
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office) (© Copyright, 1961, by the American Chemical Society)

VOLUME 83

JUNE 19, 1961

NUMBER 11

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF COLUMBIA UNIVERSITY, NEW YORK, N. Y., AND OF THE UNIVERSITY OF OREGON, EUGENE, OREGON]

Effects of Substituents on the Radical Exchange Reaction between Benzyl Iodide and Iodine

BY IRWIN J. GARDNER¹ AND RICHARD M. NOYES²

RECEIVED DECEMBER 5, 1960

The previously unknown compounds *p*-nitro, *p*-methyl and *p*-methoxybenzyl iodide have been prepared. The *p*-methoxy compound decomposes rapidly in the presence of iodine, but the exchange of elementary iodine with the other two compounds and with unsubstituted benzyl iodide has been studied photochemically in ethylene dichloride. The exchange mechanisms are entirely free radical and apparently involve comparable contributions from a direct substitution by iodine atoms and from the abstraction of iodine to form benzyl radicals, although the direct substitution reaction is not established with certainty. Electron-withdrawing substituents accelerate the radical abstraction of iodine, but they slow the abstraction of benzylic hydrogen. Apparently electron withdrawal facilitates radical abstraction of a group that would tend to ionize as a negative entity and depresses radical abstraction of a group that would tend to ionize as a positive entity. In air saturated ethylene dichloride at 30°, oxygen and $1.4 \times 10^{-4} M$ iodine compete for benzyl radicals with about equal efficiency.

Introduction

At room temperature, benzyl iodide exchanges photochemically with elementary iodine.³ All of the kinetic evidence indicates that free radical processes are responsible for the reaction and that at least a major contributing mechanism involves the formation of benzyl radicals by attack of iodine atoms on benzyl iodide molecules.

The original study left two questions about this reaction unanswered. (1) How is the rate affected by substituents on the benzene ring? (2) To what extent does exchange involve direct substitution by iodine atoms without intermediate formation of benzyl radicals? The present investigation was undertaken to provide answers to these questions.

Effects of Aromatic Substituents on Radical Reactions.—It has long been known that different substituents can profoundly affect the rates and equilibria of reactions of aromatic compounds. For non-radical reactions, these effects can be rationalized well in terms of the abilities of dif-

ferent groups to donate or withdraw electrons by induction and resonance.⁴ It has even been possible to assign to each group at a particular position a measure of its ability to accept or donate electrons.⁵ For a specific reaction, the importance of electron density can be determined empirically by measuring rates with a few substituents, and the rates with other substituents can be estimated with considerable confidence. The treatment is not always simple when resonance effects are important, but electron-donating and electron-withdrawing substituents invariably affect rates in opposite directions.

The situation with regard to radical reactions is confused. Jaffé⁶ reported over twenty radical reactions whose rates satisfy the Hammett⁵ equation reasonably well. The majority (including dissociations, induced decompositions and abstractions of non-aromatic hydrogen atoms) had negative ρ values indicating that the rates were increased by electron-donating substituents. Small positive ρ values for some copolymerizations indicated an increase by electron-withdrawing substituents, the magnitude of the effect being less than for the

(1) Esso Research and Engineering Company, Linden, N. J. Based in part on the Ph.D. Dissertation of Irwin J. Gardner. The original dissertation and microfilms thereof are available from the Library of Columbia University.

(2) To whom inquiries should be sent: Department of Chemistry, University of Oregon, Eugene, Oregon.

(3) M. Gazith and R. M. Noyes, *J. Am. Chem. Soc.*, **77**, 6091 (1955).

(4) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, New York, 1953, Chapter VI.

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, N. Y., 1940, Chapter VII.

(6) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

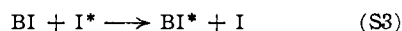
ionization of benzoic acid. An autoxidation reaction and a decomposition of an iodine(III) ester had positive ρ values greater than unity.

Although many radical reactions fit the sort of pattern observed with polar reactions, there are exceptions. Thus both electron-donating and electron-withdrawing substituents increase the degree of dissociation of hexa-arylethanes.⁷ Similarly, both Hey,⁸ *et al.*, and Dannley,⁹ *et al.*, report that both electron-donating and electron-withdrawing substituents increase the reactivity of aromatic compounds with phenyl radicals.

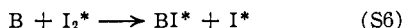
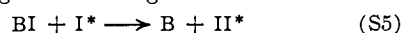
It is clearly desirable to obtain more information to aid the development of a pattern for substituent effects in aromatic radical reactions.

Direct Substitution and Abstraction Exchange Mechanisms.—Let a solution contain a substituted or unsubstituted benzyl iodide, BI, and isotopically labelled elementary iodine, and let it be illuminated by light that is capable of dissociating the absorbing species.

Isotopic exchange can arise in principle from either or both of two mechanisms. There can be a direct substitution of iodine by an elementary process



There can also be abstraction of iodine to form a carbon radical intermediate that undergoes a second step completing the exchange.



In these equations, the asterisks denote iodine atoms initially present in the element.

If chains are long, the rates of steps (S5) and (S6) are equal, and the two mechanisms exhibit identical kinetics. However, oxygen in the system can react with benzyl radicals so as to inhibit step (S6). If it can be demonstrated that oxygen is so efficient that it can completely inhibit exchange by the carbon radical mechanism, any residual exchange that is not influenced by oxygen concentration will presumably go by the direct substitution step (S3). Hence the extent of exchange uninhibited by oxygen can be used to answer the second of the questions posed above.

Formulation of Problem

Absorption of Light.—If a monochromatic beam of intensity I_0 einsteins/cm.² sec. falls upon a solution of thickness L cm. and if only benzyl iodide and iodine absorb at this wave length, the change of intensity with distance is given by

$$-\frac{dI}{dx} = (\alpha_{\text{I}_2}[\text{I}_2] + \alpha_{\text{BI}}[\text{BI}])I \quad (1)$$

where the α 's refer to specific absorbing species. Let

$$f = \frac{1 - e^{-(\alpha_{\text{I}_2}[\text{I}_2] + \alpha_{\text{BI}}[\text{BI}])L}}{(\alpha_{\text{I}_2}[\text{I}_2] + \alpha_{\text{BI}}[\text{BI}])L} \quad (2)$$

(7) M. F. Roy and C. S. Marvel, *J. Am. Chem. Soc.*, **59**, 2622 (1937); F. L. Allen and S. Sugden, *J. Chem. Soc.*, 440 (1936).

(8) D. R. Augood, D. H. Hey and G. H. Williams, *J. Chem. Soc.*, 2094 (1952); D. H. Hey, B. W. Pengilly and G. H. Williams, *ibid.*, 6 (1955).

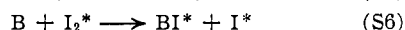
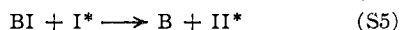
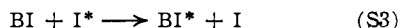
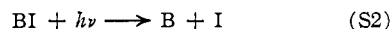
(9) R. L. Dannley, E. C. Gregg, Jr., R. E. Phelps and C. B. Coleman, *J. Am. Chem. Soc.*, **76**, 445 (1954); R. L. Dannley and E. C. Gregg, Jr., *ibid.*, **76**, 2997 (1954).

where f will differ little from unity for a weakly absorbing solution. Finally, let q_{I_2} be the average rate of absorption by iodine in einsteins/liter sec. Then

$$q_{\text{I}_2} = 1000 I_0 \alpha_{\text{I}_2} [\text{I}_2] f \quad (3)$$

where the factor 1000 is for ml./liter. A similar expression can be written for absorption by benzyl iodide.

Exchange in Degassed Systems.—If isotopic substitutions are included, the following processes can take place in an illuminated degassed solution of benzyl iodide and iodine



Let R_{ex} be the rate of the exchange process



The above mechanism predicts that

$$R_{\text{ex}} = k_6[\text{B}][\text{I}_2] + \{k_3[\text{BI}][\text{I}] + k_5[\text{B}][\text{I}]\} \frac{2q_{\text{I}_2}\phi_{\text{I}_2} + k_4[\text{I}_2][\text{I}] + k_6[\text{B}][\text{I}_2]}{2q_{\text{I}_2}\phi_{\text{I}_2} + q_{\text{BI}}\phi_{\text{BI}} + k_3[\text{BI}][\text{I}] + k_4[\text{I}_2][\text{I}] + k_6[\text{B}][\text{I}_2]} \quad (5)$$

where the ϕ 's are quantum yields for dissociation of the indicated species. The term multiplying the brackets arises because the isotopic distribution in iodine atoms is not quite identical with that in iodine molecules; the need for this type of term has been discussed previously.¹⁰

Equation 5 is complex. However, it can be simplified by three assumptions that must ultimately be justified by experimental test.

Assumption (a) is that

$$2q_{\text{I}_2}\phi_{\text{I}_2} + k_4[\text{I}_2][\text{I}] + k_6[\text{B}][\text{I}_2] \gg q_{\text{BI}}\phi_{\text{BI}} + k_3[\text{BI}][\text{I}] \quad (6)$$

This assumption is equivalent to saying that the isotopic composition of iodine atoms is the same as of molecules; it reduces the ratio in equation 5 to unity.

Assumption (b) is that

$$k_3[\text{BI}][\text{I}] + k_6[\text{B}][\text{I}_2] \gg k_5[\text{B}][\text{I}] \quad (7)$$

This assumption will certainly be satisfied if chain lengths for exchange are large compared to unity, and it may be satisfied under other conditions also.

Assumption (c) is that

$$k_4[\text{BI}][\text{I}] = k_6[\text{B}][\text{I}_2] \quad (8)$$

This assumption implies that chain lengths are long for exchange by the carbon radical mechanism.

If all three of these assumptions are valid, equation 5 becomes

$$R_{\text{ex}} = (k_3 + k_5)[\text{BI}][\text{I}] \quad (9)$$

In a system of this sort, the total rate of formation of radicals of all types can be equated to

(10) R. M. Noyes and J. Zimmerman, *J. Chem. Phys.*, **18**, 656 (1950).

total rate of destruction. Then

$$q_{12}\phi_{12} + q_{B1}\phi_{B1} = k_7[I]^2 + k_8[B][I] + k_9[B]^2 \quad (10)$$

With the aid of equation 8, this rearranges to

$$[I] = \sqrt{\frac{q_{12}\phi_{12} + q_{B1}\phi_{B1}}{k_7 + k_8 \frac{k_6[BI]}{k_6[I_2]} + k_9 \frac{k_6^2[BI]^2}{k_6^2[I_2]^2}}} \quad (11)$$

Equations 9 and 11 can be combined to give the rate of exchange in terms of species present in macroscopic amounts. The combination is aided by defining the quantities:

$$g = 1 + \frac{\alpha_{B1}\phi_{B1}[BI]}{\alpha_{12}\phi_{12}[I_2]} \quad (12)$$

$$M_p = k_6 \left(\frac{1000I_0\alpha_{12}\phi_{12}}{k_9} \right)^{1/2} \left(1 + \frac{k_8}{k_6} \right) \quad (13)$$

$$N_p = k_6 \left(\frac{1000I_0\alpha_{12}\phi_{12}}{k_7} \right)^{1/2} \left(1 + \frac{k_8}{k_5} \right) \quad (14)$$

$$\Phi = \frac{k_8}{2\sqrt{k_7k_9}} \quad (15)$$

$$Q = [I_2]/[BI] \quad (16)$$

Of these quantities, g is a correction factor that is never very different from unity in our experiments, and M_p and N_p are limiting rate constants for exchange in excess benzyl iodide and iodine, respectively.

In terms of these quantities, equation 9 becomes

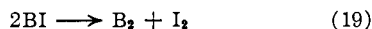
$$R_{ex} = \frac{N_p(fg)^{1/2}[BI][I_2]^{1/2}}{\sqrt{1 + \frac{2\Phi N_p}{M_p Q} + \frac{N_p^2}{M_p^2 Q^2}}} = \frac{M_p(fg)^{1/2}[I_2]^{1/2}}{\sqrt{1 + \frac{2\Phi M_p Q}{N_p} + \frac{M_p^2 Q^2}{N_p^2}}} \quad (17)$$

Either expression can be rearranged to give

$$\frac{[BI]^2[I_2]fg}{R_{ex}^2} = \frac{1}{N_p^2} + \frac{2\Phi}{M_p N_p Q} + \frac{1}{M_p^2 Q^2} \quad (18)$$

The quantities on the left side of equation 18 are capable of experimental measurement, and the values at different concentrations can be expressed as a quadratic function in $1/Q$. The fit of this quadratic expression permits evaluation of M_p , N_p and Φ .

Iodine Production in Degassed Systems.—The above mechanism implies that exchange is accompanied by the process



which causes a net chemical change in the system. The rate of this process is given by

$$\frac{d[I_2]}{dt} = k_9[B]^2 = \frac{q_{12}\phi_{12} + q_{B1}\phi_{B1}}{1 + \frac{2\Phi M_p Q}{N_p} + \frac{M_p^2 Q^2}{N_p^2}} \quad (20)$$

This equation suggests two limiting forms. At extremely low concentrations of iodine it reduces to

$$\frac{d[I_2]}{dt} = q_{B1}\phi_{B1} \quad (21)$$

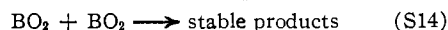
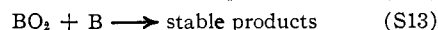
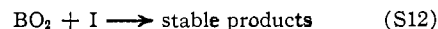
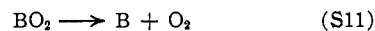
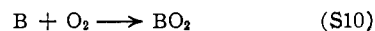
as would be anticipated. At moderately high concentrations of iodine, it reduces to

$$\frac{d[I_2]}{dt} = \frac{1000I_0fg\alpha_{12}\phi_{12}k_8^2k_9[BI]^2}{k_6^2k_7[I_2]} \quad (22)$$

Hence the rate of iodine production falls off as the

concentration of iodine increases, and a state is reached where step (S9) is very improbable.

Exchange in Presence of Oxygen.—If the solution also contains oxygen, these additional processes are possible



The chief effect of the added steps is to place iodine and oxygen in competition for benzyl radicals by steps (S6) and (S10), respectively. Let x be the fraction of the time that a benzyl radical reacts with oxygen rather than with iodine. Then

$$x = \frac{k_{10}[O_2]}{k_8[I_2] + k_{10}[O_2]} = \frac{1}{1 + k_8[I_2]/k_{10}[O_2]} \quad (23)$$

The mechanism involving all possible steps is too complicated for useful quantitative comparisons. However, the importance of various steps can be tested by examining three limiting types of situation:

(a) **Comparative Effects of Air and Oxygen.**—

Under some conditions, addition of oxygen can cut the rate of exchange to less than 1% of the value in degassed solutions. Hence in the presence of oxygen the concentration of benzyl radicals must be very much less than that of BO_2 peroxy radicals. If formation of a peroxy radical is reversible, a given BO_2 has more chance of decomposing by step (S11) than it does of reacting by any of the steps (S12–S14). For such a reversible situation, the concentration of free benzyl radicals should be about five times as great in a solution saturated with air as in one saturated with oxygen at one atmosphere. This factor of five should be reflected in the relative rates of exchange under conditions where chains in a degassed solution are long.

Even if the formation of BO_2 is not reversible, the factor of five between air and oxygen saturated solutions should still be observed if exchange goes only by the sequence (S5–S6) and does not contain a contribution from (S3). Exchange would then result from the competition of steps (S6) and (S10) for benzyl radicals with step (S10) being the more probable.

The above arguments lead to the conclusion that failure of oxygen to reduce the exchange rate to one fifth that of air indicates both that the formation of BO_2 is essentially irreversible and that the direct substitution step (S3) is making a significant contribution to the exchange reaction.

If, as is indeed observed, exchange in oxygen is somewhat less than that in air, it implies that step (S10) is not entirely efficient at competing with step (S6). Some of the exchange then takes place by step (S3) with iodine atoms that have been produced photochemically, and some takes place by either (S3) or (S6) through the action of radicals whose past history involved formation of a benzyl radical at some time since the photochemical generation of that chain. Exchange by radicals whose past history includes benzyl forma-

tion will be inhibited five times as efficiently by oxygen as by air. Let $R_{\text{ex}}(\text{residual})$ be the exchange by step (S3) by photochemically produced iodine atoms such that it could not be inhibited by oxygen regardless of partial pressure. Then

$$R_{\text{ex}}(\text{residual}) = R_{\text{ex}}(\text{oxygen}) - 0.25[R_{\text{ex}}(\text{air}) - R_{\text{ex}}(\text{oxygen})] \quad (24)$$

(b) **Exchange at Low Benzyl Iodide Concentrations.**—It is possible to have benzyl iodide concentrations so low that the quantum yield for exchange in degassed solution is less than the quantum yield for iodine dissociation. Almost all radicals are then produced by light absorption by molecular iodine, and the concentration of iodine atoms will be almost the same whether the solution is degassed or saturated with oxygen. For this situation, $R_{\text{ex}}(\text{degassed})$ will equal $(k_3 + k_5)[\text{BI}][\text{I}]$, and $R_{\text{ex}}(\text{residual}) = k_3[\text{BI}][\text{I}]$. Then

$$\frac{R_{\text{ex}}(\text{residual})}{R_{\text{ex}}(\text{degassed})} = \frac{k_3}{k_3 + k_5} = y \quad (25)$$

where y is the probability that an iodine atom will react by step (S3) rather than by step (S5).

(c) **Exchange at High Benzyl Iodide Concentrations.**—Let R_i be the rate of photochemical production of iodine atoms. Then

$$R_i = 2q_{12}\phi_{12} + q_{\text{BI}}\phi_{\text{BI}} \quad (26)$$

If the concentration of benzyl iodide is high, every iodine atom produced photochemically will eventually react by step (S5) to form a benzyl radical, and its subsequent fate will involve the competition of steps (S6) and (S10). The number of exchanges by step (S3) that a photochemically produced iodine atom undergoes before it reacts by step (S5) is given by

$$y + y^2 + y^3 + y^4 + \dots = \frac{y}{1-y} \quad (27)$$

Then we can write

$$\frac{R_{\text{ex}}(\text{residual})}{R_i} = \frac{y}{1-y} \quad (28)$$

This expression permits an estimate of y independent of the method suggested by equation 25. Of course knowledge of y permits calculation of the desired ratio k_3/k_5 .

The same type of argument can also be used to estimate the relative efficiencies of oxygen and iodine molecules at trapping benzyl radicals. At high concentrations of benzyl iodide, benzyl radicals are produced from photochemically generated species at a rate $R_i + q_{\text{BI}}\phi_{\text{BI}}$, the extra term arising because photolysis of benzyl iodide gives both an iodine atom and a benzyl radical, and R_i gives only the rate of production of iodine atoms that subsequently react to form benzyl radicals. In the presence of air, a fraction $1 - x$ of these benzyl radicals react with iodine by step (S6) and in doing so cause exchange. They also produce iodine atoms that have been shown above to cause $y/(1-y)$ exchanges per iodine atom produced. The exchange caused by benzyl radicals or species produced from them is $R_{\text{ex}}(\text{air}) - R_{\text{ex}}(\text{residual})$. Then

$$\begin{aligned} R_{\text{ex}}(\text{air}) - R_{\text{ex}}(\text{residual}) &= (R_i + q_{\text{BI}}\phi_{\text{BI}})(1-x) \left(1 + \frac{y}{1-y}\right) \\ &= (R_i + q_{\text{BI}}\phi_{\text{BI}}) \frac{1-x}{1-y} \end{aligned} \quad (29)$$

Hence x becomes the only unknown and the desired efficiency can be calculated.

Iodine Production in Presence of Oxygen.—If step (S10) is irreversible, oxygen becomes an efficient scavenger for benzyl radicals produced in step (S5). At sufficiently high concentrations of benzyl iodide, every iodine atom produced photochemically in the system eventually causes production of an iodine molecule by the sequence (S5, S10). Then

$$\frac{d[\text{I}_2]}{dt} = q_{12}\phi_{12} + q_{\text{BI}}\phi_{\text{BI}} \quad (30)$$

Measurements of iodine production at known light intensities then permit determination of quantum yields for dissociation of the absorbing species. The method is similar to the allyl iodide scavenging technique previously developed.¹¹

Experimental

Materials.—Benzyl iodide was prepared from benzyl alcohol and hydriodic acid by the method of Norris¹² as described previously.³ It melted sharply at 24.00° and boiled at 80.25° at 5 mm. The refractive index was n_D^{20} 1.6315.

Anal. Calcd. for $\text{C}_7\text{H}_7\text{I}$: C, 38.56; H, 3.24; I, 58.20. Found: C, 38.40; H, 3.18; I, 58.00.

p-Nitrobenzyl iodide was prepared by refluxing the chloride briefly with sodium iodide in aqueous acetone. The yellow precipitate was recrystallized from alcohol and melted 127.18–127.69°.

Anal. Calcd. for $\text{C}_7\text{H}_6\text{NO}_2\text{I}$: C, 31.96; H, 2.30; N, 5.33; I, 48.25. Found: C, 32.20; H, 2.41; N, 5.34; I, 48.52.

p-Methylbenzyl iodide was prepared from the bromide by action of sodium iodide in ether-acetone. The precipitate was extracted with anhydrous ether and the extract was washed with cold aqueous sodium sulfite. It was dried over anhydrous sodium sulfite and the ether was evaporated. The residue was recrystallized from anhydrous ether at Dry Ice temperatures. The colorless crystals melted 49.00–49.40°.

Anal. Calcd. for $\text{C}_8\text{H}_9\text{I}$: C, 41.40; H, 3.91; I, 54.69. Found: C, 41.58; H, 4.08; I, 54.83.

There was no difference between analyses for total halide and for iodine, so bromide had been quantitatively removed.

p-Methoxybenzyl iodide was prepared in two steps from anisyl alcohol. First the chloride was prepared from the alcohol by the method of Quelett and Allard.¹³ The chloride was then converted to the iodide in ether-acetone by much the same procedure used with the *para*-methyl compound. The colorless solid melted 32.5–32.8°.

Anal. Calcd. for $\text{C}_8\text{H}_9\text{OI}$: C, 38.73; H, 3.66; I, 51.16. Found: C, 38.97; H, 3.74; I, 51.14.

There was no evidence for residual chloride. Although the desired compound obviously was prepared, it was too unstable for use in the exchange experiments.

p-Aminobenzyl iodide could not be prepared. The failure is not surprising in view of the extreme reactivity observed for the *p*-methoxy compound.

Ethylene dichloride (1,2-dichloroethane) was used as solvent in all experiments because *p*-nitrobenzyl iodide was not sufficiently soluble for kinetic studies in hexachlorobutadiene, the solvent used in previous work with benzyl iodide.³ Prepurified commercial material was distilled, and the fraction boiling 83.5–83.7° was retained. It contained about 4×10^{-8} mole/liter of material capable of reacting with iodine. This estimate of impurity was obtained both by measuring the amount of radioactive iodine becoming organically bound in a solution initially containing only iodine and also by measuring the apparent induction period for the photochemical decomposition of the benzyl iodides in the absence of iodine.

(11) F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

(12) J. F. Norris, *Am. Chem. J.*, **38**, 638 (1907).

(13) R. Quelett and J. Allard, *Bull. soc. chim.*, [5] **4**, 1468 (1937)

Resublimed reagent grade iodine was used without further purification. Solutions were activated with small quantities of aqueous carrier-free iodine-131 obtained from the United States Atomic Energy Commission. Moisture was subsequently removed by filtering the activated solutions through paper. Additional drying over anhydrous magnesium sulfate did not affect the rates of exchange.

Apparatus and Procedure.—Experiments were carried out in cylindrical cells 2.0 cm. long and 1.8 cm. in diameter fitted with side arms in which the contents could be frozen during degassing. The cells could be mounted reproducibly either in a thermostat on an optical bench or in a Beckman spectrophotometer. While in the thermostat, they could be illuminated with light of 5461 Å. isolated with filters from a thermostated AH-4 mercury arc. The absolute intensity of the light was measured with a thermopile-galvanometer system calibrated against a standard lamp, and a photo tube was used for monitoring.

In order to prepare for a run, solutions were mixed in the desired concentrations and an amount just sufficient to fill the cell was introduced into the side arm. The "air" runs were then illuminated without further treatment. The "oxygen" runs were saturated with a stream of tank oxygen dried over calcium chloride and bubbled first through a portion of a solution identical with that to be used in the run. The "degassed" runs were frozen to Dry Ice temperature, evacuated with a mercury diffusion pump and then melted and agitated; the cycle of freezing and evacuation was repeated five times.

Each photochemical decomposition run then was illuminated and analyzed for iodine at frequent intervals by measuring the absorbance at 500 m μ .

After illumination, each exchange experiment was chilled and opened. The solution was then extracted with aqueous sulfite, and the organic and aqueous layers were separated and washed with water and carbon tetrachloride, respectively. The radioactivity in each solution was measured with a thin-walled counter, and empirical counting corrections were applied for the differences in solvent density. Simultaneous radioactivity measurements were made on a sample of the same solution which had had identical treatment except for illumination. The rate of photochemical exchange was computed with standard equations.

Results of this separation procedure could be reproduced to within 1%. Several exchange runs were analyzed spectrophotometrically for iodine before the cells were opened; these analyses never indicated significant concentration changes during a run.

Results

Extinction Coefficients.—Solutions of iodine and of several benzyl iodides were measured spectrophotometrically at 546 m μ , the wave length used for the illuminations. Solutions of iodine were also measured at 500 m μ , the wave length used for the analyses. The solutions fitted Beer's law satisfactorily, and the extinction coefficients, $E = \alpha/2.303$, were computed from the standard equation $\log(I_0/I) = EcL$. The results are presented in Table I.

TABLE I

EXTINCTION COEFFICIENTS AND QUANTUM YIELDS FOR DISSOCIATION IN ETHYLENE DICHLORIDE				
Substance	λ , m μ	E , l./mole cm.	ϕ	$\phi\alpha$
Iodine	500	965 \pm 2		
	546	504 \pm 5	0.13	150
Benzyl iodide	546	0.086	.091	0.0180
<i>p</i> -Nitrobenzyl iodide	546	.068	.11	.0172
<i>p</i> -Methylbenzyl iodide	546	.192	.065	.0288

In the exchange experiments, concentrations of benzyl iodide were sometimes as much as 1000 times those of iodine. However, the extinction coefficient of iodine is so large that this species was always responsible for at least 85% of the light absorbed.

Iodine Production in Presence of Oxygen.—Oxygenated solutions of each of the three benzyl iodides were illuminated with light of known intensity at 30°, and iodine concentrations were measured frequently. After a time necessary for consumption of the reactive impurity in the solvent, iodine was produced at a constant rate as illustrated in Fig. 1. Since the concentration of iodine was so low that virtually all of the incident light was absorbed by the benzyl iodide, the $q_L\phi_{I_2}$ term in equation 31 could be neglected and the quantum yield for benzyl iodide dissociation could be calculated directly. The results of these measurements also are presented in Table I.

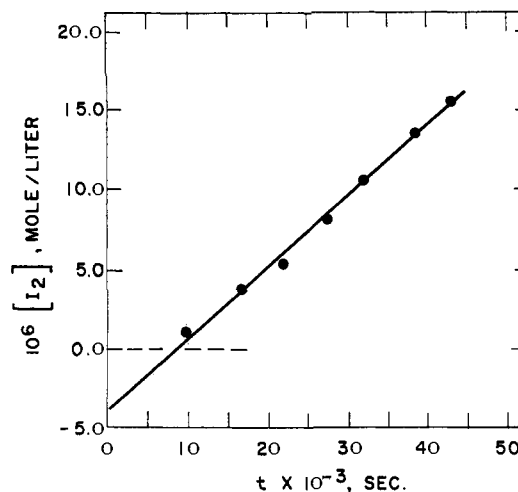


Fig. 1.—Iodine production during illumination of oxygenated solution containing 0.190 mole/liter of unsubstituted benzyl iodide. Incident light intensity was 7.63×10^{13} quanta/cm.² sec. at 5461 Å. Note induction period suggesting impurity reacting with 3.6×10^{-4} mole per liter of iodine at start of illumination.

In the solution containing unsubstituted benzyl iodide, the illumination was continued for so long a period that much of the light was being absorbed by the produced iodine. The rate of iodine production increased as illustrated in Fig. 2. The increased rate could be fitted very closely to that predicted if $\phi_{I_2} = 0.13$, and this value is included in Table I.

The quantum yields, ϕ_{BI} , are computed from the conventional definition of probability of dissociation per quantum absorbed. Table I also contains a column listing $\phi_{BI}\alpha_{BI}$. This quantity is proportional to the probability of dissociation per quantum incident on a given number of molecules of substance. The low quantum yield for dissociation of *p*-methylbenzyl iodide apparently is due to absorption of light by processes not affecting the C-I bond, and this compound actually shows a greater probability of dissociation per incident flux available.

Iodine Production in Degassed Solution.—A degassed solution of unsubstituted benzyl iodide showed no measurable iodine production after 41 hr. of illumination of the intensity used in the exchange experiments. Since 10^{-6} mole/liter of

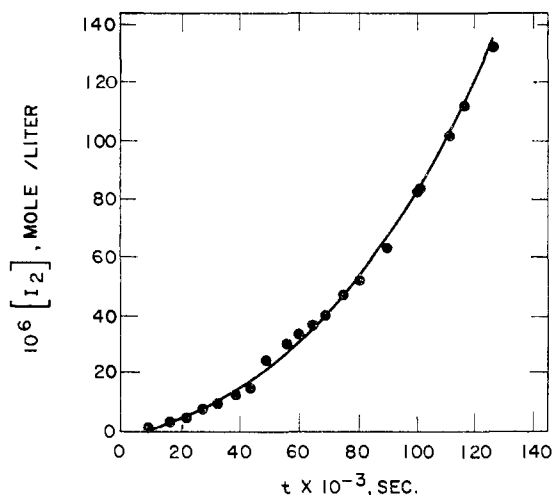


Fig. 2.—Iodine production during continued illumination of solution used in Fig. 1. The increasing rate of iodine production is due to photochemical dissociation of iodine as well as benzyl iodide.

iodine could have been detected readily, benzyl iodide was present in at least a 10^5 -fold molar excess over iodine. This observation implies that step (S9) has a surprisingly low rate constant for a radical-radical reaction; the implications are discussed in more detail below.

TABLE II

EXCHANGE OF UNSUBSTITUTED BENZYL IODIDE, CORRECTED TO 2.75×10^{-10} EINSTEINS/CM.² SEC. INCIDENT INTENSITY

$10^4 [I_2]$, mole/l.	$10^4 [BI]$, mole/l.	Q	$10^8 R_{ex}$, mole/l. sec.		
			Degassed	Air	Oxygen
20°					
1.90	948	0.00201	38.1		
1.02	190	.00537	2.66		
1.90	190	.0100			0.454
1.94	190	.0102			.441
0.680	7.59	.0896	0.451		
1.02	5.69	.180	.263		
1.94	5.69	.341	.385		
1.94	1.71	1.14			.0490
30°					
1.00	948	0.00105	24.6		
1.44	948	.00152	111	1.45	0.794
1.32	190	.00697		1.61	.972
1.44	190	.00760	44.6		
1.25	142	.00879	11.2		
2.04	190	.0108	28.9	1.86	.981
1.32	37.9	.0348	4.57		.372
1.32	19.0	.0697	4.10		
1.00	7.58	.132	2.39		
1.04	1.71	.608	0.266	0.0761	.0642
40°					
1.00	948	0.00105			0.457
1.02	948	.00108	19.2		
1.15	948	.00121	16.7		
1.92	948	.00203	90.3		
1.92	190	.0102	13.11		
1.00	37.9	.0263			0.323
1.92	37.9	.0507	7.98		
1.00	7.58	.132	1.15		

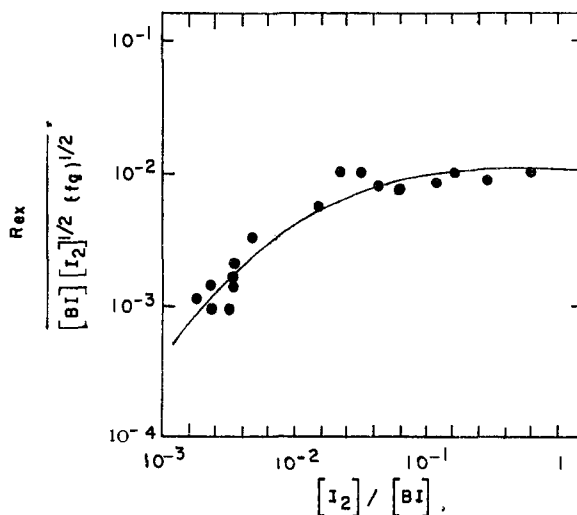


Fig. 3.—Applicability of equation 18 to the exchange of *p*-nitrobenzyl iodide with iodine at 30°. The curve has been computed for the reported values of the kinetic parameters.

Iodine Production during Intense Illumination.—Another degassed solution containing 0.1896 *M* benzyl iodide was illuminated by two 100-watt lamps placed on opposite sides and the whole surrounded by reflecting aluminum foil. Iodine production was observed under this intense illumination, but after 26 hr. the concentration of 2.7×10^{-4} *M* iodine was not changing at a detectable rate. Infrared spectra of the solution revealed no features that were not due to the starting materials; dibenzyl could not have been detected at the concentration it had presumably attained.

An oxygenated solution of benzyl iodide was also illuminated under approximately the same conditions. A steady state concentration of 1.2×10^{-3} *M* iodine was attained in a few hours. The solution absorbed strongly at 5.9 microns, presumably because of benzaldehyde.

Exchange Kinetics.—The results of a number of exchange experiments with unsubstituted benzyl iodide are presented in Table II. These experiments were carried out at two different incident light intensities of 1.66×10^{14} and 7.63×10^{13} quanta/cm.² sec. Since the analysis indicates that exchange rate should be proportional to the square root of incident light intensity, all of the rates in Table II have been corrected by this assumption to correspond to 1.66×10^{14} quanta/cm.² sec. (2.75×10^{-10} einsteins/cm.² sec.). This is the light intensity used in the experiments with *p*-nitrobenzyl iodide which are reported in Table III; a plot in Fig. 3 illustrates the fit to a modification of equation 18.

During the experiments with *p*-methylbenzyl iodide, some difficulty was encountered with the behavior of the amplifier circuit for monitoring light intensity. Hence studies with this compound were conducted by following each run with a control experiment employing unsubstituted benzyl iodide under nearly identical conditions. The results are presented in Table IV.

The degassed runs were fitted to equation 18, data in different ranges of Q being used to calcu-

TABLE III
EXCHANGE OF *p*-NITROBENZYL IODIDE AT 2.75×10^{-10}
EINSTEINS/CM.² SEC. INCIDENT INTENSITY

10 ⁴ [I ₂], mole/l.	10 ⁴ [BI], mole/l.	Q		10 ⁸ R _{ex} , mole/l. sec. Degassed	Air
		20°			
1.54	762	0.00202	137		
1.08	173	.00624	75.7		
1.44	11.6	.124	9.15		
1.44	1.16	1.24	0.944		
		30°			
2.70	1520	0.00178	250		
1.07	452	.00236	67.8	0.504	
1.07	452	.00236	41.3		
0.525	173	.00303	12.3		
.552	151	.00366	18.0		
.552	151	.00366	15.8		
.552	151	.00366	23.8		
1.49	302	.00493	115	0.281	
2.07	173	.0156	138		
1.98	86.7	.0228	114		
1.98	60.9	.0325	65.9		
1.98	45.7	.0433	45.9		
2.33	35.8	.0651	37.0		
1.48	11.6	.128	11.0		
2.70	17.3	.156	23.6		
0.525	1.73	.303	1.05		
0.733	1.16	.632	0.952		
		40°			
1.88	1530	0.00122	223	2.17	
1.92	60.9	.0315	72.3		
1.92	15.2	.126	17.1	2.81	
1.92	1.73	1.11	2.76	0.478	

TABLE IV
COMPARATIVE EXCHANGE OF UNSUBSTITUTED AND *p*-
METHYLBENZYL IODIDES AT 30°

10 ⁴ [I ₂], mole/l.	10 ⁴ [BI], mole/l.	Q	10 ⁸ R _{ex} , mole/l. sec.		
			Unsub- stituted degassed	<i>p</i> -Methyl- De- gassed	Air
1.39	606	0.00229		18.6	
1.39	592	.00234	15.0		
2.00	474	.00422	24.8		
2.47	485	.00509		46.8	
1.85	97.0	.0190		2.24	0.375
1.85	94.8	.0195	1.15		
1.50	24.2	.0618		0.365	
1.50	23.7	.0632	0.637		
1.85	19.4	.0953		.133	

TABLE V
PARAMETERS FOR DEGASSED EXCHANGE

Compound	Temp., °C.	N _p	M _p	Φ
Benzyl iodide	30	0.0019	0.52	2.5
<i>p</i> -Nitrobenzyl iodide	20	.007		
	30	.0099	.51	0.5
	40	.011		
<i>p</i> -Methylbenzyl iodide	30	.0008	.67	

late the "best" values for the three parameters. The results are presented in Table V. The confidence in these values varies considerably, but it is always best at 30° where the most measurements were made. N_p is the rate constant at low concentrations of organic iodide; it is probably known within 10% for the *p*-nitro compound and 20%

for the unsubstituted. M_p, the rate constant at high benzyl iodide concentrations, is much more sensitive to impurities and may be uncertain by 40%. The parameter Φ is least well defined and is only known to about a factor of two. Hence we cannot say with confidence that Φ values differ significantly from unity.

Discussion

Quantum Yield for Iodine Dissociation.—At 30° and 5461 Å., the observed quantum yield for iodine dissociation is 0.13. A recently developed theory¹⁴ which treats the solvent as a viscous continuum predicts a quantum yield of 0.080 for a solvent of viscosity 0.0070 poise. The predictions of the theory have tended to be low in hydrocarbons and high in completely chlorinated solvents. The somewhat low prediction in this partially chlorinated solvent helps to establish the range of validity of theories describing molecular behavior in terms of the macroscopic viscosity of the solvent.

Importance of Direct Substitution.—The experiments with unsubstituted benzyl iodide clearly show that substitution of oxygen for air cuts the rate of exchange by no more than a factor of two. Hence the arguments developed previously indicate that the direct substitution mechanism (S3) contributes to exchange as well as the iodine abstraction mechanism (S5-6).

For the unsubstituted compound, the argument of equation 25 applied to the lowest concentration of BI gives $y = 0.23$ and $k_3/k_5 = 0.30$. The argument of equation 28 applied to the highest concentration of BI gives $y = 0.38$ and $k_3/k_5 = 0.61$. The agreement is only fair but certainly supports the interpretation that k_3 is comparable to but somewhat less than k_5 . Since even at the lowest concentration of benzyl iodide about half of the photochemically produced iodine atoms caused exchange in the degassed system, addition of oxygen probably did significantly deplete the concentration of free iodine atoms. Hence the $y = 0.23$ value would be expected to be somewhat low. We believe the computation at high benzyl iodide concentration is the more reliable.

The *p*-nitrobenzyl iodide experiments were not conducted with both air and oxygen. However, if the additional effect of oxygen compared to air is the same as with the unsubstituted compound, k_3/k_5 at 30° is about the same for both compounds. The data do not permit estimation of k_3/k_5 for *p*-methylbenzyl iodide.

Although application of our observations to the proposed mechanism indicates unequivocally that k_3 is significant, an alternative explanation is possible. If benzyl peroxy radicals can react with iodine molecules as



there would be a residual exchange that could not be inhibited by increasing oxygen pressure. Step (S15) is probably quite endothermic, and we prefer to regard the residual exchange as due to step (S3). The question probably could be settled by additional experiments that were not performed.

(14) R. M. Noyes, *Z. Elektrochem.*, **64**, 153 (1960).

Effect of Substitution on Reactivity.—For different benzyl iodides, the value of N_p is proportional to $k_3 + k_5$. The data in Table V show a clear effect of substitution with the rate being accelerated by the electron-withdrawing nitro group and slowed by the electron-donating methyl group. Application of the Hammett equation⁵ gives $\rho = +1.1$.

This effect of substitution is opposite in sign to the effects on hydrogen abstraction reported by Jaffe.⁶ It is also opposite in sign to the observations of Kooyman, *et al.*,¹⁵ and of Johnston and Williams¹⁶ on radical abstraction of benzylic hydrogen. These substituent effects are directly opposite to those observed for ionic dissociation of the same bonds. Thus electron-withdrawing groups like *p*-nitro greatly increase the acidity of benzoic acids while they decrease the ease of radical abstraction of benzylic hydrogen. On the other hand, electron-donating groups certainly would increase the rate of unimolecular solvolysis of benzyl iodide even though they decrease the rate of radical abstraction.

The difference can be rationalized in terms of bond polarities. The hydrogen end of a benzylic C-H bond is positive because of hyperconjugation. If the hydrogen is to be removed with an accompanying electron rather than as a proton, the reaction will be aided by increased electron density at the site. On the other hand, the iodine end of the C-I bond is negative, and groups that withdraw electrons from this region will facilitate a reaction in which one of the bonding electrons must be retained by the carbon. This argument suggests as a general rule that electron donation will facilitate radical abstraction of a group that would tend to ionize as a positive entity while electron withdrawal will facilitate radical abstraction of a group that would tend to ionize as a negative entity. Additional evidence on this matter would be of interest.

If the reactions of benzyl radicals with each other (S9) are controlled by diffusion and little influenced by structure, the values of M_p in Table V indicate the effect of substitution on k_6 . The effects are small and not of clear significance but seem to be opposite in direction to the effects on k_5 . This result is expected. Steps (S5) and (S6) must go through identical transition states. A substituent that tends to stabilize a benzyl radical more than a benzyl iodide molecule will increase k_5 and decrease k_6 . The arguments of Hammond¹⁷ indicate that the common transition state more closely resembles a benzyl radical and iodine molecule than it does an iodine atom and benzyl iodide molecule. Our observations are in complete accord with this prediction.

Rate Constants for Propagation Steps.—The rate constant, k_7 , for iodine atom recombination has not been measured in ethylene dichloride. However, values in similar solvents¹⁸ indicate that it is not very different from 8×10^9 liter/mole sec.

(15) E. C. Kooyman, R. van Helden and A. F. Bickel, *Koninkl. Ned. Akad. Wetenschap.*, Proc. **56B**, 75 (1953).

(16) K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1446 (1960).

(17) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(18) H. Rosman and R. M. Noyes, *ibid.*, **80**, 2410 (1958).

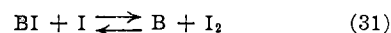
Then the value of N_p for unsubstituted benzyl iodide in ethylene dichloride at 30° indicates that $k_3 + k_5 = 2.6 \times 10^4$ liter/mole sec.

The value obtained previously for the same quantity in hexachlorobutadiene at 36° is¹⁹ 7.1×10^4 . The difference is a little large to be due entirely to the temperature change, and the solvent effect suggests that the transition state actually has a lower dipole moment than the original benzyl iodide molecule; this conclusion is consistent with the substituent effects discussed above.

Corresponding values of $k_3 + k_5$ at 30° in ethylene dichloride are 1.38×10^5 liter/mole sec. for *p*-nitrobenzyl iodide and 1.1×10^4 for *p*-methylbenzyl iodide.

The value of $k_3/k_5 = 0.61$ for the unsubstituted benzyl iodide permits individual values of these rate constants to be calculated easily.

The quantity $N_p/M_p = (k_5/k_6)\sqrt{k_9/k_7}$. It is almost but not quite equal to the equilibrium constant for the reaction



The value for unsubstituted benzyl iodide in ethylene dichloride at 30° is 0.00367, while the value in hexachlorobutadiene at 36° is³ 0.0113. The difference partly reflects a temperature effect and partly the greater dipole moment of benzyl iodide than of benzyl radical. Other values in ethylene dichloride at 30° are 0.0194 for the *p*-nitro compound and 0.0012 for the *p*-methyl. The *p*-nitro group seems to stabilize the benzyl radical, while the *p*-methyl group causes a slight destabilization. This conclusion is opposite to the effects of substituents on radical stability claimed by Huang and Singh.²¹

Rate Constants for Termination Steps.—In the previous study,³ termination steps (S7) and (S8) were assumed to involve equal reactivities, and the value of Φ was used to calculate the rate of step (S9) involving two benzyl radicals. Equation 20 suggests that k_9 could be measured independently by studying iodine production in a degassed solution. However, no iodine was produced at the illumination levels of our experiments. Some iodine was produced under intense illumination as described above, but the kinetics of approach to the steady state cannot be reconciled to the mechanism developed in this paper and indicated in equation 22. The results can be explained if benzyl radicals can slowly attack solvent to produce species capable of reacting with molecular iodine. The reaction is obviously much slower than the exchange reaction of interest here and does not interfere with the main conclusions of this paper.

Validity of Assumptions.—During the formulation of the problem, three assumptions were made about magnitudes of rate constants. Assumption (a) (equation 6) depends upon the magnitude of k_4 which has been shown¹⁰ to be about 7×10^7 liter/mole sec. in another solvent. Then the left side

(19) This value is the same as that given in ref. 3 but has been recalculated with the use of improved values of k_7 (ref. 18) and of ϕ_1 (ref. 20). The effects of the changes almost exactly compensate!

(20) L. F. Meadows and R. M. Noyes, *J. Am. Chem. Soc.*, **82**, 1872 (1960).

(21) R. L. Huang and S. Singh, *J. Chem. Soc.*, 3183, 3190 (1959).

of equation 6 is greater than the right by a factor of about eight under the worst conditions encountered in this paper.

Assumption (b) (equation 7) is clearly satisfied by the fact that chain lengths were of the order of a hundred for the highest concentrations of benzyl iodide, and lower concentrations would reduce both sides of the equation proportionately.

Assumption (c) (equation 8) must be satisfied if chain lengths are long. Even at low benzyl iodide concentrations where chain lengths can be less than unity, assumption (c) must hold if $k_6[B][I_2] \gg k_8[B][I]$ as implied in assumption (b).

Competition of Iodine and Oxygen for Benzyl Radicals.—The argument of equation 29 can be applied to the highest concentration of unsubstituted benzyl iodide at 30°. If $y = 0.38$, then $x = 0.53$. Thus in an air saturated solution containing $1.4 \times 10^{-4} M$ iodine, $k_6[I_2]/k_{10}[O_2] = 0.89$ and

iodine and oxygen compete with about equal effectiveness. The data of Sibbett and Noyes²² indicate that in air saturated hexane $4 \times 10^{-4} M$ iodine competes for allyl radicals with about the same efficiency as oxygen. The similarity of the results helps to support the rather complex interpretations that have been developed.

Acknowledgments.—The experimental work was carried out at Columbia University and was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314. Some of the interpretive work on the data was carried out at the University of Oregon and was also supported in part by the Atomic Energy Commission under Contract AT(45-1)-1310. The Esso Research and Engineering Company also facilitated some of the preparation of the manuscript.

(22) D. J. Sibbett and R. M. Noyes, *J. Chem. Soc.*, **75**, 763 (1953).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, BROOKHAVEN NATIONAL LABORATORY, UPTON, NEW YORK, AND BOSTON UNIVERSITY, BOSTON, MASSACHUSETTS]

The Effect of Ion Pairing on the Reactivity of Anionic Nucleophiles. I. The Exchange Reaction of *p*-Nitrobenzyl Bromide with Bromide Ion in Liquid Sulfur Dioxide Solution¹

BY NORMAN N. LICHTIN AND K. NARAYANA RAO²

RECEIVED OCTOBER 1, 1960

The kinetics of exchange of *p*-nitrobenzyl bromide with Br⁻² provided in the form of LiBr, KBr, (CH₃)₄NBr and (C₂H₅)₄NBr has been investigated over a wide range of ionophore concentrations at 0° and, with KBr, at -10.2° and +10.75° as well. Neither of the rate expressions, $R_o = k_2(RBr)(MBr)_s$, where (RBr) and (MBr)_s are stoichiometric concentrations of aralkyl bromide and ionophore, respectively, or $R_o = k_1(RBr)$ correlates the data satisfactorily; k_2 decreases with increasing (MBr)_s while k_1 increases to a much greater degree. The data establish that the variation of k_2 with (MBr)_s is not a salt effect. The rate data have been analyzed with the aid of the thermodynamic dissociation constants of the ionophores evaluated from conductance data by Shedlovsky's procedure and of activity coefficients calculated by means of the De-

bye-Hückel equation and are consistent with the rate law $R_o = k_f(RBr)(Br^-) + k_p(RBr)(M^+Br^-)$ which ascribes different reactivities to free and paired ions. The magnitudes of k_p , but not of k_f , depend to a substantial degree on the values assigned to α_{DH} , the Debye-Hückel "distance of closest approach." Calculations carried out with an IBM 650 computer show that no value of the Debye-Hückel α -parameter in the range from 0 to 30 Å. provides a uniquely superior correlation of the data. The validity of the analysis in terms of k_f and k_p is supported by the fact that k_f is independent of the nature of the cation. In contrast, k_p varies with the nature of the cation in the same sense as does K_d : more tightly bound ion pairs are less reactive. These results support the view that the discrimination between free and paired ions provided by conductivity measurements serves to identify species which differ in their kinetic reactivity but they yield no critical information concerning the precise nature of the paired species. The data are equally consistent with Fuoss' "ions in contact" model or with Bjerrum's original statistical model. The data indicate that SN-1 contribution to the reaction is negligible or, at most, minor. The data are not capable of discriminating between the analysis in terms of k_f and k_p and a treatment based on catalysis by free cation of displacement by free anion.

Introduction

It has been known for a long time that, particularly in smenogenic³ solvents, reactions of ionic reagents display dependence of specific rate on concentration of the ionophore.³ The increase in second order specific rate with decrease in concentration of ionophore which is observed in many reactions between neutral molecules and ionic reagents was reported⁴ as early as 1890 and was

explored extensively by Acree and his students during the first two decades of this century.⁵ Acree⁵⁻⁷ employed his "dual hypothesis," represented essentially by equation 1, where α is the degree of dissociation, to account for these results by assigning different specific rates to free ion (k_f) and associated species (k_p). Although Brønsted

$$k_2^{obsd.} = \alpha k_f + (1 - \alpha)k_p \quad (1)$$

rejected⁸ Acree's analysis and regarded it as based on "a misunderstanding of salt effect," it has been subsequently accepted by a number of workers.

(1) Research carried out under the auspices of the U. S. Atomic Energy Commission.

(2) Based on a dissertation submitted by K. N. Rao in fulfillment of a requirement for the Ph.D. degree granted by Boston University in June, 1960. Cf. N. N. Lichtin and K. N. Rao, Abstracts of the 134th meeting of the American Chemical Society, Chicago, Ill., Sept. 1958, p. 12-S for a preliminary communication.

(3) R. M. Fuoss, *J. Chem. Ed.*, **32**, 527 (1955).

(4) W. Hecht, M. Conrad and C. Bruckner, *Z. physik. Chem.*, **5**, 289 (1890).

(5) Cf. H. C. Robertson and S. F. Acree, *J. Am. Chem. Soc.*, **37**, 1902 (1915).

(6) J. H. Shroder and S. F. Acree, *J. Chem. Soc.*, 2582 (1914).

(7) E. K. Marshal and S. F. Acree, *J. Phys. Chem.*, **19**, 589 (1915).

(8) J. N. Brønsted and E. A. Guggenheim, *J. Am. Chem. Soc.*, **49**, 2557 (1927).