Polar Exchange of Iodine Molecules with Substituted Benzhydryl Iodides

W. J. Muizebelt and Richard M. Noyes

Contribution from the Department of Chemistry, University of Oregon, Eugene, Oregon 97403, and the Department of Organic Chemistry, University of Nijmegen, Nijmegen, The Netherlands.

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Abstract: The previously unknown benzhydryl iodide, $(C_6H_5)_2CHI$, and its *p*-chloro and *m*-chloro derivatives have been prepared. As had been anticipated, even in solvents of very low dielectric constant the dominant mechanism of isotopic exchange with elementary iodine does not involve free atoms but passes through a very polar transition state containing one or more iodine molecules. Rates of exchange are several times as fast in carbon tetrachloride as they are in hexane, the difference being due to variation in entropy of activation. Sensitivity of rate to change in solvent is somewhat greater than for the exchange of iodine with benzoyl iodides, but it is much less than the sensitivity to solvent of the rate of quaternization of tertiary amines; it is proposed that both dipole moments and also polarizabilities of transition states must be considered in order to explain effects of changing solvent on rates of such reactions. The rate of exchange is strongly depressed with chlorine substitution consistent with a Hammett ρ of about -4, but effects of substituents are somewhat less than on the exchange of benzoyl iodides. The reaction appears to be well suited for the study of effects of changing solvent and of aromatic substitution on rates of formation of ion-pair transition states in solvents of very low dielectric constant.

Organic iodine compounds undergo isotopic exchange with elementary iodine in nonpolar solvents. For many compounds, the exchange mechanism is a free-radical process initiated by iodine atoms. However, some iodides exchange by a very different mechanism whose rate is more than first order in *molecular* iodine, is little accelerated by light, and is very dependent upon the dielectric constant of the solvent. This polar mechanism is thought to pass through a transition state having charge distribution approximating that of an ion pair.

The polar mechanism has previously been observed for *t*-butyl[1] and benzoyl[2,3] iodides. The organic portions of these molecules can accommodate positive charge easily. Such an interpretation suggests that benzhydryl iodide, $(C_6H_5)_2CHI$, should also exchange by this polar mechanism and that derivatives of this compound might be useful to study effects of aromatic substitution on rates of very polar reactions in solvents of low dielectric constant. The present paper describes experiments confirming this prediction.

Experimental Section

Materials. To prepare the previously unknown benzhydryl iodide, a solution of 10 g of $(C_6H_5)_2CHOH$ in 50 ml of ethanol was mixed with 30 ml of 57% aqueous HI. An oil separated immediately, and the temperature rose to about 50°. The oil was quickly dissolved in hexane, washed with aqueous Na_2SO_3 to remove iodine, and dried over magnesium perchlorate for 0.5 hr. The $(C_6H_5)_2CHI$ was crystallized by cooling to $-80°$ and was recrystallized from hexane at the same temperature.

Benzhydryl iodide is quite unstable, and decomposition is accelerated greatly by light or oxygen. Crystals were stored under hexane at $-80°$ in complete darkness. A sample dried under nitrogen melted with decomposition at 41–43°. Weighed samples were analyzed by hydrolyzing with sodium hydroxide in alcohol-water to which a little sodium sulfite had been added, and then titrating the resulting iodide ion potentiometrically with silver nitrate. Different preparations contained 97–98.5% of the theoretical amount of iodide.

The *meta* and *para* isomers of $(C_6H_5)(C_6H_4Cl)CHI$ were prepared from the corresponding benzhydrols in a similar way. They were liquids at room temperature and the best preparations contained only 96 and 93%, respectively, of the theoretical amount of iodine. Since kinetic runs with samples of different purity gave identical results, it appears unlikely that the impurities affected the rate of exchange.

Hexane and 1,2-dichloroethane solvents were stirred with concentrated sulfuric acid for several hours, washed with sodium carbonate solution and water, dried over calcium chloride, and distilled. Analytical reagent carbon tetrachloride was purified by distillation only.

Procedure. The experimental procedure was similar to that used previously.[2,3] Solutions of benzhydryl iodide and elementary iodine were mixed and thermostated in flasks carefully wrapped with aluminum foil to exclude light. At zero time, the elementary iodine was isotopically labeled by adding a small known volume of 10^{-4} *M* iodine solution that had been shaken with an aqueous solution of carrier-free iodine-131 and subsequently dried over magnesium perchlorate.

At appropriate time intervals, aliquots were removed and extracted with chilled aqueous sulfite in order to remove the elemental iodine. The radioactivity of the residual organic layer was then determined with a thin-walled liquid-jacketed Geiger counter, and the rate of exchange, v, was calculated by conventional procedures. Separate tests demonstrated that benzhydryl iodide was not significantly hydrolyzed even by shaking for 5 min longer than was necessary to extract the iodine.

Solutions that had not been dried with magnesium perchlorate exchanged more rapidly than dried solutions did and gave erratic results. Spectrophotometric measurements demonstrated that the iodine concentration did not change during these runs. However, exposure of a reaction mixture to daylight resulted in iodine production. The limiting amount of iodine produced photochemically agreed well with that calculated from analysis of the benzhydryl iodide by hydrolysis and potentiometric titration of iodide ion. Because benzhydryl iodides are so sensitive to photochemical decomposition, the effect of light on the rate of exchange was not studied.

Results

The rate data for the three compounds in two solvents each are presented in Figures 1–6 as plots of $v/[\mathrm{BzhI}] \cdot [\mathrm{I_2}]$ against $[\mathrm{I_2}]$, where BzhI denotes a benzhydryl iodide compound. Exchange rates are calculated in mol/l. sec, and concentrations are expressed in mol/l.

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[1] J. E. Bujake, Jr., and R. M. Noyes, *J. Amer. Chem. Soc.*, 83, 1555 (1961).

[2] A. Goldman and R. M. Noyes, *ibid.*, 79, 5370 (1957).

[3] D. W. Hamilton and R. M. Noyes, *ibid.*, 91, 1740 (1969).

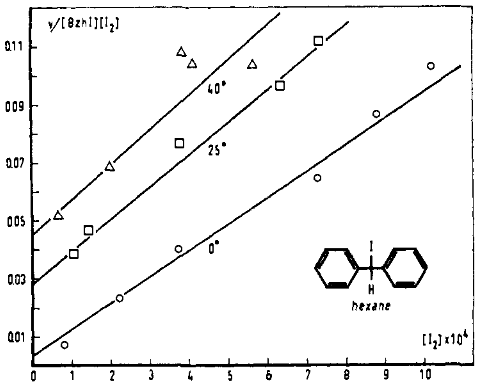

Figure 1. Rate data for exchange of benzhydryl iodide with iodine in hexane.

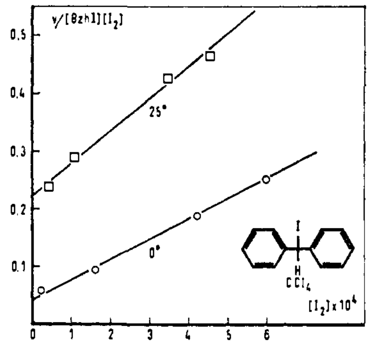

Figure 2. Rate data for exchange of benzhydryl iodide with iodine in carbon tetrachloride.

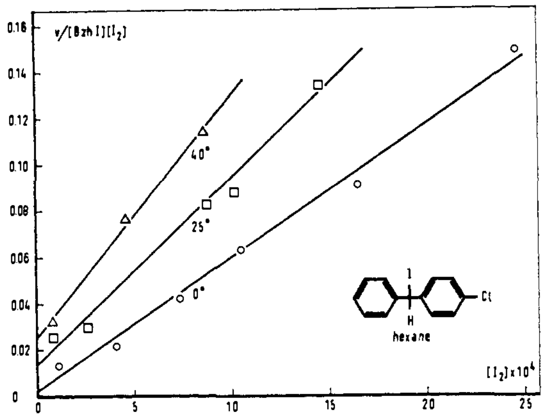

Figure 3. Rate data for exchange of *p*-chlorobenzhydryl iodide with iodine in hexane.

The linear behavior of most plots is consistent with a rate equation of the form

$$v = k_1[\mathrm{BzhI}][\mathrm{I}_2] + k_2[\mathrm{BzhI}][\mathrm{I}_2]^2 \qquad (1)$$

For the slower exchange of *m*-chlorobenzhydryl iodide in hexane, the rate could be followed at much higher iodine concentrations than were permissible for other reactions, and a term in $k_3[\mathrm{BzhI}][\mathrm{I}_2]^3$ made a dominant contribution to the rate.

Because the benzhydryl iodides exchange so rapidly, it was not possible to vary their concentrations by more than a factor of 6, and the points in most of the figures represent solutions of 0.005–0.02 mol/l. Points at the

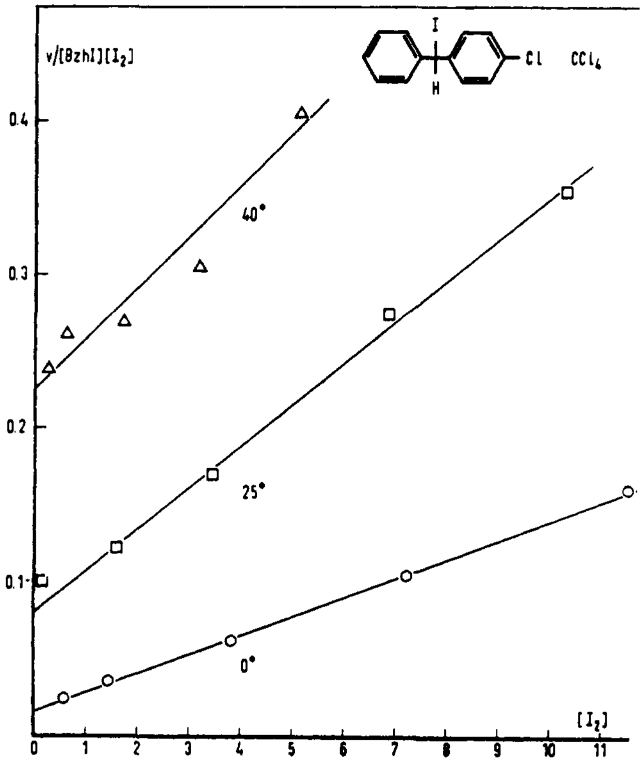

Figure 4. Rate data for exchange of *p*-chlorobenzhydryl iodide with iodine in carbon tetrachloride.

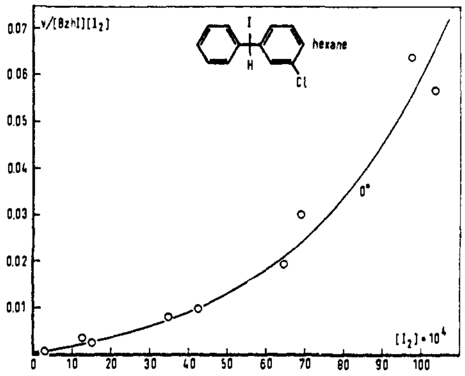

Figure 5. Rate data for exchange of *m*-chlorobenzhydryl iodide with iodine in hexane.

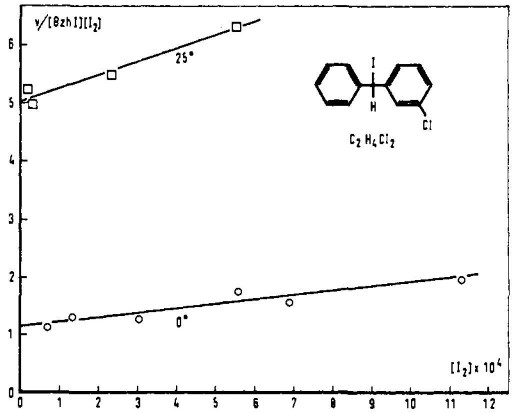

Figure 6. Rate data for exchange of *m*-chlorobenzhydryl iodide with iodine in dichloroethane.

Table I. Rate Constants for Exchange of Benzhydryl Iodides

Solvent	Temp, °C	k_1, l./mol sec	k_2, l.^{2}/mol^2 sec	k_3, l.^{3}/mol^3 sec
Benzhydryl Iodide				
C_6H_{14}	40.0	0.045 ± 0.002	120 ± 15	
	25.0	0.028 ± 0.002	113 ± 5	
	0.0	0.0033 ± 0.0015	90 ± 3	
CCl_4	25.0	0.222 ± 0.005	567 ± 30	
	0.0	0.042 ± 0.005	350 ± 20	
p-Chlorobenzhydryl Iodide				
C_6H_{14}	40.0	0.025 ± 0.002	105 ± 5	
	25.0	0.013 ± 0.003	82 ± 3	
	0.0	0.0025 ± 0.003	57 ± 3	
CCl_4	40.0	0.226 ± 0.008	330 ± 30	
	25.0	0.080 ± 0.006	270 ± 20	
	0.0	0.017 ± 0.0015	123 ± 3	
m-Chlorobenzhydryl Iodide				
C_6H_{14}	0.0	0.0003 ± 0.00015	1.3 ± 0.3	420 ± 50
$C_2H_4Cl_2$	25.0	5.05 ± 0.15	2300 ± 300	
	0.0	1.17 ± 0.08	700 ± 200	

Table II. Parameters Based on Temperature Dependence of Rate Constants

Solvent	Rate constant	Log *A*	*E*, kcal/mol	$\Delta S^{\ddagger}$, cal/(mol deg)
Benzhydryl Iodide				
C_6H_{14}	k_1	6.3 ± 1.0	11 ± 2	−32 ± 5
	k_2	3.0 ± 0.7	1.3 ± 1.0	−47 ± 3
CCl_4	k_1	7.4 ± 1.0	10 ± 2	−27 ± 5
	k_2	5.0 ± 0.7	3 ± 1	−38 ± 3
p-Chlorobenzhydryl Iodide				
C_6H_{14}	k_1	5.4 ± 1.0	10 ± 2	−36 ± 5
	k_2	3.8 ± 0.3	2.6 ± 0.5	−43 ± 1.4
CCl_4	k_1	7.3 ± 0.7	11.3 ± 1.0	−27 ± 3
	k_2	5.4 ± 0.3	4.1 ± 0.5	−36 ± 1.4
m-Chlorobenzhydryl Iodide				
$C_2H_4Cl_2$	k_1	7.6 ± 0.9	9.4 ± 1.5	−25 ± 4
	k_2	9.0 ± 1.3	7.7 ± 2	−19 ± 6

lower concentrations tend to lie slightly below the lines drawn to fit all points, but the deviations are hardly significant. The influence of the concentration of organic iodide on the rate constant for exchange is definitely smaller than the effect observed with benzoyl iodides.[2,3] More precise determination of the magnitude of the effect would require measurements of the very fast rates at higher concentrations.

As is apparent from the figures, eq 1 usually describes the kinetics satisfactorily to concentrations of iodine as low as 10^{-4} mol/l., while data on benzoyl iodides[2,3] are complicated by a term that is zero order in iodine and that becomes important at concentrations of the order of 10^{-3} mol/l.

Because of the above differences, benzhydryl iodides seem to be more satisfactory than benzoyl iodides for studying effects of substituents on rates of exchange in very nonpolar solvents. However, benzhydryl iodides tend to exchange at faster rates, and it was impossible to study the unsubstituted compound in chlorobenzene or in dichloroethane because exchange was complete in less than 2 min.

Values of the rate constants derived from the data in the figures are presented in Table I. The estimated uncertainties are based on deviations of individual points from the best two- or three-parameter fit of the data. Table II presents the parameters obtained from fitting the rate constants to the Arrhenius equation and from calculating the entropy of activation by standard procedures.

Discussion

Mechanism. This work was initiated in the expectation that a polar exchange mechanism would be favored by the resonance stabilization of the benzhydryl carbonium ion. The anticipated very polar transition state is indicated by the strong effect of chlorine substitution on the rate of exchange, by the great variation of rate with dielectric constant of solvent, and by the very negative entropies of activation. The k_1 term in eq 1 presumably involves a path through a transition state of the form $(C_6H_5)_2HC^+\cdots I_3^-$ in which the incipient carbonium ion is migrating from one end to the other of the incipient triiodide ion. Rate contributions from larger numbers of iodine molecules may involve incipient ions like I_5^- or else may involve polarization stabilization by a separate nonexchanging iodine molecule of the positive organic portion of the transition state. Since kinetics measure only the empirical formulas of transition states, we are unable to locate the other iodine molecule more precisely.

Effects of Changing Solvent. Reactions with large charge separation in the transition state are uncommon in solvents of very low dielectric constant. The present reaction is an exception because both the benzhydryl carbonium ion and the triiodide negative ion can dissipate their charges over such large regions that local concentrations are much less than in smaller and less polarizable ions. That considerable charge separation has taken place is indicated by the fact that for unsubstituted benzhydryl iodide k_1 is about ten times as great in carbon tetrachloride as in hexane, while k_2 is about four times as great. Although these factors are much larger than the rate ratios observed for radical and other nonpolar reactions in these solvents, they are much smaller than the factor of 140 observed by Lassau and Jungers[4] for the ratio in rates of quaternization of tertiary amines by methyl iodide in the same two solvents.

The entropies of activation are more negative in hexane than in carbon tetrachloride and more negative for k_2 than for k_1. Energies of activation are smaller for k_2 than for k_1 but show rather little solvent effect. Hence the effects of solvent on rate of reaction are primarily due to variations in the entropy of activation. By contrast, *p*-chlorobenzoyl iodide exchanges more rapidly in dichloroethane than in hexane because of a variation in energy of activation.[3] Considerably more information will be needed in order to understand the effects of changing solvent on these very polar reactions, but the benzhydryl iodide reactions reported here appear to be more sensitive to changing solvent than are the reactions of benzoyl iodides.[2,3]

As Lassau and Jungers[4] have pointed out, the dielectric constant of solvent is insufficient as a single parameter to explain variations in rate of quaternization of amines. The limited data now available on polar iodine exchanges also suggest that different reactions passing through polar transition states may not respond in comparable ways to changing solvent. Dipole

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(4) C. Lassau and J. C. Jungers, *Bull. Soc. Chim. Fr.*, 2678 (1968).

moment of transition state has sometimes been used as a theoretical parameter, but it need not be independent of changing solvent even if the basic mechanism is unaffected by such change. As a minimum, it appears that the separation of charge (dipole moment) and the polarizability of the transition state will both have to be considered before it is possible to explain effects of several aprotic solvents on the rates of several polar reactions. More data will be needed to define the range of the problem.

Effects of Substituents. The rates are reduced by chlorine substitution in one of the aromatic rings, the effect being much larger for *meta* than for *para* substitution. The direction of the rate change is that anticipated for the charge distribution proposed for the transition state, and the magnitude is perhaps somewhat less than that from substitution in benzoyl iodide.[3] Somewhat surprisingly, the effect of chlorine substitution appears to be greater in carbon tetrachloride than in hexane.

The rates in hexane can be roughly correlated with σ^+ values[5] to give a ρ of about -4, but more compounds must be studied before a really quantitative discussion of substituent effects is possible. Unfortunately, strongly electron-withdrawing substituents such as *p*-nitro and *p*-cyano apparently render benzhydryl iodide so unstable to radical decomposition that the desired compounds cannot be synthesized and studied.[6]

In spite of these synthetic complications, it is obvious that the benzoyl and benzhydryl iodides exchange with iodine by very polar mechanisms even in solvents of low dielectric constant. These reactions appear to offer exceptionally good opportunities to study substituent and solvent effects on transition states more polar than can usually be formed in such solvents.

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(5) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(6) Observations of Dr. J. A. Hemmingson.

Formation of an Intermediate in Nucleophilic Substitution at Dicoordinated Sulfur

Ennio Ciuffarin and Franco Griselli

Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy. *Received July 29, 1969*

Abstract: The rate of reaction between *p*-nitrobenzenesulfenyl choride and aniline has been measured in benzene at 20° with a stopped-flow spectrophotometer. In the absence of additives the pseudo-second-order rate coefficient, k_2, tends to a limiting value with increasing aniline concentration. In the presence of tetra-*n*-butylammonium perchlorate, k_2 either is independent of the concentration of nucleophile, or, at very low salt concentration, increases slightly. The data are interpreted in terms of a two-step mechanism.

The bulk of the existing evidence concerning direct nucleophilic displacement reactions at dicoordinated sulfur is adequately fitted by a synchronous bimolecular mechanism. The small substituent effects[1-6] and large steric effects[7] which have been measured for a variety of reactions at dicoordinated sulfur have all been taken as proof of synchronous, direct displacement similar to the SN2 mechanism for sp^3 carbon.[8]

On the other hand, a report has recently appeared[9] where evidence is presented for the formation of a metastable intermediate in nucleophilic substitution at dicoordinated sulfur. It has been suggested[9] that the intermediate can either be an ion pair or an addition complex. Moreover, the formation of addition complexes as intermediates has also been proposed by Kwart[6] in the chlorination of phenyl sulfenyl chlorides and by Trost[10] in the reaction of sulfonium salts with organolithium compounds.

However, the bulk of information pointing to a synchronous, direct displacement compared to the relatively scarce and indirect evidence for the formation of an intermediate could lead one to believe that the formation of an intermediate is never possible. While we are still pursuing a larger objective, that of finding the reasons for sulfur ambivalent behavior, we now wish to report new and conclusive evidence for the formation of an intermediate in nucleophilic substitution at dicoordinated sulfur. Part of the significant facts pertinent to this investigation have been summarized previously.[9]

Results and Discussion

The rate of reaction of *p*-nitrobenzenesulfenyl chloride, Ar′SCl, with aniline, ArNH$_2$, was measured in

(1) J. L. Kice and J. M. Anderson, *J. Org. Chem.*, 33, 3331 (1968).

(2) A. Ceccon and A. Fava, unpublished data cited in ref 3.

(3) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).

(4) L. Di Nunno, G. Modena, and G. Scorrano, *Ric. Sci.*, **36**, 825 (1966).

(5) C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

(6) E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.*, **90**, 378, 386 (1968).

(7) A. Fava and A. Iliceto, *ibid.*, **80**, 3478 (1958).

(8) Data by L. Senatore, E. Ciuffarin, and A. Fava, *ibid.*, 92, 3035 (1970), from our own laboratory regarding the Brønsted coefficients for both entering and leaving group are also consistent with a SN2 mechanism.

(9) E. Ciuffarin and G. Guaraldi, *ibid.*, **91**, 1745 (1969).

(10) B. M. Trost, R. LaRochelle, and R. C. Atkins, *ibid.*, **91**, 2175 (1969).