[Contribution from the Department of Chemistry, University of Notre Dame]

Diffusion Kinetics of Atom-Radical Recombination in Radiative Neutron Capture by Halogens in Liquid Alkyl Halides[1]

By J. C. Roy, R. R. Williams, Jr., and W. H. Hamill

Received February 20, 1954

The effects of added halogens and haloölefins have been measured upon distribution of halogen radioactivity between organic and inorganic components following neutron capture in some alkyl halides. A simple, approximate treatment of atom-radical dissociation–recombination by diffusion is proposed to explain these effects. It is postulated that each nuclear process produces *effectively* one atom–radical pair and decreased recombination due to added halogen results from competition with diffusion controlled recombination. A different type of mechanism is proposed to account for the effects of added haloölefins in liquid alkyl halides since the olefins are effective at mole fractions 10^{-7}–10^{-4} compared to 10^{-4}–10^{-2} for halogens. For ethyl bromide–dibromoethylene the competing reactions would be: $C_2H_2Br_2 + Br^* \rightarrow C_2H_2BrBr^* + Br$; $C_2H_5Br + Br^* \rightarrow C_2H_4Br + HBr^*$. The results indicate an activation energy difference of *ca.* 11 kcal.

Introduction

Several recent studies[2-7] demonstrate marked effects upon the chemical processes which follow thermal neutron capture for small additions of various solutes and a variety of explanations have been proposed[2,4-6,8,9] to account for such effects. This report describes additional experiments, mostly with systems of liquid ethyl bromide and ethyl iodide, to measure more carefully some of these effects and proposes a simple treatment.

This work is not concerned with hot atom effects as such and it is assumed that the portion of the total halogen activity produced which responds to small amounts of additives represents radioactive atoms of thermal energies. Designating the organic yield in pure liquid halide by A_0, the asymptotic limits with added haloölefin by $A_{\max}$ and with added halogen by $A_{\min}$, and any intermediate value by A one distinguishes two additional sub-classes of radioactive atoms (Fig. 1). The radioactive thermal atoms, X^*, corresponding to $A_0 - A_{\min}$ are considered to combine with organic radicals; in the pure liquid those corresponding to $A_{\max} - A_0$ are considered to remain in the inorganic fraction in the pure liquid either because the organic radicals are otherwise removed or because X^* enters stable inorganic combination. It will appear later that for the systems being considered one may postulate that each nuclear process produces *effectively* one atom-radical pair and that the component of activity $A_0 - A_{\min}$ in the pure liquid results from diffusion controlled recombination, as described by Noyes.[10] Added free halogen would then be regarded as competing with X^* for the organic radical. The treatment here proposed for such systems is adapted from one recently developed by Samuels and Magee[11] for diffusion controlled recombination of several atom-radical pairs produced within a small initial volume.

Consider a large number of replicas of a system immediately subsequent to a valence bond rupture by a dissociative process. Let the initial mean separation of the two recombining particles be $\bar{R}_0$, any subsequent net displacement by diffusion R at time t, the relative velocity v, the collision cross section $\sigma = \pi d^2$, the assumed Gaussian particle distribution $\phi(R)$ and the probability of recombination by diffusion W. The probability of finding both particles in a differential spherical annulus $\mathrm{d}V$ is $2\phi^2(\mathrm{d}V)^2$ and the probability of their colliding is $\sigma v/(\mathrm{d}V/\mathrm{d}t)$ times as great.

For the ensemble of systems in which the fraction W of recombinations have occurred the rate of recombination over all R becomes

$$(1 - W)^{-1}\,\mathrm{d}W/\mathrm{d}t = P_1\sigma v \int_0^\infty \phi^2 4\pi R^2 \mathrm{d}R \equiv f(R) \quad (1)$$

where

$$\phi(R) = \pi^{-1.5}\bar{R}^{-3}\exp(-R^2/\bar{R}^2) \quad (2)$$

and P_1 is the probability of recombination during an encounter or set of collisions.[12] The effect of an added solute which is capable of reacting with a recombining particle is introduced by the approximation that $1 - W$ is diminished at each displacement by a factor $1 - P_2X$ where X is mole fraction of solute and P_2 is the probability of reaction per encounter. The exaggeration of solute reaction so introduced can be minimized later by confining analysis to small X. Since the number of displacements n is vtL^{-1}, where L is the mean free path, the ultimate extent of recombination within the diffusion sphere is given by

$$\int_{W_0}^{W_\infty} \mathrm{d}W(X)/(1 - W(X)) = \int_0^\infty (1 - P_2X)^{vt/L} f(\bar{R})\mathrm{d}t \quad (3)$$

The initial separation is accounted for by the fiction of equivalent diffusion in time τ, *i.e.*, $n_0 = v\tau L^{-1}$. The integral of equation 3 after some minor approximations is

$$\ln \frac{1 - W_0(X)}{1 - W_\infty(X)} = \frac{\sigma P_1}{\pi L^2(2\pi n_0)^{1/2}}\left[\frac{1 - (\pi n_0 P_2 X)^{1/2} + n_0P_2X}{1 - n_0P_2X}\right] \quad (4)$$

---

[1] From the doctoral dissertation of Jean-Claude Roy, University of Notre Dame, June, 1954.

[2] W. H. Hamill and R. R. Williams, Jr., *J. Chem. Phys.*, **22**, 53 (1954).

[3] F. S. Rowland and W. F. Libby, *ibid.*, **21**, 1495 (1953).

[4] J. M. Miller and R. W. Dodson, *ibid.*, **18**, 865 (1950).

[5] S. Goldhaber and J. E. Willard, This Journal, **74**, 318 (1952).

[6] G. Levey and J. E. Willard, *ibid.*, **74**, 6161 (1952).

[7] R. R. Williams, Jr., W. H. Hamill, H. A. Schwarz and E. J. Burrell, *ibid.*, **74**, 5737 (1952).

[8] W. F. Libby, *ibid.*, **69**, 2523 (1947); M. S. Fox and W. F. Libby, *J. Chem. Phys.*, **20**, 487 (1952).

[9] W. H. Hamill, R. R. Williams, Jr., H. A. Schwarz and E. E. Voiland, AECU-1321, Technical Information Service, Oak Ridge, Tennessee.

[10] (a) R. M. Noyes, *J. Chem. Phys.*, **18**, 999 (1950); (b) private communication, to be published.

[11] A. H. Samuels and J. L. Magee, *ibid.*, **21**, 1080 (1953); A. H. Samuels, Ph.D. dissertation, University of Notre Dame, June, 1953.

[12] E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 1225 (1937).

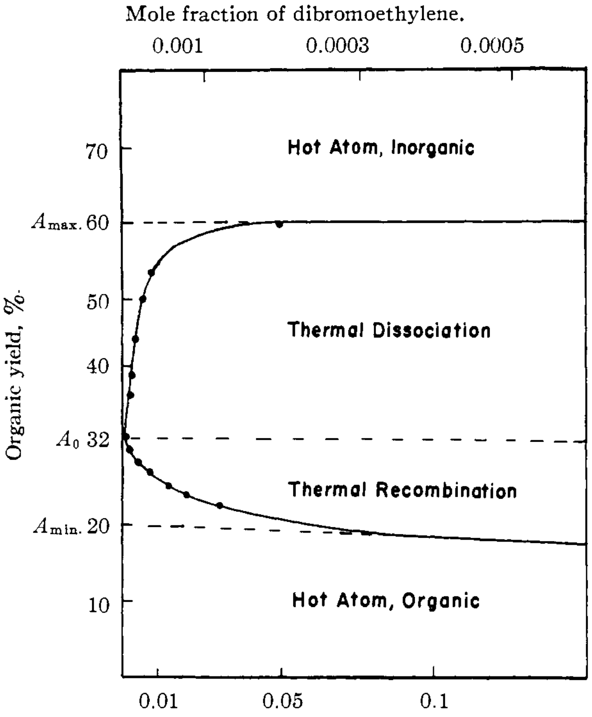

Fig. 1.—Organic yield of Br^{80} for ethyl bromide with solute at 0°: upper curve, with dibromoethylene; lower curve, with bromine.

The factor of the term in brackets, $g(X)$, is evidently

$$\ln\,(1 - W_0(0))/(1 - W_\infty(0))$$

For $W_0 = 0$, we have

$$\lambda_1(W) \equiv \ln(1 - W_\infty(X))/\ln(1 - W_\infty(0)) = g(X) \quad (5)$$

At small X

$$g(X) \cong 1 - (\pi n_0 P_2 X)^{1/2}$$

and a plot of $\lambda_1(W)$ *vs.* $X^{1/2}$ yields a tentative value of n_0P_2 from the limiting slope. Rearranging 5 and inserting the trial value of n_0P_2 we finally obtain

$$\lambda_2(W) \equiv (1 + n_0P_2X) - (1 - n_0P_2X)\lambda_1(W) = (\pi n_0 P_2 X)^{1/2} \quad (6)$$

which is employed to interpret the present experiments. In this application it is considered that (see Fig. 1)

$$W_\infty(X) = (A - A_{\min})/(A_{\max} - A_{\min})$$

and that

$$W_\infty(0) = (A_0 - A_{\min})/(A_{\max} - A_{\min})$$

According to Williamson and LaMer[13] the effect of collision sets upon reaction probability, P_r, during an encounter is given by

$$P_r = \frac{A_r\exp(-E_r/RT)}{A_r\exp(-E_r/RT) + A_d\exp(-E_d/RT)} \quad (7)$$

where subscripts r and d refer to reaction and diffusion.

The predicted dependence of W upon X for equation 6 appears in Fig. 2 for several values of the parameters. It is clear that if any appreciable activation energy is required for recombination, then conventional steady state kinetics will apply; similarly, unless the diffusing particle is capable of reacting with solute very efficiently it will not be possible to demonstrate the effect under consideration. When $P_1 \cong 1$ and $P_2 \cong 1$ it is seen (Fig. 2) that 50% efficiency of solute occurs typically at $X \cong 10^{-3}$.

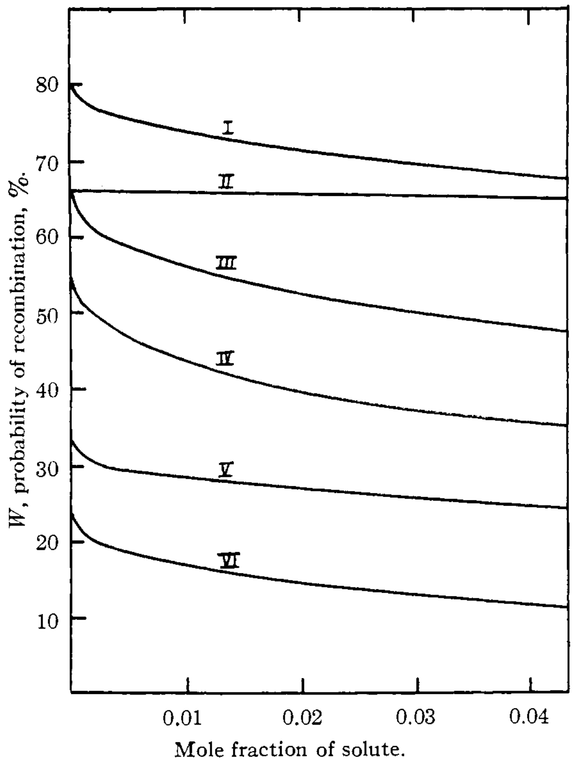

Fig. 2.—The predicted dependence by equation 4 of W, the probability of recombination, upon the mole fraction of solute for various values of the parameters: I, $P_2 = 1$; $L = \bar{R}_0 = 0.5d$; II, $P_2 = 0.1$; $L = 0.5d$, $\bar{R}_0 = 0.75d$; III, $P_2 = 1$; $L = 0.5d$, $\bar{R}_0 = 0.75d$; IV, $P_2 = 1$; $2L = \bar{R}_0 = d$; V, $P_2 = 1$; $L = \bar{R}_0 = d$; VI, $P_2 = 1$; $L = d$, $\bar{R}_0 = 1.5d$.

Experimental

Purification of Reagents.—Ethyl iodide was purified in the early experiments substantially according to the methods of Goldhaber and Willard.[5] For all work with added solutes, preliminary purification was followed by addition of a small amount of free bromine and illumination for several hours with a tungsten lamp. After appropriate washing and drying it was distilled at 20:1 reflux ratio in a 3-foot column packed with glass helices. Ethyl bromide was purified by ozonization,[5] washing, drying and fractional distillation. Eastman C.P. grade of α,β-dibromoethylene was used as received after demonstrating absence of impurities which could add radioactive bromine in the dark.[7] J. T. Baker reagent grade bromine and iodine were used as received.

Neutron Irradiation.—All neutron irradiations were performed with a 300-mg. Ra-Be source with a total neutron intensity of *ca.* 10^6 sec.$^{-1}$ Early runs were performed in open soft glass or fused quartz tubes but all later measurements involving temperature effects were performed with the sample in the annulus of a quartz tube and the source in the central well. In order to obtain reliable measurements of temperature dependence it was necessary to use every precaution to reproduce all experimental conditions, other than temperature. High and low temperature runs of ethyl iodide–iodine (−78°, 25°), ethyl bromide–bromine

---

(13) B. Williamson and V. K. LaMer, THIS JOURNAL, **70**, 717 (1952).

(−78°, 0°) and ethyl bromide–dibromoethylene (0°, 25°) were performed with aliquot portions at each concentration. In solutions with added free halogen additional runs were also made at the higher temperature. Temperature was controlled by placing the sample being irradiated in a Dewar flask with water and ice or Dry Ice and acetone.

Extraction and Counting.—Additional free halogen was added to the solution in all runs following irradiation and part of this solution was counted in a liquid sample type Geiger counter with an annular jacket. The rest of the irradiated sample was extracted with dilute sulfite-halide solution and the organic layer counted as before. Corrections for background, decay and coincidence were applied. The small Br^{80} (4.4 hr.) activity produced during 15 min. irradiations was allowed for in measuring Br^{80} (18 min.) activity after transient equilibrium was reached.

Miscellaneous.—Very dilute solutions were prepared by repeated dilution of more concentrated solutions. Liquid solutes were measured in micro-pipets; iodine was weighed. Solvents were measured by volume.

In three runs at 25° with ethyl iodide in a quartz tube containing a little mercury the sample was degassed by repeated evacuation, then sealed and illuminated at 2537 Å. until a deep iodine color was produced in order to scavenge any residual oxygen. Iodine was then removed by shaking with the mercury. The average yield, $A_0 = 0.389$, was not significantly different from otherwise similar runs in air. All subsequent runs were made with solutions exposed to air.

Iodine-131 was obtained by allocation of the AEC from Carbon and Carbide Chemicals Corp., Oak Ridge, Tenn.

Results and Discussion

The results obtained in this work for the organic yields in ethyl iodide, with and without addition of iodine, differ slightly from those of Willard and coworkers.[5,6] Treatment of ethyl iodide with sulfuric acid alone led to an organic yield of 0.400 with an average deviation of ±0.004. Additional treatment with bromine changed these results to 0.386 and ±0.002, respectively. Further tests were made at 5×10^{-4} M iodine, containing I^{131}. Purified ethyl iodide, not treated with bromine, exchanged *ca.* 1% in the dark at 25° after one hour, with little or no exchange thereafter. Purified ethyl iodide also treated with bromine gave 0.0% exchange under similar conditions. The impurities most likely to increase retention are certain haloolefins[7]; Sibbett and Noyes[14] have just shown that allyl iodide and iodine atoms exchange very efficiently. Measurements reported below demonstrate that minute additions of this reagent to alkyl iodides prior to neutron irradiation greatly increase the organic yield of I^{128}. Treatment with bromine presumably eliminates such impurities. Unlike ethyl iodide, ethyl bromide appeared never to be quite free of similar impurities even after prolonged photobromination and limiting values of A_0 were obtained by adding a little bromine ($X \simeq 10^{-5}$).

The results obtained in this work for systems with added free halogen are qualitatively similar to earlier measurements of this type[2-7] in that 50% of the maximum possible decrease in organic yield is attained by adding *ca.* 3×10^{-3} mole fraction of solute. Allyl iodide in ethyl iodide and α,β-dibromoethylene in ethyl bromide, however, produce the corresponding increase at *ca.* 10^{-5} mole fraction and attain limiting yields at *ca.* 10^{-4} mole fraction. The former results can be understood in terms of recombination by equation 8.

$$R + X^* \longrightarrow RX^* \qquad (8)$$

within a short diffusion path; added halogen competes by reaction[15] 9.

$$R + X_2 \longrightarrow RX + X \qquad (9)$$

Unless X_2 intervenes before R undergoes *ca.* 10^3 encounters its effect will be negligible.[10] Since E_{act} for reaction 9 is probably less than E_{act} for diffusion, then by equation 7 nearly every encounter should be effective and 10^{-3} is the approximate lowest mole fraction of halogen which could produce an appreciable effect upon recombination. This agrees well with experiment. Since added olefins exert a considerable effect at concentrations well below this limiting value but exhibit no effect at 10^{-3}–10^{-2} mole fraction, although they are known to exchange with X* with very low activation energy[7,16] it is very improbable that they are competing with diffusion controlled recombinations, such as reaction 10, which presumably define the ultimate inorganic yield.

$$R + R \longrightarrow R_2 \qquad (10)$$

Because the present evidence is contrary to any such reaction it follows that each elementary reaction system contains *effectively* just one atom-radical pair. Earlier discussions of the chemical consequences of neutron capture in liquids have postulated large local concentrations of molecular fragments[6,8] and it is indeed unexpected to find the contrary in these systems. It is interesting that the addition of 10^{-3} to 10^{-2} mole fraction of allyl chloride to carbon tetrachloride[2] prior to neutron bombardment increases the organic yield while similar additions of chlorine decrease it but, unlike the present work, smaller concentrations of allyl chloride are quite ineffective. The reaction kinetics of chlorine with allyl chloride are not known and it does not necessarily follow that reaction 10 is to be inferred.

In the system ethyl bromide–α,β-dibromethylene it is likely that Br* which escapes recombination by reaction 8 will produce HBr*, barring intervention by a solute, in preference to reaction with other atoms or free radicals. This would be consistent with the generally observed independence of organic yield upon gamma flux. Small additions of haloölefin would tend to enhance the organic yield by exchange. If, then, we postulate the competition between reactions 11 and 12

$$C_2H_5Br + Br^* \longrightarrow C_2H_4Br + HBr^* \qquad (11)$$

$$C_2H_2Br_2 + Br^* \longrightarrow C_2H_2BrBr^* + Br \qquad (12)$$

for times long compared to diffusive recombination, it follows that

$$\frac{\text{rate (11)}}{\text{rate (12)}} = \frac{k_{11}(C_2H_5Br)}{k_{12}(C_2H_2Br_2)}$$

The results of this series of measurements, Fig. 3 lowest curve, are seen to conform adequately with this description. Additional partial evidence of the

---

[14] D. J. Sibbett and R. M. Noyes, This Journal, **75**, 763 (1953).

[15] Although added halogen certainly lowers the probability of recombination by exchange with X*, the effect will be treated, for simplicity, in terms of eq. 9 only.

[16] Sibbett and Noyes, ref. 14, found that the rate of exchange of iodine atoms with allyl iodide was 1/16 of that with iodine; previous work in these laboratories (*cf.* ref. 7) agreed with H. Steinmetz and R. M. Noyes, This Journal, **74**, 4141 (1952), that the rate constant for exchange of bromine atoms with α,β-dibromoethylene was 1/3 of that with bromine at 35°.

competitive character of the reactions in such systems was obtained from runs with solutions containing both bromine and α,β-dibromoethylene, reported in Table I.

TABLE I

EFFECTS OF COMBINED ADDITION OF Br_2 AND $C_2H_2Br_2$ TO C_2H_5Br AT 0°

N_{Br_2}	5×10^{-5}	5×10^{-4}	5×10^{-3}
$N_{C_2H_2Br_2}$	1.5×10^{-4}	1.5×10^{-4}	1.5×10^{-4}
$A_{obsd.}$	0.570	0.410	0.286
$A_{calcd.}$ (for same Br_2, no $C_2H_2Br_2$)	.310	.300	.280
$A_{calcd.}$ (for same $C_2H_2Br_2$, no Br_2)	.60	.60	.60

From the approximation $k_{11}/k_{12} \simeq \exp(E_{11} - E_{12})/RT$ and the slope of the lowest curve, Fig. 3, we find $E_{11} - E_{12} \simeq 8$ kcal. Finally, with four aliquot portions of a solution of dibromoethylene in ethyl bromide ($X = 4.5 \times 10^{-5}$) the measured organic yields were 0.495 and 0.435 at 25°, 0.572 and 0.540 at 0°; $E_{11} - E_{12} \simeq 11$ kcal. Considering the uncertainty of the measurements, which is characteristic of very dilute solutions of dibromoethylene and of allyl iodide, these values support the proposed mechanism.

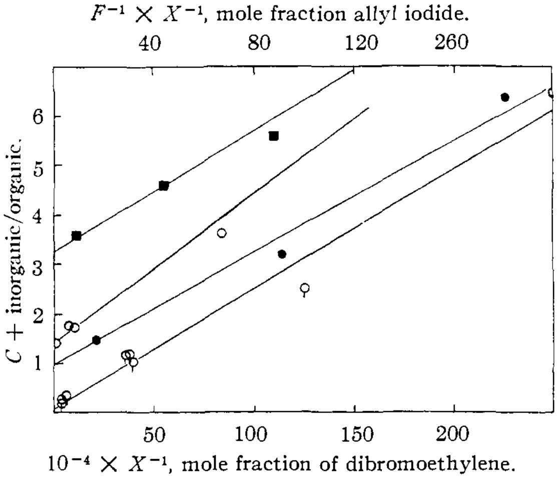

Fig. 3.—Ratio of (inorganic yield)/(organic yield) *vs.* mole fraction of haloölefin, lower scale of abscissas; flagged circles, ethyl bromide solvent, dibromoethylene solute at 0°, $C = 0$; upper scale of abscissas; solid circles, *n*-butyl iodide solvent, allyl iodide solute, $C = 1$, $F = 25$; open circles, ethyl iodide solvent, allyl iodide solute at 25°, $C = 1$, $F = 10^3$; squares, methyl iodide solvent, allyl iodide solute at 0°, $C = 3$, $F = 2 \times 10^3$.

The measured distributions of radiohalogen between organic and inorganic fractions as a function of added free halogen are represented in Table II and in Figs. 1, 4, 5. Additional similar measurements from the recent literature have also been employed except that in Fig. 5 the calculations for butyl iodide have been based upon our own lower value of A_0. The ability of equation 6 to describe these various results is qualitatively demonstrated by the linearity of $\lambda_2(W)$ *vs.* $X^{1/2}$ in Figs. 4, 5. The values of the parameters are, of course, rather more

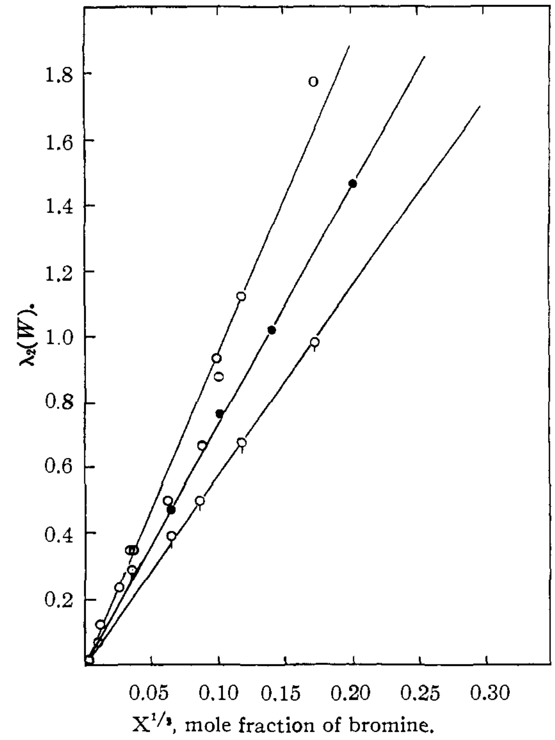

Fig. 4.—Test of equation 6 for alkyl bromides with added bromine: upper curve, ethyl bromide, 0°; middle curve, propyl bromide, 25°; lower curve, ethyl bromide, −78°.

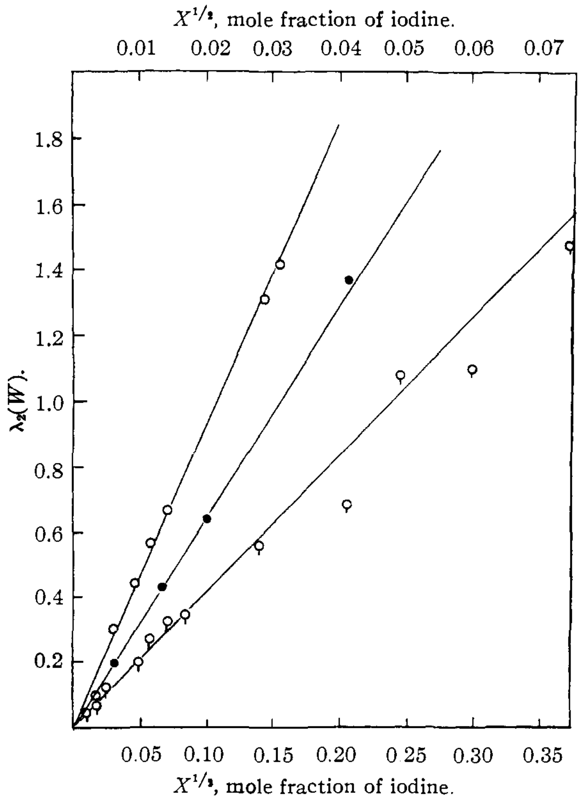

Fig. 5.—Test of equation 6 for alkyl iodides with added iodine at 25°: lower scale, open circles, methyl iodide; solid circles, *n*-butyl iodide; upper scale, flagged circles ethyl iodide.

TABLE II

INTERPRETATION OF EFFECTS OF ADDED SOLUTES

Substance	Temp., °C.	A_0	10^2 $A_{\min}$	$A_{\max}$	Slope	Intercept	ρ_0	γ
C_2H_5I	20	38.6	25	70	20	0.35	3.6	0.32
	−78	37.0	25					
C_2H_5Br	0	31.8	20	60	9.4	.35	2.5	.47
	−78	34.5	20	60	5.7	.45	1.7	.54
n-C_3H_7Br[a]	25	34.0	22	60	7.2	.38	2.1	.51
n-C_4H_9I[b]	20	37.0	25	56	6.4	.49	1.7	.47
CH_3I[b]	0	56.0	36	95	9.2	.42	2.3	.43
	−46	57.5		95				

[a] Data of Rowland and Libby, ref. 3. [b] Data on the effects of free halogen on the retention were taken from the work of Levey and Willard, ref. 6.

significant. To simplify this evaluation let it be assumed that $P_1 = P_2 = 1$, replace $n_0^{1/2}$ by $\bar{R}_0/L$ and employ the reduced parameters $\rho_0 = \bar{R}_0/d$, $\gamma = L/d$. From the preceding considerations it follows that

$$-\ln(1 - W_\infty(0)) = -\ln(A_{\max} - A_0)/(A_{\max} - A_{\min}) = (\sqrt{2}\pi\rho_0\gamma)^{-1}$$

Combining these results with the slopes of Figs. 4, 5, *viz.* $\sqrt{\pi}\rho_0/\gamma$ we obtain the values of the reduced parameters which are listed in the last two columns of Table II. In view of the uncertainties involved the range of values obtained for the initial separation and mean free path are quite gratifying. It is clearly desirable to test the preceding diffusion equation in a more nearly appropriate system where there is less uncertainty regarding the initial act. Suitable data are, unfortunately, scarce and such a test has thus far been completed only for the photolysis of tribromide ion with bromide ion as the solute[17] and Mn(II) as scavenger.

The primary process is

$$Br_3^- + h\nu \longrightarrow Br_2^- + Br$$

and the effect of the solute in preventing recombination is probably

$$Br + Br^- \longrightarrow Br_2^-$$

followed by

$$Mn(II) + Br_2^- \longrightarrow Mn(III) + 2Br^-$$

We find for this reaction $\rho_0 \simeq 0.6$, $\gamma \simeq 0.5$. Details of this and other related work will be published.

Acknowledgments.—The authors wish to thank Dr. C. E. McCauley for helpful discussions and Dr. R. M. Noyes for his detailed criticism of this paper. This research was supported in part by the AEC under contract At(11-1)-38.

[17] A. C. Rutenberg and H. Taube, THIS JOURNAL, **73**, 4426 (1951).

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Kinetics of Reactions between Neptunium Ions. The Neptunium(IV)–Neptunium(VI) Reaction in Perchlorate Solution

BY J. C. HINDMAN, J. C. SULLIVAN AND DONALD COHEN

RECEIVED JANUARY 14, 1954

An investigation of the mechanism of the reaction Np(IV) + Np(VI) $\rightleftarrows$ 2Np(V) has been undertaken in perchlorate media. The rate law for the forward reaction is given by: $-\,d(Np^{+4})/dt = k_1^0[Np^{+4}][NpO_2^{++}][H^+]^{-2}$. At 25° and $\mu = 2.00$, k_1^0 is 2.69 mole l.$^{-1}$ min.$^{-1}$; ΔH^* is 24.6 kcal.; ΔS^* is 17.8 cal./deg. and ΔF^* is 19.3 kcal. At 25° and $\mu = 1.00$, k_1^0 is 3.13 mole l.$^{-1}$ min.$^{-1}$. The effect of ionic strength has been measured. Two alternative mechanisms for the reaction are postulated.

Few quantitative investigations have been made of the kinetics of reactions in which neptunium ions participate. Huizenga and Magnusson[1] have reported that the oxidation of Np^{+4}(aq.) by Fe^{+3} (aq.) appears to proceed by a mechanism involving a hydrolyzed species of neptunium(IV). The exchange reaction between Np^{+4}(aq.) and NpO_2^+ (aq.) has been found to be a complex reaction involving two different paths depending on the acid concentration range.[2] Although the disproportionation reaction of neptunium(V) to give neptunium(IV) and -(VI) has been reported[3] at high acid, the experimental conditions make it difficult to interpret the results in any detail. To further extend our information in this field, the investigation of the reaction between Np^{+4}(aq.) and NpO_2^{++}(aq.) was undertaken. Details of this investigation are reported in the present communication.

Experimental

The neptunium stock solutions in perchloric acid were prepared electrolytically from a neptunium(V) stock in perchloric acid according to previously described methods.[4] The reaction solutions were prepared volumetrically using standardized solutions of sodium perchlorate, perchloric acid and neptunium(IV). A two-centimeter silica absorption cell was used for the reaction vessel. After spectrophotometric measurement of the density of the neptunium(IV) band at 724 mμ[3] to give a value for the initial optical density, the neptunium(VI) was added. The progress of the reaction was followed by monitoring the neptunium (IV) band at 724 mμ. Small corrections were made for the absorption of the neptunium(V) produced in the reaction. The temperature in the thermostatic cell compartment of the Cary recording spectrophotometer was maintained to ±0.1°.

The acid concentration in the reaction solution was checked after completion of the reaction by titration with standard alkali.[2]

Results and Discussion

Effect of Metal Ion.—The stoichiometry of the reaction with respect to each of the metal ions was determined by experiments in which the concentra-

---

[1] J. R. Huizenga and L. B. Magnusson, THIS JOURNAL, **73**, 3202 (1951).

[2] J. C. Sullivan, D. Cohen and J. C. Hindman, *ibid.*, in press (1954).

[3] R. Sjoblom and J. C. Hindman, *ibid.*, **73**, 1744 (1951).

[4] D. Cohen and J. C. Hindman, *ibid.*, **74**, 4679, 4682 (1952).