Some of the same arguments make it hard to understand how the abstraction mechanism can be important for all compounds at all temperatures. Unless reported carbon–iodine bond dissociation energies are badly in error, some other explanation must be found for the oxygen inhibition. The results could be accommodated by the reversible formation of an IO_2 intermediate that was about half as reactive as a free atom, but a considerable body of evidence at lower temperatures[23] argues against the existence of such an intermediate.

A reasonably satisfactory explanation of all of our observations is possible if carbon–iodine bond dissociation energies are not much more than about 45 kcal./mole instead of the higher values claimed and if the effects of α-methyl replacement on the rate of nucleophilic substitution is primarily a steric inhibition of solvation rather than a steric hindrance for attack on the carbon undergoing the substitution. However, these revisions of current ideas are too drastic to accept without more evidence than we have accumulated here.

Chain Initiating Reactions.—Calculated values of R_1 are based on extrapolations of over a hundred degrees of measurements made at lower temperatures. They serve only to indicate orders of magnitude, but the calculations certainly indicate that chain lengths often are quite short. In fact,

(23) (a) J. Zimmerman and R. M. Noyes, J. Chem. Phys., 18, 658 (1950); (b) D. J. Sibbett and R. M. Noyes, THIS JOURNAL, 75, 763 (1953); (c) F. W. Lampe and R. M. Noyes, ibid., 76, 2140 (1954).

it is hard to explain some of the oxygen kinetics unless iodine atom production is somewhat faster than our computed values of R_1. If iodine atoms are produced by uncatalyzed dissociation of I_2 molecules, the activation energy must be at least 3 kcal./mole greater than the gas phase bond dissociation energy. Such a difference is quite plausible.

Decomposition Reactions.—The rates of decomposition are too scattered for us to draw any reliable mechanistic conclusions. The irreproducibility of these measurements suggests that trace impurities are at least partly involved in the processes causing iodine production. However, it may be significant that decomposition rates are lower for methyl and neopentyl iodides than for the others. These compounds do not have hydrogens on carbons beta to iodine, and they are the only compounds studied that cannot undergo processes like P1 and P2 mentioned in the discussion of isopropyl iodide.

Mechanisms of Exchange Reactions of t-Butyl Iodide with Elementary Iodine

BY JOHN E. BUJAKE, JR.,[1] AND RICHARD M. NOYES[2]

t-Butyl iodide exchanges with elementary iodine near room temperature by two parallel non-radical mechanisms that are not influenced by light. The *bimolecular* mechanism is first order each in t-butyl iodide and in molecular iodine and at 25° is significant only in the solvents chlorobenzene and ethylene dichloride that have dielectric constants greater than 5. The rate depends on dielectric constant more strongly than has been found for other reactions known to form ion pairs, and it is proposed that the exchange involves an ion pair intermediate $C_4H_9{}^+I_3{}^-$. The *termolecular* mechanism is first order in t-butyl iodide and second order in molecular iodine and shows a dependence on dielectric constant comparable to that for reactions forming ion pairs. It is proposed that the exchange involves either nucleophilic attack by an iodine molecule on a $C_4H_9I_3$ neutral complex or by an $I_3{}^-$ component of an ion pair on the $C_4H_9I_2{}^+$ component. Cooling solutions to Dry Ice temperatures causes complete exchange apparently induced on the surface of iodine precipitated by the cooling. At 25°, the exchange of t-butyl iodide with 0.02 M iodine in hexachlorobutadiene is 7×10^6 times as fast as the exchange of isopropyl iodide under the same conditions as predicted by extrapolation from 130°. This extreme difference in reactivity suggests that for reactions proceeding through ionic or ion-pair intermediates the effects of structure on reactivity will be most pronounced in less polar solvents because in these solvents the separation of charge is promoted less by solvation and more by the nature of the species in which charge separation is occurring.

Introduction

The work described here is part of a systematic study of the exchange of elementary iodine with various alkyl iodides that was undertaken to learn more about the effects of changing structure on the parameters affecting rates of radical reactions. All of the primary and secondary iodides that were studied[3] did indeed appear to exchange by radical

processes initiated by free iodine atoms. However, t-butyl iodide exchanged much more rapidly than these other iodides. The reaction obviously received negligible contribution from free radical processes and involved a highly polar transition state. It has seemed appropriate to report these observations separately from the others.

Experimental

Materials.—Commercial t-butyl iodide was vacuum distilled. The distilled material remained colorless for several

(1) Based in part on the Ph.D. Dissertation of John E. Bujake, Jr. 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) J. E. Bujake, Jr., M. W. T. Pratt and R. M. Noyes, THIS JOURNAL, 83, 1547 (1961).

weeks at −5° or for a few hours at room temperature. Gas chromatography indicated impurities of the order of a few parts per thousand. Separate portions were prepared by this distillation at frequent intervals, and no significant difference was observed in the exchange rates of samples from different distillations.

The solvents hexachlorobutadiene-1,3 and ethylene dichloride have been described previously.[3] Commercial hexane and chlorobenzene were purified by successive agitation with concentrated sulfuric acid, sodium carbonate solution and water. They were then dried with calcium chloride and distilled.

Procedure.—Samples could not be frozen and degassed as was possible for solutions of the other iodides[3] because the freezing induced a very rapid exchange. Hence all runs were carried out in contact with air. Solutions were mixed and thermostated either in an ice-water slush or in conventional water thermostats, and aliquots were withdrawn at suitable times. Identical results were obtained with individual ampules instead of aliquots.

The solutions were extracted with aqueous sulfite, and the aqueous layer was counted as described previously.[3] Subsequent extraction of the radioactive organic layer demonstrated that hydrolysis of t-butyl iodide was negligible during the separation. The rate of exchange, R_{ex}, was calculated by conventional procedures.

For runs with the less polar solvents, the concentration of iodine was measured spectrophotometrically before and after a run, and the rate of decomposition, R_d, was calculated as twice the rate of production of molecular iodine.

Results

The results of individual runs are presented in Tables I and II. The kinetics of the exchange reaction fell into two rather distinct classifications depending on the dielectric constant of the solvent. The less polar solvents hexane and hexachlorobutadiene-1,3 had dielectric constants at 25° of 1.9 and 2.6, respectively. Exchange in these solvents was first order in t-butyl iodide and almost second order in molecular iodine. If the data were fitted to the equation

$$R_{ex} = k_a\,[t\text{-BuI}][I_2] + k_b\,[t\text{-BuI}][I_2]^2 \qquad (1)$$

values of k_a were not significantly different from zero at 25°. However, significant values of k_a were obtained in hexachlorobutadiene at higher temperatures.

The more polar solvents chlorobenzene and ethylene dichloride had dielectric constants at 25° of 5.5 and 10.1, respectively. Exchange in these solvents was somewhat more than first order in molecular iodine but was not as nearly second order as in the less polar solvents. The rate was first order in t-butyl iodide in the range 0.01 to 0.05 mole/liter, but at 0.25 mole/liter the rate was less than that for a first order extrapolation from lower concentrations. Since this behavior is of the sort to be expected if a significant fraction of the iodine is present as a complex with t-butyl iodide, equation 1 was modified to

$$R_{ex} = \frac{k_a\,[t\text{-BuI}][I_2]}{1 + K[t\text{-BuI}]} + \frac{k_b\,[t\text{-BuI}][I_2]^2}{\{1 + K[t\text{-BuI}]\}^2} \qquad (2)$$

where the terms in brackets are total concentrations of the appropriate species. Reasons for choosing this form of equation are presented below.

The parameters k_a and k_b were evaluated for the less polar solvents by a least squares fit of $R_{ex}/[t\text{-BuI}][I_2]$ against $[I_2]$. For the more polar solvents, the data for 0.01 and 0.05 M t-butyl iodide were fitted to equation 1, and the data for 0.25 M were fitted separately. The parameters for the two fits were used to estimate the best value of K

REACTIONS OF t-BUTYL IODIDE (t-BuI) IN LESS POLAR SOLVENTS

Temp., °C.	[I₂] × 10⁴, mole/l.	[t-BuI], mole/l.	$10^8 R_{ex}$, mole/l. sec.	$10^8 R_d$, mole/l. sec.	$10^8 R_{ex}$ (calcd.)
			Hexane, D_{25} = 1.9		
25.0	5.31	0.250	0.425	0.0133	0.453
	5.59	.0500	0.0803	.0370	0.1002
30.5		.0500	1.058	.0165	1.582
30.9		.0099	0.350	.0538	0.323
30.9		.250	7.30	....	7.81
110		.0498	21.7	.444	17.5
114		.249	80.0	....	90.5
193		.250	300	....	254
252		.250	397	−28.1	429
			Hexachlorobutadiene-1,3, D_{25} = 2.6		
25.0	6.5	0.0100	0.0327	....	0.0121
	6.5	.0500	.0808	....	.0600
	6.5	.250	.845	0.215	.291
	55.5	.250	8.47	0.969	13.56
	79.8	.250	21.0	2.83	27.4
	81.6	.0500	4.90	1.90	5.94
	160	.0500	23.7	1.00	22.3
	165	.250	114	23.6	114
	254	.250	282	18.4	267
	400	.250	683	47.8	659
40.0	6.64	0.0100	0.0630	....	0.0502
	6.64	.0500	0.262	....	0.251
	7.53	.250	1.57	0.515	1.48
	55.5	.0100	1.10	....	1.40
	57.0	.250	35.3	2.83	36.7
	57.5	.0500	7.80	1.13	7.46
	123	.250	141	....	153
	245	.250	637	11.1	575
	453	.250	1870	44.4	1920
60.0	6.1	0.0100	0.823	....	0.748
	6.1	.0500	3.27	....	3.68
	6.1	.250	17.2	....	17.1
	55.8	.0500	49.7	....	49.1
	55.8	.250	217	....	229
	241	.250	2030	....	2170

on the assumption that the fit with dilute t-butyl iodide gave k_a and k_b. This value of K then was used to fit the more dilute data to equation 2, and the k_a and k_b obtained from this fit were combined with the fit of the 0.25 M data to give a better value of K. This value then could be applied to the more dilute data, and the process repeated as often as necessary.

The results of these fits are presented in Table III. The error limits are probable errors estimated from the fit of individual data. Values of K are reported for the less polar solvents even though they are clearly without significance. The reaction in ethylene dichloride at 25° was so fast that only one run was carried out with 0.25 M t-butyl iodide; hence K can only be estimated very roughly for this system. The values of the parameters from Table III were used to calculate the rates presented in the last columns of Tables I and II.

When data were available at more than one temperature, the rate constants k_a and k_b were fitted to the Arrhenius equation, and the entropies of activation also were calculated at 25°. The results are

TABLE II

EXCHANGE OF *t*-BUTYL IODIDE (*t*-BuI) IN MORE POLAR SOLVENTS

Temp., °C.	$[I_2] \times 10^4$, mole/l.	[*t*-BuI], mole/l.	$10^8 R_{ex}$, mole/l. sec.	$10^8 R_{ex}$, (calcd.)
	Chlorobenzene, $D_{25} = 5.5$			
25.0	10.0	0.0100	6.77	6.25
	10.0	.0500	34.7	29.8
	10.0	.250	116.5	121.9
	50.0	.0100	37.2	40.7
	50.0	.0500	183	193
	50.0	.250	758	758
	150	.0500	790	904
	150	.250	3270	3390
	250	.0500	2180	2050
	250	.250	7770	7520
	Ethylene dichloride, $D_{25} = 10.1$			
0.0	10.0	0.0100	9.59	10.02
	10.0	.0500	45.0	43.9
	10.0	.250	108	135
	50.0	.0100	45.7	61.0
	50.0	.0500	288	261
	50.0	.250	840	758
	125	.0500	1050	852
	125	.250	2370	2280
	250	.0500	2250	2360
	250	.250	5770	5860
25.0	24.0	0.0100	148	123
	24.0	.0500	633	601
	24.0	.250	2700	2650
	60.0	.0100	392	381
	60.0	.0100	347	381
	60.0	.0500	1620	1850
	60.0	.0500	1650	1850
	150.0	.0500	7170	6780

TABLE III

KINETIC PARAMETERS FOR EXCHANGE OF *t*-BUTYL IODIDE (*t*-BuI)

Solvent	Temp., °C.	$10^4 k_a$, l./mole sec.	k_b, l.²/mole² sec.	K, l./mole
Hexane	25.0	0.21 ± 0.18	0.0275 ± 0.0015	0.1 ± 0.3
Hexachlorobutadiene	25.0	0.075 ± .085	.0171 ± .0005	0.1 ± .2
	40.0	.51 ± .14	.0362 ± .0008	0 ± .1
	60.0	11.6 ± .4	.116 ± .004	0.4 ± .8
Chlorobenzene	25.0	58.4 ± 4.6	.484 ± .039	1.1 ± .4
Ethylene dichloride	0.0	98 ± 7	.583 ± .058	3.5 ± 1.3
	25.0	436 ± 37	3.40 ± .50	0.6 ± 0.8

TABLE IV

TEMPERATURE DEPENDENCE OF RATE CONSTANTS

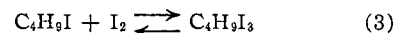| Parameter and dimensions	Solvent	log A	E, kcal./mole	ΔS^* cal /mole deg.
k_a, l./mole sec.	Hexachlorobutadiene	(17.6 ± 1.4)	(31.3 ± 2.2)	(+20 ± 6)
	Ethylene dichloride	3.72 ± 0.54	9.66 ± 0.70	−43.5 ± 2.5
k_b, l.²/mole² sec.	Hexachlorobutadiene	6.09 ± .18	10.75 ± 0.26	−32.7 ± 0.8
	Ethylene dichloride	8.90 ± .85	11.4 ± 1.1	−19.8 ± 3.9

comparable dark run reported in Table I. The rate of decomposition was 3.83×10^{-8} mole/l. sec. compared to 1.90×10^{-8} reported in Table I. The light does not accelerate the exchange reaction, although it does seem to increase the rate of decomposition. Since illumination must have increased the concentration of free atoms by at least three powers of ten, the test demonstrates the unimportance of radical exchange processes under these conditions.

Discussion

Types of Exchange Processes.—The exchange reaction is clearly not of the same type as the radical reactions of the primary and secondary iodides.[3] The low activation energies, the large influence of changing solvent and the absence of photochemical acceleration all demonstrate that iodine atoms are not the active species.

At least in the more polar solvents, the exchange seems to involve two parallel processes which are first order and second order in molecular iodine, respectively. The dependence of the rate on *t*-butyl iodide concentration also indicates the presence of significant concentrations of complexes. The complex formation and the parallel kinetic processes are conveniently discussed separately.

The Formation of Complexes, K.—At the highest concentration of *t*-butyl iodide, the exchange rate does not increase as much as predicted for a first order process. This behavior is that to be expected if there were an equilibrium of the form

$$C_4H_9I + I_2 \rightleftharpoons C_4H_9I_3 \qquad (3)$$

Since complexing is significant only at high concentrations of organic iodide when it is present in con-

presented in Table IV. The values for k_a in hexachlorobutadiene are anomalous; they are placed in parentheses and discussed further below.

Although the kinetics are not indicative of a radical reaction, a specific test was made for photochemical acceleration. A solution containing 8×10^{-3} M iodine and 5×10^{-2} M *t*-butyl iodide in hexachlorobutadiene was allowed to react at 25° while a 100 watt light was six inches from the reaction vessel. The rate of exchange was 4.10×10^{-8} mole/l. sec. compared to 4.90×10^{-8} for a

siderable excess over the iodine, the chief kinetic effect is a reduction in the apparent concentration of iodine. Then

$$[I_2] = \frac{[I_2]_0}{1 + K[t\text{-BuI}]} \qquad (4)$$

where K is the equilibrium constant for reaction 3, and $[I_2]_0$ is the total concentration of dissolved iodine and the quantity reported in Tables I and II. This equation is the reason for the correction by which equation 2 differs from equation 1.

The presence of complexes was also indicated by the fact that t-butyl iodide caused solutions of iodine to be browner than otherwise. We did not attempt to evaluate the equilibrium constants independently, but Keefer and Andrews[4] have examined some of these equilibria spectrophotometrically. They report $K = 1.33$ for t-butyl iodide and iodine in heptane at 25°. It is hard to reconcile this figure with our kinetic observations in hexane unless the exchange reaction of $RI_3 + RI_3$ goes with very nearly the same rate constant as does the reaction of $RI_3 + I_2$. Our kinetic data indicate that complexing increases with polarity of solvent, and Keefer and Andrews[4] suggest that the shift of charge is in the direction to make the iodine more negative.

The Bimolecular Mechanism, k_a.—The bimolecular process is first order each in t-butyl iodide and in molecular iodine and is extremely dependent on the nature of the solvent. Thus the existence of this process cannot be claimed with certainty in the less polar solvents, while in ethylene dichloride it is responsible for over half of the exchange even at iodine concentrations as high as 0.01 M.

If the dielectric constant of the medium is the only factor influencing rate of reaction, one can regard $d \ln k/d[(D - 1)/(2D + 1)]$ as a measure of the increase in polarity during a reaction of neutral molecules.[5] If the anomalously low rates in hexachlorobutadiene are neglected, this quantity is between 30 and 40 for k_a; and still larger values are indicated by including hexachlorobutadiene. Values of the same quantity are in the range 13 to 20 for reactions like the attack of pyridine on benzyl bromide,[6] the reaction of triphenylphosphine with sulfur[7] and the exchange of iodine with benzoyl iodide.[8] All of these processes are thought to involve formation of ions or ion pairs. The value of this quantity was 7.7 for the degassed exchange of methyl iodide[3]; this reaction presumably involves a radical rather than an ionic abstraction.

The entropy of activation of -43 cal./mole deg. in ethylene dichloride is also unusually low for a bimolecular reaction and is the sort of value to be anticipated for a reaction producing ions. All of the evidence points to a very considerable separation of charge in the transition state, and the bimolecular mechanism apparently involves the formation of an ion pair intermediate $C_4H_9{}^+I_3{}^-$ in which at least the end iodines of the $I_3{}^-$ group become indistinguishable.
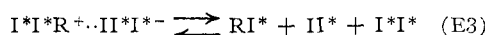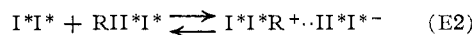
Of course our data provide no information as to the stereochemistry of the exchange reaction. The mechanism proposed here predicts that for an optically active iodide the bimolecular exchange mechanism would lead either to retention of configuration or to racemization depending upon how free the members of the ion pair became; it

excludes the possibility of inversion in excess of retention of configuration.

The Termolecular Mechanism, k_b.—The termolecular process is second order in molecular iodine. Although it is less sensitive than the bimolecular process to changes in medium, the rate constant varies over a hundredfold for the solvents studied. The quantity $d \ln k/d[(D - 1)/(2D + 1)]$ is not well defined but appears to be between 20 and 30, and the entropies of activation are quite low in the two solvents for which temperature dependence was studied.

All of these observations suggest that this mechanism involves considerable separation of charge in the transition state but that the influence on the surrounding solvent molecules is somewhat less than for the bimolecular mechanism because the additional iodine molecule makes the transition state itself larger and more polarizable.

Of course our observations do not indicate whether the stereochemistry of the reaction favors retention or inversion of configuration of carbon. Both Corey and Wechter[9] and Beringer and Schultz[10] studied halogen substitution reactions of 2-iodoöctane and concluded that inversion predominated. We therefore propose that the termolecular exchange involves nucleophilic attack on carbon analogously to a mechanism first proposed by Keefer and Andrews.[11] The sequence is

$$RI + I^*I^* \rightleftharpoons RII^*I^* \qquad (E1)$$

$$I^*I^* + RII^*I^* \rightleftharpoons I^*I^*R^+\cdots II^*I^{*-} \qquad (E2)$$

$$I^*I^*R^+\cdots II^*I^{*-} \rightleftharpoons RI^* + II^* + I^*I^* \qquad (E3)$$

The intermediate formed in step E2 has been written as an ion pair rather than separated ions. The principle of microscopic reversibility requires that each process be going at equal rates in both directions so that equal numbers of exchanges involve the attack of an iodine molecule on an RI_3 complex and the attack of an $I_3{}^-$ ion on an $RI_2{}^+$ ion.

The exchange kinetics do not indicate any paths requiring more than two iodine molecules in the transition state. However, freezing the solutions to Dry Ice temperature induces a rapid exchange. Solid iodine precipitates in these cold solutions, and either the crystal surfaces or the nuclei of a few molecules appear to be very efficient at exchanging. Rapid exchange is also induced by freezing solutions of iodine and benzoyl iodide,[8] and this exchange reaction also becomes anomalously rapid in homogeneous solutions of iodine that are nearly saturated. Some years ago, Sibbett and Noyes[12] were frustrated in attempts to freeze and degas exchange solutions containing iodine and allyl iodide. The difficulties were ascribed to the sealing operation, but hindsight suggests that there may have been erratic heterogeneous induced exchange. Allyl, benzoyl and t-butyl iodides are the only compounds we have studied for which the exchange kinetics contained contributions from molecular iodine, and it is undoubtedly significant that compounds of

(4) R. M. Keefer and L. J. Andrews, THIS JOURNAL, **74**, 1891 (1952).

(5) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., New York, N. Y., 1941, p. 423.

(6) Ref. 5, p. 421.

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

(8) A. Goldman and R. M. Noyes, *ibid.*, **79**, 5370 (1957).

(9) E. J. Corey and W. J. Wechter, *ibid.*, **76**, 6040 (1954).

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

(11) R. M. Keefer and L. J. Andrews, *ibid.*, **75**, 543 (1953).

(12) D. J. Sibbett and R. M. Noyes, *ibid.*, **75**, 761 (1953).

these types are the only ones for which we have observed significant exchange during the operations of freezing and degassing.

Comparison with Primary and Secondary Iodides.—Probably the most startling feature of these observations is the dramatic rate increase accompanying the introduction of a third methyl group at the reaction center. The rate of exchange of t-butyl iodide with 0.02 M iodine in hexachlorobutadiene at 25° is 7 × 10⁶ times as fast as the rate predicted for isopropyl iodide under the same conditions by extrapolation of the measurements at higher temperatures! This factor is probably at least as great as has ever been claimed for the relative rates of these two compounds for the same net reaction.

Although t-butyl and isopropyl compounds show considerable reactivity differences for many processes, the contrast shown here is remarkable. We believe that the natural difference in reactivity of the two compounds is greatly enhanced because when we are studying a very polar reaction in solvents with dielectric constants less than 10. These solvent molecules do not have large permanent dipole moments, and solvation energies of ions and ion pairs will be much less than in more polar solvents. Hence in these solvents the ability to form an ion pair will be strongly influenced by the extent to which charge can be diffused on the surface of the reacting species itself. Because of increased hyperconjugation, the t-butyl group can diffuse positive charge better than the isopropyl group can, and the difference between the two groups will be more enhanced the less the solvent molecules themselves are able to accommodate themselves to charge separation during reaction.

Of course the comparison of relative rates is not entirely reliable when an extrapolation of over 100° is involved. At 130°, isopropyl iodide exchanges by a radical mechanism with an activation energy of about 30 kcal./mole, but the dominant mechanism at 25° could easily be by a polar mechanism like that of t-butyl iodide with an activation energy of about 10 kcal./mole. Then the exchange rates of the two iodides at the lower temperature might differ by somewhat less than the factor of 10⁶ even though the tertiary iodide obviously exchanges very much more easily. It may be significant that isopropyl iodide in ethylene dichloride at the lowest temperature studied was the only one of the primary and secondary iodides for which the rate of exchange seemed to be more than half order in iodine[3]; these are the conditions where a parallel polar mechanism would have been expected to make its greatest contribution to the kinetics.

Similarly, our data do not show that t-butyl iodide could not exchange by a radical mechanism but merely that the polar processes are much more rapid under the conditions employed. These polar processes have very low activation energies, and extrapolation to 180° indicates that for 0.001 M iodine at this temperature exchange of t-butyl iodide by the termolecular mechanism would only be about a factor of two faster than the oxygen inhibited exchange of isopropyl iodide by the radical mechanism. If t-butyl iodide were sufficiently stable for study at elevated temperatures, it would be surprising if it did not also exchange by a radical mechanism.

In fact, it is tempting to assign a radical mechanism to some of the exchange of t-butyl iodide in hexachlorobutadiene at 60°. When measurements in this solvent are fitted to equation 1, the apparent value of k_a is clearly without significance at 25° and is barely significant at 40°. The small number of runs at 60° indicates a significant intercept when $R_{ex}/[t\text{-BuI}][I_2]$ is plotted against $[I_2]$, but Table IV shows that a fit of these data to the Arrhenius equation gives an implausibly large value for the A term. Because a test at 25° failed to indicate photochemical acceleration at a fairly high iodine concentration, no particular precautions were taken to avoid exposure to light during reaction. The apparent anomalies in k_a would be removed if the runs at 60° were subject to a photochemical acceleration which would have been important only at the lowest iodine concentration.

If the ideas developed here are correct, highly polar reactions in solvents of low dielectic constant should be extremely sensitive to structural changes that affect diffusion or localization of charge in the transition state. Thus t-butyl bromide should exchange with bromine less easily than the reaction studied here, and the addition of the more polarizable iodine might catalyze the ability of bromine to exchange by the termolecular mechanism. Such an effect already has been observed in the exchange reactions of benzoyl halides.[8] Similarly, ring substituents in benzoyl iodide should have extremely large effects on the exchange of this compound with iodine in non-polar solvents. Some of these predictions are currently being tested at the University of Oregon.