	1.50
Isopropyl	6	6.20	9.48	3.36	3.06	6.42	.866	2.84
n-Butyl	2	3.26	9.30	1.75	3.78	5.52	.250	1.51
Isobutyl	1	1.86	8.88	1.43	3.72	5.16	.061	0.43
sec-Butyl	5	5.00	9.34	2.28	3.53	5.80	.627	2.72

[a] ½ I_2 produced per 100 e.v. absorbed. [b] For alkyl iodides with no HI or I_2 added prior to irradiation. Some of these values are taken from reference 1. [c] Net rate of iodine production by hot processes.[18] [d] The factor ½ is required to convert from G_I to $G_{\text{free radical}}$ because in the presence of excess HI two iodine atoms are formed for each thermal radical, as indicated by equations 5 and 10 of the text. [e] Total rate of production of iodine by hot processes.[18] [f] Given by $(G_{\text{norm}} - G_{\text{min}})/(G_{\text{max}} - G_{\text{min}})$. [g] This column is the value of column 3 minus column 5 and represents the *G* value for the reaction of thermal radicals with HI in the absence of initially added scavengers.

28 for the concentrations of HI and I_2 as a function of the time of radiolysis, but the equation obtained cannot be integrated. (Iodine must be added initially to study the exchange, hence the HI, I_2 and total exchange rates will all vary with the time of irradiation.) By assuming that the various rates are constant over short periods of irradiation and using iterative calculations, the fractional exchange which will be observed over longer periods may be predicted. This calculation was performed using an initial iodine concentration of 8.4 μmoles for comparison with the data in Table I. The results of the calculation are shown by curve A of Fig. 2. The predicted exchange rate averaged over the first 5 minutes was 0.128 and over the first 60 minutes 0.113 μmole/min. The experimental points of curve B of Fig. 2 show that exchange occurred considerably faster than predicted.

The solid line of curve B, which fits the experimental data, was obtained in a semi-empirical manner as follows: the iterative calculations described above were repeated, assuming that there is a constant component to the exchange rate of 0.020 μequivalents/min. which is independent of HI or I_2 concentration, *i.e.*, which is the result of exchange by a "hot" process. Thus the rate over the first 5 minutes was taken to be 0.148 and over the first 60 minutes 0.133 μequivalent/min.; values are given in Table I for comparison with the earlier calculations. It is believed that these numbers represent better values for experimental exchange rates than those calculated from equation 2. The short irradiation values based on the latter are unduly influenced by exchange induced in preparing and analyzing the samples (about 0.5 to 1%) and the long irradiation values are subject to error because equation 2 does not take into account the competition of HI with I_2 for C_2H_5 radicals.

There is no obvious reason why the exchange rate predicted by equation 26 (curve A, Fig. 2) should be in error by as much as 20% unless some step which contributes to exchange but does not affect HI or I_2 concentrations has been omitted from the postulated mechanism. This point of view is strengthened by the fact that the derived equations predict the iodine production rate during the same set of exchange experiments within 1 or 2%. Various speculations as to the basis for the discrepancy are possible. For example, it might be explained if excited ethyl iodide molecules with too little energy to produce radicals have a much higher "rate constant" for undergoing exchange with I_2 than for degradation of the energy in non-reactive collisions with other ethyl iodide molecules.

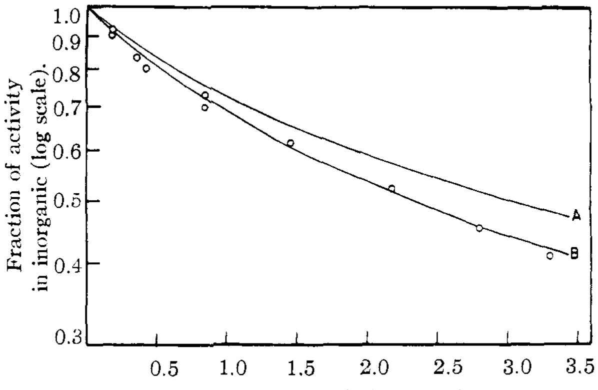

Fig. 2.—Exchange of radioiodine during the radiolysis of ethyl iodide solutions which initially contained about 8.4 × 10^{-4} molar iodine. Points are from experimental data. Curve A was calculated by equation 30; curve B was calculated by a semi-empirical method described in the text.

This hypothesis is attractive because the high energy electrons in the system undoubtedly dissipate much of their energy in producing low lying excited states of ethyl iodide. It might predict a concentration dependence but this would probably be difficult to observe because the excess exchange in only a small fraction of the total exchange yield. If thermal ethyl radicals can abstract I as well as H from HI, the rate of exchange in the presence of HI would be higher than predicted but the increase would be expected to be a function of the [HI]/[I_2] ratio.

Effect of Added HI and I_2 on the Radiolysis of Other Alkyl Iodides.—The data of Table II show that the influence of added HI and I_2 on the radiolysis of six additional alkyl iodides is qualitatively similar to the effect on ethyl iodide but quantitatively different.

Of particular interest is the fact that added iodine appears to reduce the iodine yield from methyl iodide, since this implies that HI is a product of the radiolysis. The effect seems to be greater than can be attributed to experimental error.

According to the discussions above the rate of iodine production in ethyl iodide and presumably in the other alkyl iodides must depend on: (1) the net rate of I_2 production in the spurs; (2) the rate of production of thermal radicals in the spurs; (3) the ratio of HI to I_2 production. The question may be raised as to which of these factors is responsible for the fact that G_{I_2} with no added scavengers increases with increasing number of β-hydrogens in the molecule.[2,23] From Table II it may be seen that the effect is not attributable to the rate of thermal radical production (columns 2 and 6), that the net rate of I_2 production in the spurs does increase with increase in the β-hydrogen content, except in going from C_2H_5I to *sec*-C_4H_9I, (column 5) and that the ratio of thermal radical reaction with HI to reaction with I_2 also increases (column 7). The *G* value for reaction of thermal radicals with HI shows the smoothest increase as a function of the number of β-hydrogens in the molecule (column 8). Column 7 gives the total rate at which iodine is produced in the spurs by reactions 5 and 6, including the iodine which back reacts via the exchange reaction 9. As the carbon chain length of the alkyl iodide increases the number of bonds in the molecule other than the C–I bond increases. As a result of this the rate for C–I bond rupture might be expected to decrease; this was found experimentally. It can also be seen that the secondary iodides (isopropyl and *sec*-butyl) show slightly higher rates of C–I bond rupture than the corresponding primary compounds, which might be expected on the basis of bond strengths.

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(23) E. L. Cochran, W. H. Hamill and R. R. Williams, Jr., THIS JOURNAL, **76**, 2145 (1954).

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The Formation of Thallium Chloride Complexes and their Extraction into Ether[1]

BY DONALD L. HORROCKS AND A. F. VOIGT

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The extraction of thallium(III) chloride into isopropyl ether has been studied using tracer techniques with Tl^{204}. Appreciable extraction occurs under conditions of high acidity, and the extraction is markedly dependent upon the ionic strength of the solution. In order to study the effect of varying acidity and chloride concentration over a wide range, the study was run at rather high ionic strength. The temperature coefficient and heat of extraction were determined in the range of 20–30°. The empirical formula of the extracted species was found to be $HTlCl_4$ and a higher complex, H_2TlCl_5, was found not to be extractable. At low chloride concentrations and low acidity the extraction cannot be explained completely by this mechanism and it is postulated either that $TlCl_3$ extracts or that $HTlCl_4$ ionizes in ether under these conditions.

The extraction of thallium(III) from hydrohalic acids into ether has been reported by several investigators.[2–6] It has been developed into an analytical method for separating thallium from most elements, except iron(III), gallium(III), gold(III), and some others. Aside from noting the optimum conditions for complete extraction of the thallium, no investigations of the nature of the extraction process have been made. This research was undertaken to obtain information about the thallium compound present in the ether phase, the dependence of the extraction upon the concentrations of acid and chloride, the temperature coefficient of the extraction and the extraction equilibrium constant. These should be of interest in comparison with the analogous Fe(III) which has been shown to extract into ether as $HFeCl_4$.[7]

Preliminary investigations of the extraction of thallium(III) from $HClO_4$–LiCl–$LiClO_4$ solutions into isopropyl ether showed appreciable extraction only at relatively high acid and chloride concentrations and also showed that the extraction depends very markedly upon the ionic strength. It was thus necessary to perform the investigations in solutions of constant, high ionic strength. On the other hand the sensitivity of the tracer method made it possible to do the experiments at low concentration, about 10^{-3} *M*, of thallium.

The results of these conditions was that the determination of the activity coefficients of the various ionic species was difficult, but not as difficult as it would have been at higher thallium concentrations. In estimating activity coefficients it was necessary to make some assumptions which may not be completely valid.

The distribution of thallium between phases was measured by tracer techniques over a range of

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(1) Based in part on a thesis presented by Donald L. Horrocks to Iowa State College in partial fulfillment of the requirements for the Ph.D. degree, November, 1955.

(2) Rothe, *Stahl und Eisen*, **12**, 1052 (1892); **13**, 333 (1893).

(3) (a) A. A. Noyes, W. C. Bray and E. B. Spear, THIS JOURNAL, **30**, 489, 515, 559 (1908); (b) E. H. Swift, *ibid.*, **46**, 2375 (1924).

(4) I. Wada and R. Ishii, *Bull. Inst. Phys. Chem. Res. Tokyo*, **13**, 264 (1934); [*C. A.*, **28**, 3334 (1934)].

(5) H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

(6) H. M. Irving and F. J. C. Rossottl, *Analyst*, **77**, 801 (1952).

(7) N. H. Nachtrieb and J. C. Conway, THIS JOURNAL, **70**, 3547 (1948).