[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Mechanisms of Exchange Reactions between Acyl Halides and Molecular Halogens

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Benzoyl iodide and bromide undergo isotopic exchange with elementary iodine and bromine, respectively, in non-polar solvents at room temperature. The data can be accounted for satisfactorily by means of two parallel mechanisms, each containing one molecule of benzoyl halide and either one or two molecules of halogen in the transition state. Radical processes make no significant contribution to the rate even when the solutions are illuminated, but the rates are very sensitive to traces of moisture. The exchange of benzoyl iodide involves a very negative entropy of activation, and its rate depends as strongly on dielectric constant as do the rates of reactions that are known to form discrete ion pairs. The transition state for the bimolecular exchange mechanism seems to be very close to that involved in forming the ion pair $C_6H_5CO^+I_3^-$. Very low concentrations of iodine can strongly catalyze the exchange between benzoyl bromide and bromine, but the mechanism of the catalysis has not been elucidated. Acetyl iodide exchanges with iodine either by a very rapid homogeneous process or by a heterogeneous process induced during precipitation of iodine by cooling to Dry Ice temperatures.

Introduction

Several previous publications from this Laboratory have been concerned with elucidating the mechanisms of isotopic exchange reactions of elementary bromine and iodine with various organic halides. All of the compounds studied previously contained only carbon and hydrogen in addition to halogen. Although the reactions exhibited a wide range of kinetic behavior, all of the compounds appeared to undergo at least part of their exchange by free radical mechanisms. In addition, allyl iodide[2] exchanged with molecular iodine, and iodobenzene[3] underwent exchange by a non-radical mechanism that has not yet been completely elucidated.

The present paper describes an extension of these studies to the acyl halides in which the oxygen exerts a very polar influence. The exchange reactions of these compounds appear to go entirely by non-radical mechanisms and exhibit features different from any we have observed previously.

Experimental

Materials.—Benzoyl iodide was prepared from the action of excess hydrogen iodide on benzoyl chloride as described by Staudinger and Anthes.[4] The anhydrous hydrogen iodide was obtained by a modification of the method of Meyer.[5] It was generated by the reaction of aqueous suspensions of iodine and phosphorus, freed of iodine and phosphonium iodide, dried and introduced into the benzoyl chloride until twice the stoichiometric amount had been added. The product was shaken with mercury to remove iodine, and purified by vacuum distillation. The fraction finally taken boiled at 91.5–92.0° at 4 mm. The pure material was quite sensitive to air oxidation, so it was usually dissolved in a solvent soon after preparation. The resulting solution was then sealed under nitrogen and stored at −5° until it was ready for use. Solutions were analyzed by hydrolyzing with aqueous alkali, removing the organic solvent, and titrating the acidified solution with silver nitrate using eosin as indicator.[6] Analyses by this method checked to 0.4% or better with concentrations calculated from the weights of benzoyl iodide used to make up the solutions.

Acetyl iodide was prepared from acetyl chloride and hydrogen iodide by the same procedure. The fraction taken boiled at 53–54° at 145 mm.

Reagent grade resublimed iodine was used without further purification. Since the magnesium sulfate drying agent seemed to adsorb some iodine, concentrations of dilute solutions had to be measured spectrophotometrically rather than calculated from the weight of dissolved material. Solutions in various solvents were activated by shaking with aqueous carrier-free iodine-131 obtained on allocation by the United States Atomic Energy Commission.

Benzoyl bromide was obtained from Eastman Kodak Co. and purified by distillation. The portion boiling between 107.3 and 107.5° was used for the experiments. Solutions were analyzed by the same hydrolysis procedure employed with benzoyl iodide.

N.F. grade bromine was distilled from anhydrous calcium bromide. Solutions were analyzed iodometrically with standardized thiosulfate.

Solutions of bromine in carbon tetrachloride were activated for exchange studies by shaking with aqueous solutions of KBr^{82} prepared by neutron activation and obtained on allocation by the United States Atomic Energy Commission. The activated solutions were dried with magnesium sulfate.

The solvents used in the iodine studies were hexane, carbon tetrachloride, chlorobenzene and 1,2-dichloroethane. Only carbon tetrachloride was used in the bromine studies. The solvents were purified either with acidic permanganate or concentrated sulfuric acid, dried and distilled. Experiments with radioactive halogen showed that no solvent contained more than 5×10^{-7} mole/liter of material capable of forming organically bound halogen under the most severe conditions used in our experiments.

Procedure.—Kinetic runs on the exchange reactions were carried out at 0, 25 and 40° either in an ice-bath or a conventional water thermostat. The flasks contained two separate compartments so that solutions could be pipetted and thermostated before they were mixed rapidly by inverting and shaking. During a run, six aliquot samples were pipetted into separatory funnels containing slightly acidified aqueous sulfite, and the free halogen was reduced and extracted. Usually the radioactivity was only counted in the organic layer, but frequent checks in which both layers were counted usually agreed to within 1% with the total activity measured on the original solution.

The procedure was tested for possible difficulties. When a solution of radioactive benzoyl iodide was shaken with aqueous sulfite under especially severe conditions, only 1% of the activity was transferred to the aqueous layer. Similarly, it was demonstrated that iodide ion did not exchange significantly with benzoyl iodide during the conditions of the separation. Finally, straight lines were obtained for several half-lives when the logarithm of the distance from exchange equilibrium was plotted against time. Since these straight lines extrapolated to a few per cent. of apparent exchange at zero time, the method apparently caused a little induced exchange that was unimportant for the evaluation of the slopes of the semi-logarithmic plots. Similar tests of the exchange between benzoyl bromide and bromine indicated that the separation procedure was also valid for this reaction.

The kinetic data suggested the desirability of making some additional measurements. The spectrophotometric measurements were made with either a Cary recording spectrophotometer or a Beckman quartz DU spectrophotometer. Measurements of dielectric constant were made with a standard heterodyne-beat apparatus in which changes in

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[1] Based on the Ph.D. dissertation of Alex Goldman. The original dissertation and microfilms thereof are available from the Library of Columbia University.

[2] D. J. Sibbett and R. M. Noyes, THIS JOURNAL, **75**, 761 (1953).

[3] S. Levine and R. M. Noyes, to be published.

[4] H. Staudinger and E. Anthes, *Ber.*, **46**, 1417 (1913).

[5] L. Meyer, *ibid.*, **20**, 3381 (1881).

[6] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, p. 572.

capacity of the cell were balanced against opposing changes in the setting of a precision condenser. The differences in capacity of the meshed and unmeshed positions of a variable condenser were read both when the condenser was in air and immersed in the liquid of interest.

Results

Studies with Acetyl Iodide.—A preliminary attempt was made to study the exchange of acetyl iodide and iodine in hexane. However, we were unable to find a chemical procedure for separating the species. The iodine could be removed by freezing the solution to Dry Ice temperatures and filtering, and radioactive measurements by this procedure always indicated complete exchange. Subsequent studies with benzoyl iodide indicated accelerated exchange whenever traces of solid iodine were present. The experiments with acetyl iodide indicate only that either homogeneous or induced exchange is very rapid.

Exchange of Benzoyl Iodide.—The exchange reaction between benzoyl iodide and iodine was studied in hexane at 0, 25 and 40°, and it was also studied at 25° in carbon tetrachloride, chlorobenzene and 1,2-dichloroethane. The rate of exchange seemed slightly more than first order in benzoyl iodide and between first and second order in iodine. Except at very low iodine concentrations, the data could be fitted fairly satisfactorily by an expression of the form

$$R = k_1[\mathrm{BzI}][\mathrm{I_2}] + k_2[\mathrm{BzI}][\mathrm{I_2}]^2 \qquad (1)$$

In this equation, R is the rate of exchange calculated by conventional equations and BzI is benzoyl iodide.

In order to evaluate rate constants, $R/[\mathrm{BzI}][\mathrm{I_2}]$ was plotted against $[\mathrm{I_2}]$. Figure 1 illustrates such a plot for all data in hexane with 0.201 M benzoyl iodide. Because of the lower solubility of iodine at 0°, the data at this temperature could not be carried to as high concentrations. At each temperature, values of k_1 and k_2 were then obtained for each concentration of benzoyl iodide by a least squares fit to a plot like Fig. 1, the data at the very lowest concentrations of iodine being neglected. The results are summarized in Table I.

TABLE I

RATE CONSTANTS FOR EXCHANGE OF BENZOYL IODIDE AND IODINE

Solvent	Temp., °C.	[BzI], mole/l.	$k_1 \times 10^3$, l./mole sec.	k_2, l.^{2}/mole^2 sec.
C_6H_{14}	40.0	0.201	16.8	1.68
		.0402	11.1	0.724
		.01005	9.73	.579
C_6H_{14}	25.0	0.201	9.32	1.38
		.0402	8.35	0.638
		.01005	7.87	.438
		.00396	6.88	.389
C_6H_{14}	0.0	0.201	3.21	0.803
		.0402	3.39	.453
CCl_4	25.0	0.1787	11.5	2.14
		.0357	9.49	1.32
C_6H_5Cl	25.0	[a]	134	11.6
$C_2H_4Cl_2$	25.0	[a]	556	72.5

[a] Only a few runs were made in these solvents, and no attempt was made to separate the effects of changing benzoyl iodide concentration. Because of the greater dielectric constants of these solvents, the effects of benzoyl iodide concentration probably were less.

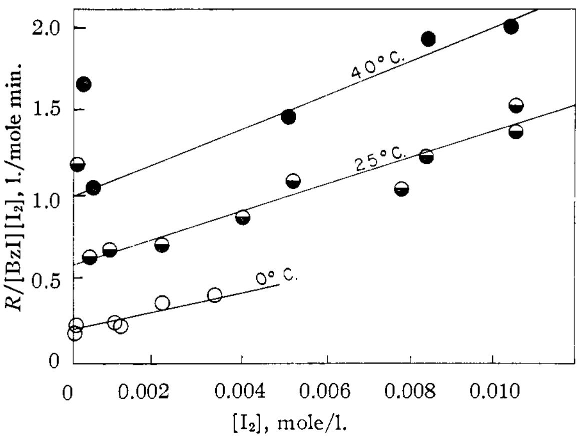

Fig. 1.—Exchange of iodine with 0.201 M benzoyl iodide in hexane.

The deviations at iodine concentrations below 5×10^{-4} M could be fitted fairly satisfactorily if an additional term $k_0[\mathrm{BzI}]$ were added to equation 1. This term had a trivial influence on all except one or at most two points in any series, so the above method of evaluating k_1 and k_2 was satisfactory. Except for lower values at 0°, values of k_0 were all within a factor of three of 10^{-6} sec.$^{-1}$ and have not been tabulated because they were so poorly defined by the few points involving contributions by this term. The mechanistic significance of this term is not clear, but we are inclined to ascribe it to effects of hydrolysis as described below.

The data in hexane suggest that the rate of exchange is proportional to more than the first power of benzoyl iodide concentration. The less extensive runs in other solvents indicate a strong dependence on dielectric constant that is summarized in Table II. Some of the more concentrated solutions of benzoyl iodide in hexane had almost the same dielectric constants as more dilute solutions in carbon tetrachloride and exchanged with almost identical rate constants. It therefore appears that the variation in rate constants indicated in Table I is a medium effect due to changing dielectric constant rather than an order greater than unity in benzoyl iodide.

TABLE II

EFFECT OF DIELECTRIC CONSTANT ON EXCHANGE OF IODINE WITH 0.2 M BENZOYL IODIDE AT 25°

Solvent	Dielectric constant of benzoyl iodide soln.	Relative rate constants k_1	k_2
C_6H_{14}	2.13	1	1
CCl_4	2.45	1.3	1.7
C_6H_5Cl	5.5	14	8
$C_2H_4Cl_2$	10.1	60	53

The rate constants that were evaluated at three temperatures were fitted to the standard Arrhenius equation $k = Ae^{-E/RT}$, and the values of the parameters are summarized in Table III along with entropies of activation calculated from the usual formulation of absolute reaction rate theory. The indicated uncertainties are probable errors estimated from the fit of individual runs to equation 1.

Exchange of Benzoyl Bromide.—The exchange reaction between benzoyl bromide and bromine

TABLE III

PARAMETERS FOR TEMPERATURE DEPENDENCE OF BENZOYL IODIDE-IODINE EXCHANGE IN HEXANE

Rate constant	[BzI], mole/l.	E, cal./mole	A		$\Delta S^{\ddagger}$, cal./mole deg.
k_1	0.201	7050 ± 370	$10^{3.15 \pm 0.28}$	l./mole sec.	−46
	.0402	5060 ± 330	$10^{1.59 \pm 0.25}$		−53
k_2	0.201	3040 ± 540	$10^{2.36 \pm 0.39}$	l.^{2}/mole^2 sec.	−50
	.0402	1890 ± 1460	$10^{1.18 \pm 1.05}$		−55

could only be studied in carbon tetrachloride because the other solvents of this study were attacked by bromine. The reagent solutions were more concentrated than those used for the benzoyl iodide exchange because the rates of the benzoyl bromide reactions were considerably slower. No attempt was made to study the effect of dielectric constant on rate, but the effect of benzoyl bromide concentration suggested that k_2 was more dependent than k_1 on changes in dielectric constant.

The kinetics appeared to be identical to those for the benzoyl iodide exchange even to the apparent need to add a term k_0[BzBr] to treat bromine concentrations less than 0.01 M. Values of k_1 and k_2 are summarized in Table IV; values of k_0 were within a factor of two of 1.5×10^{-6} sec.$^{-1}$ and hence were the same as or slightly larger than those for benzoyl iodide.

TABLE IV

RATE CONSTANTS FOR EXCHANGE OF BENZOYL BROMIDE AND BROMINE IN CARBON TETRACHLORIDE

Temp., °C.	[BzBr], mole/l.	$k_1 \times 10^5$, l./mole sec.	$k_2 \times 10^3$, l.^{2}/mole^2 sec.
40.0	0.966	26.1	6.51
	.271	23.4	1.83
	.0551	20.7	1.58
25.0	0.966	6.52	2.29
	.271	6.00	0.716
	.0551	10.9	1.04

The parameters for temperature dependence are presented in Table V. The large estimated uncertainties reflect the disadvantages of basing activation quantities on measurements at two temperatures only 15° apart.

TABLE V

PARAMETERS FOR TEMPERATURE DEPENDENCE OF BENZOYL BROMIDE-BROMINE EXCHANGE

Rate constant	[BzBr], mole/l.	E, cal./mole	A		$\Delta S^{\ddagger}$, cal./mole deg.
k_1	0.966	17,200 ± 3400	$10^{8.4 \pm 2.4}$	l./mole sec.	−22
	.271	16,800 ± 7200	$10^{8.1 \pm 5.0}$		−23
k_2	0.966	12,900 ± 1000	$10^{6.8 \pm 0.7}$	l.^{2}/mole^2 sec.	−29
	.271	11,600 ± 2800	$10^{5.4 \pm 2.0}$		−36

Effects of Light.—All of the exchange reactions that we have studied previously have been sensitive to photochemical influences. Test runs were made under dark and light conditions on both the benzoyl iodide and benzoyl bromide exchanges. The rates of light and dark runs were identical within a few per cent. and showed no consistent tendency for one or the other to be faster. Any contribution of halogen atoms to the exchange is too small to detect under the conditions of our experiments.

Effects of Moisture.—The kinetic studies reported above were made with dried solutions. When about 10 mg./50 ml. (roughly 0.01 M) water was added to a solution that was 0.0402 M in benzoyl iodide and 0.00418 M in iodine, the rate of exchange was increased by a factor of 2.5. When the same amount of water was added to a solution that was 0.966 M in benzoyl bromide and 0.0157 M in bromine, the data were scattered but indicated that the rate of exchange was increased several fold.

The increases in rate may be merely a dielectric constant effect accentuated by a preferential interaction with the very polar water molecules. In addition, they may involve a very rapid catalysis by hydrogen iodide or hydrogen bromide formed by hydrolysis of the benzoyl halide. Available data indicate a very rapid homogeneous exchange between hydrogen halide and free halogen,[7] and the hydrogen halide might well also exchange rapidly with an acyl halide.

In the preceding discussion, the anomalously fast exchange at very low halogen concentrations has been formally described by adding a term that is zero order in halogen. The extreme sensitivity to moisture suggests that this additional term may be associated with the hydrolysis reaction. We were not able to develop a simple procedure for testing this hypothesis by studying the reaction at low halogen concentrations without letting the solutions come in contact with the air of the laboratory. At higher concentrations of halogen, the reproducibility of the kinetics indicates that stray moisture probably was not a major problem, although the sensitivity to water is probably the major obstacle to improving the precision of the measurements reported here.

Tests for Nuclear Halogenation.—The exchange measurements only determine radioactive halogen atoms that have become organically bound and are no longer extractable with aqueous sulfite. It is assumed that the only reaction is exchange, but halogenation of the benzene ring could also form organically bound halogen. To test this possibility, a sample of benzoyl iodide was allowed to stand with radioactive iodine until 80% exchange had occurred. The benzoyl iodide was then hydrolyzed with hot alkali, acidified and extracted with water. Less than 1% of the activity remained in the organic layer, so the original formation of organic iodide appears to have been a true exchange reaction. A similar test with benzoyl bromide and bromine gave even more definite evidence that the kinetic data reported above measured a simple exchange reaction without complication from halogenation of the aromatic nucleus.

Evidence for Complex Formation.—Since the benzoyl iodide exchange included contributions from terms that were higher than first order in iodine, it seemed plausible that some of the exchange might involve reaction of iodine with a complex formed from benzoyl iodide and iodine. Qualitative evidence for such a complex was provided by color changes when chilled solutions of benzoyl iodide and iodine were mixed. A spectrophotometric study by the method of continuous vari-

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(7) H. Jacobson, *J. Chem. Phys.*, **18**, 994 (1950).

ations[8] did indeed suggest an interaction between the species, but the precision was too poor to draw any quantitative conclusions about the stoichiometric formula or equilibrium constant for complex formation.

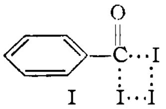
Iodine Catalysis of Bromide Exchange.—Since several bromine reactions are catalyzed by iodine, a few experiments were made in which small amounts of iodine were added to exchange runs containing benzoyl bromide and radioactive bromine in concentrations at least 10 times as great. When iodine was 0.004 *M*, the rate of bromine exchange seemed to be increased about 70 fold at 25° and 20–30 fold at 40°. When the iodine was 0.0008 *M*, the rate was increased about 10 fold at 25° and 5 fold at 40°. The experiments did not constitute a complete kinetic study but did suggest that changing concentrations of bromine and benzoyl bromide had rather little effect on the factor by which added iodine increased the rate of exchange. The temperature dependence suggested that the activation energy was only about 2500 cal./mole for the catalyzed reaction.

The test for nuclear halogenation was applied to a solution in which exchange had been catalyzed by iodine. Although most of the radioactivity could be hydrolyzed fairly easily, about 8.5% remained organically bound and presumably was attached to the aromatic nucleus. This side reaction indicates that a more thorough experimental procedure is necessary for a quantitative treatment of the kinetics of the iodine catalyzed exchange.

Discussion

General Considerations.—The integral order kinetics and absence of photochemical effects definitely rule out any significant contribution from radical processes involving free halogen atoms. The detailed interpretation is somewhat complicated, but the data seem most consistent with the existence of two parallel mechanisms for exchange. One mechanism is bimolecular with a transition state containing one molecule of benzoyl halide and one molecule of halogen; the other is termolecular and contains an additional molecule of halogen in the transition state.

The Bimolecular Mechanism.—A superficially plausible mechanism of the bimolecular exchange between benzoyl iodide and iodine could involve the formation of a simple cycle configuration like I.


I

However, both the value of the Arrhenius *A* term and the effect of dielectric constant suggest that the transition state is considerably more polar than this simple representation would indicate.

The pre-exponential *A* term in the Arrhenius equation is frequently of the order of 10^{10} liter/mole sec. for reactions between neutral molecules, and deviations of more than two orders of magnitude are comparatively rare. The large probable errors in the benzoyl bromide data make it impossible to say with certainty that the *A* term is anomalously low, but the data in Table III on the benzoyl iodide exchange indicate that especially in dilute solution the *A* term is lower by several orders of magnitude than is at all customary for second-order reactions. In fact, it is almost unprecedented for a reaction with an activation energy below 10 kcal./mole to be amenable to kinetic study at room temperature by conventional methods. The very low entropies of activation are comparable to those reported[9] in similar solvents for substitution reactions that form ions or ion pairs.

The effect of dielectric constant provides at least as striking evidence for the polarity of the transition state. If the dielectric constant of the medium is the only factor influencing rate of reaction, one can write[10]

$$\frac{\mathrm{d}\ln k}{\mathrm{d}\,[(D-1)/(2D+1)]} = -\frac{N}{RT}\left[\frac{\mu_{\mathrm{A}}^{2}}{r_{\mathrm{A}}^{3}} + \frac{\mu_{\mathrm{B}}^{2}}{r_{\mathrm{B}}^{3}} - \frac{\mu_{\ddagger}^{2}}{r_{\ddagger}^{3}}\right] \quad (2)$$

This expression applies to the reaction of neutral molecules A and B to form a transition state, while *r* denotes a molecular radius and μ a dipole moment. The data in Table II fit fairly well to the predicted relationship and give $\mathrm{d}\ln k_1/\mathrm{d}[(D-1)/(2D+1)] = 19$. The Menschutkin reaction of pyridine with benzyl bromide has been studied in benzene–alcohol mixtures of roughly the same range of dielectric constants, and a similar treatment of the data[11] gives $\mathrm{d}\ln k/\mathrm{d}[(D-1)/(2D+1)] = 13$. Also, for the reaction of triphenylphosphine with sulfur Bartlett and Meguerian[12] find a factor of 13 increase in rate on going from carbon tetrachloride to chlorobenzene; a factor of 11.5 is found for the values of our k_1 in the same two solvents. The Menschutkin and phosphine–sulfur reactions are postulated to involve formation of an ion pair and a zwitterion, respectively.

All of the above arguments suggest that the second-order exchange of iodine and benzoyl iodide involves a transition state as polar as that in reactions forming discrete ion-pair species. The exchange reaction may actually involve an ion-pair intermediate such as II

$$C_6H_5CO^+I_3^- \quad \mathrm{II}$$

Certainly the transition state is well on the way toward formation of such an intermediate. It is surprising that the preferred path for reaction in a solvent like hexane would involve an intermediate of this sort, and the stability of the I_3^- ion in aqueous solution is not enough to suggest that II could be formed in a process having such a low activation energy. However, we do not see any other way to account for the low *A* factor and the large dependence of the rate on the dielectric constant of the medium.

Because the bromine attacked several of the solvents used in the iodine work, it was not possible to study the effect of dielectric constant on the ex-

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[8] W. C. Vosburgh and G. C. Cooper, THIS JOURNAL, **63**, 437 (1941).

[9] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 1953, p. 128.

[10] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 423.

[11] Ref. 10, p. 421.

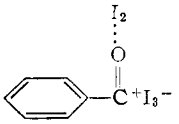
[12] P. D. Bartlett and G. Meguerian, THIS JOURNAL, **78**, 3710 (1956).

change of benzoyl bromide. The effect of added benzoyl bromide on the rate constant was not clearly different from the corresponding effect of benzoyl iodide, but the Arrhenius A factor for this reaction was larger than for the benzoyl iodide exchange. The transition state for the benzoyl bromide exchange may be less polar than for benzoyl iodide, but the kinetic behaviors are so similar that probably there is no great difference in mechanisms for the two reactions.

The Benzoyl Iodide–Iodine Complex.—Iodine is known to form complexes with various organic iodides and also with compounds containing carbonyl oxygen. Keefer and Andrews[13] have shown that for complexes with alkyl iodides the order of stabilities is in the direction to be expected if iodine is acting as an electron acceptor, and Mulliken[14] has interpreted the absorption spectra of several of these complexes in terms of a charge-transfer process leading to negative halogen.

The spectrophotometric data indicate a small but significant concentration of a complex between benzoyl iodide and iodine, but there does not seem to be any *a priori* means of deciding whether the oxygen or iodine atoms of the benzoyl iodide are complexed. As long as the equilibrium involving the complex is rapid compared to the exchange reaction, kinetic measurements can never provide any information as to whether or not the complex is an intermediate for either the bimolecular or termolecular mechanisms, but it is plausible that the termolecular mechanism involves reaction of a halogen molecule with some sort of metastable complex of benzoyl halide and halogen.

The Termolecular Mechanism.—The third-order exchange of benzoyl iodide with iodine has a very low entropy of activation, and d ln k_2/d $[(D - 1)/(2D + 1)] = 17$. These facts indicate that the termolecular transition state has about as much ion pair character as that for the bimolecular mechanism. The five iodine atoms in the transition state may be grouped in a ring or incipient I_5^- structure around the carbon at which exchange takes place. Alternatively, the second molecule of iodine may be complexed with oxygen as in III


III

In such a structure, the large polarizability of the iodine would help to delocalize the positive charge and so to stabilize the almost ion-pair transition state.

The ratio $k_2/k_1 = e^{-\Delta\Delta F^{\ddagger}/RT}$ where $\Delta\Delta F^{\ddagger}$ is the difference in free energy between a termolecular transition state and a bimolecular transition state and separate halogen molecule. The data in Tables I and IV indicate that k_2/k_1 is about ten times as large for the benzoyl iodide exchange as it is for the bromide exchange at comparable concentrations of benzoyl halide. This means that adding a molecule of iodine to the transition state for bimolecular benzoyl iodide exchange has a greater absolute effect on the free energy than adding a molecule of bromine to the transition state for bimolecular benzoyl bromide exchange, and the percentage effect on the free energy of activation is greater still. The effect is in the direction the greater polarizability of iodine would lead one to predict if the termolecular transition state looks somewhat like III. However, the argument is not compelling.

If the addition of a polarizable halogen molecule facilitates exchange, the presence of more halogen molecules might lower the energy still further. Aggregates of larger numbers of iodine molecules would have greater tendency to form in more concentrated solutions and could account for the anomalously fast rates that were obtained in solutions that were almost saturated with iodine. According to this explanation, nuclei and crystals of iodine should promote exchange very effectively. The data with acetyl iodide always indicated complete exchange when the iodine was removed by precipitation at Dry Ice temperatures, but the exchange could have been induced heterogeneously during the precipitation process.

The Iodine-catalyzed Exchange of Benzoyl Bromide.—Both chlorine and bromine liberated iodine almost instantaneously from benzoyl iodide. The equilibrium reaction

$$2C_6H_5COI + Br_2 \rightleftharpoons 2C_6H_5COBr + I_2 \qquad (3)$$

is clearly displaced far to the right, but we do not have quantitative data that unequivocally rule out benzoyl iodide as an intermediate in the iodine-catalyzed exchange of benzoyl bromide. However, the reaction from right to left in equation 2 is clearly unfavorable energetically and should go distinctly slower than the exchange of benzoyl iodide with iodine, which involves no net change in free energy. Nevertheless, in the presence of small amounts of iodine, benzoyl bromide exchanges with bromine much faster than benzoyl iodide would exchange with these catalytic concentrations of iodine.

Although it seems inescapable that both iodine and bromine are involved in the transition state for this rapid catalyzed exchange of bromine with benzoyl bromide, the kinetic data are not sufficiently extensive to provide much information about the mechanism of the reaction. It may be that IBr reacts much more effectively than Br_2 in the bimolecular mechanism. It may also be that a molecule of I_2 or IBr is much more effective than Br_2 in promoting the exchange of another molecule of Br_2 or IBr with benzoyl bromide by the termolecular mechanism.

Molecular Substitution Reactions of Saturated Iodides.—The results reported here seem somewhat related to those obtained by other workers on the substitution reactions of saturated iodides by chlorine, bromine and iodine monochloride. The kinetic studies of Keefer and Andrews[15] have demonstrated that these substitution reactions involve two molecules of halogen in the transition state and that a significant fraction of the alkyl iodide is tied up as a complex that may be an intermediate in the

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[13] R. Keefer and L. Andrews, This Journal, **74**, 1891 (1952).

[14] R. S. Mulliken, *J. Phys. Chem.*, **56**, 801 (1952).

[15] R. M. Keefer and L. J. Andrews, This Journal, **75**, 543 (1953); **76**, 253 (1954).

reaction. Both Corey and Wechter[16] and Beringer and Schultz[17] have shown that these molecular substitution reactions take place predominantly with inversion of configuration. The termolecular mechanism of exchange of the benzoyl halides may involve a process very similar to the mechanisms proposed by these authors for the substitution reactions of saturated iodides.

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NEW YORK 27, N. Y.

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[16] E. J. Corey and W. J. Wechter, THIS JOURNAL, **76**, 6040 (1954).

[17] F. M. Beringer and H. S. Schultz, *ibid.*, **77**, 5533 (1955).

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

The Deuterium Isotope Effect on the Rate of Reaction of Hydrogen and Iodine[1]

BY ELLINGTON M. MAGEE[2]

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The ratio of rate constants has been determined for the reactions $H_2 + I_2$ and $HD + I_2$. An experimental method was used whereby errors in temperature, time and concentrations were negligible. The ratios of H_2:HD were determined in the reactants and in the first product formed. The value for k_{H_2}/k_{HD} was found to be 1.55. The significance of this result is discussed in relation to past experimental and theoretical work.

Introduction

The isotope effect on the rates of chemical reactions offers an excellent method for the accurate, experimental determination of the structural parameters of the activated complex. Recent calculations have been made by Polanyi,[3] using a "calibrated" activation energy barrier, for the reactions of various hydrogen isotopes with methyl radicals. Such calculations would be possible for simpler systems, such as the reaction of hydrogen and iodine if enough experimental data were available. This paper presents some of the necessary data.

The reaction of hydrogen with iodine to form hydrogen iodide and the reverse reaction are two of the best known, homogeneous, gaseous reactions. The rates were studied in the work of Bodenstein,[4] Kistiakowsky[5] and others and a review of much of the work is given by Kassel.[6] The reaction has been found to be first order with respect to each of the two reactants and homogeneous in the concentration range of 2×10^{-5} to 1×10^{-3} mole cc.$^{-1}$ when the reaction is carried out in quartz vessels.

Several workers have measured the rate constants for the reaction of deuterium with iodine and for the reverse reaction.[7,8] The average value for k_{H_2}/k_{D_2} from ref. 7a, 7b and 8a (the value obtained in ref. 8b is believed to be erroneous[7b]) is 1.97 ± 0.08 and the corresponding average ratio, k_{HI}/k_{DI} for the reverse reaction is 1.61 ± 0.06. The theoretical values calculated for the two ratios are 2.34 and 1.92, respectively.[9] The calculated values are seen to be in some disagreement with the values found experimentally. It was hoped that a measurement of the ratio of rate constants for the two reactions

$$H_2 + I_2 \xrightarrow{k_{H_2}} 2HI \qquad (1)$$

$$HD + I_2 \xrightarrow{k_{HD}} HI + DI \qquad (2)$$

would provide data that would point out corrections to be made in the *a priori* calculation of the potential surface for the hydrogen–iodine reaction.

Experimental

The ratio of rate constants for reactions 1 and 2 could be found by determining the rate constant for each reaction and taking the ratio of the two. This procedure would involve very precise measurements and control of temperature, time and concentration. Further, HD must be prepared free of H_2 and D_2. A simpler method was devised which removed the necessity of accurate measurement and control of the experimental conditions mentioned above.

By taking the ratio of rate expressions for reactions 1 and 2, eq. 3 is obtained.

$$d(H_2)/d(HD) = [k_{H_2}/k_{HD}][(H_2)/(HD)] \qquad (3)$$

The left side of (3) can be approximated closely by R_p, defined as the ratio of $(H_2)/(HD)$ in the first products of a reaction of iodine with a mixture of H_2 and HD. The ratio $(H_2)/(HD)$ at the right of eq. 3 is defined as R_0 and is the ratio of hydrogen to deuterium hydride in the initial reactants. Then

$$k_{H_2}/k_{HD} = R_p/R_0 \qquad (4)$$

Since the reaction must proceed far enough to give sufficient product for a determination of R_p, and since k_{H_2}/k_{HD} is larger than unity, this relation is not exact. A small correction may be made easily which gives a value of k_{H_2}/k_{HD} that is accurate to well within experimental error. Integration of eq. 3 gives

$$\ln(1 - f) = (k_{H_2}/k_{HD})\ln(1 - f^{\ddagger}) \qquad (5)$$

where the f and $f^{\ddagger}$ are the fractions of the H_2 and HD which have reacted. The value of f can be estimated from the initial concentrations of the reactants, the rate constant, and the time; and it needs to be only approximately correct. To a first approximation $f^{\ddagger}$ is equal to f divided by the approximate value of k_{H_2}/k_{HD} found by eq. 4. Solution of eq. 5 then gives a value of k_{H_2}/k_{HD} which is correct except for a third-order approximation.

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[1] Presented in a thesis for the partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, June, 1956.

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