states efficiently by a collisional process. If it is assumed that the Stern–Volmer slopes for 4-stilbazole and 4,4′-BPE represent the product of $k_{\text{diff}} = 1.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$ (for *tert*-butyl alcohol) and τ_n, the lifetime of the $^1n,\pi^*$ state, lifetimes of 10^{-8} sec and 4×10^{-8} sec are obtained for 4-stilbazole and 4,4′-BPE, respectively. The overall path for deactivation probably involves three excited singlet states of the azastilbenes: the initially formed planar trans fluorescent state ($^1\pi,\pi^*$), the $^1n,\pi^*$ state, and a twisted state ($^1\pi,\pi^*$) that decays with isomerization. The trend of increased quantum efficiencies for isomerization with increasing solvent polarity for 2,2′-BPE and 4,4′-BPE can be explained by an increase in energy of the $^1n,\pi^*$ state. Such an increase would be expected to lower the activation energy to reach the twisted state.

The lifetimes and reactivity of $^3n,\pi^*$ states in aza aromatics remain an area for further investigation. Results of the present study suggest that participation of reactive $^3n,\pi^*$ states in sensitized reactions of the azastilbenes is doubtful.

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Polar Exchange of Methylbenzhydryl Iodides with Iodine in Hexane

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Abstract: *m*- and *p*-methylbenzhydryl iodides exchange with elementary iodine in hexane by a polar mechanism requiring two molecules of I_2 in the transition state. Irreproducible parallel contributions by terms of lower order in iodine could be virtually eliminated by coating the glass surface of the reaction vessel with a hydrophobic silicone preparation. These and previous observations at 0° obey the σ^+ modification of the Hammett equation with $\rho = -5.2$; this very large magnitude of substituent effects means that the *p*-methyl compound exchanges 5000 times as rapidly as the *m*-chloro one! It is suggested that the second molecule of iodine interacts with the back side of the incipient carbonium ion in a transition state resembling an $I_2 \cdot \cdot R^+\ I_3^-$ ion pair. Attempts to synthesize nitro- and cyanobenzhydryl iodides were frustrated apparently because these compounds are very sensitive to decomposition by radical mechanisms; such decomposition is to be expected for any organic iodide unless the C–I bond is appreciably stronger than the I–I bond in the element.

The effects of meta and para substituents on rates tend to be greatest for those reactions having considerable release of or demand for electrons at the reaction center. Such reactions tend to have polar transition states, and especially large substituent effects should be observed in solvents of low dielectric constant where compensatory polarization of the medium is less important. Some organic iodides undergo isotopic exchange with the element by a very polar mechanism in which the transition state approximates an ion pair,[1] and Muizebelt and Noyes[2] have shown that benzhydryl iodide and its monochloro derivatives exchange by such a mechanism even in hexane solvent. The present work was undertaken to study additional substituents and to determine the magnitudes of their effects on this very polar reaction in a solvent of very low dielectric constant.

Experimental Section

Methylbenzhydryl Iodides. A solution of 2 g of *m*- or *p*-methylbenzhydryl alcohol, $(CH_3C_6H_4)(C_6H_5)CHOH$, in 5 ml of ethanol was flushed with nitrogen and treated with 5 ml of a concentrated solution of HI in ethanol and 10 ml of 57% aqueous HI. After 3 min, 20 ml of hexane was added to extract the iodide and was separated from the alcohol 2 min later. This hexane extract was washed with dilute aqueous sodium sulfite and sodium bicarbonate and then with water, dried over magnesium perchlorate for 1 hr, and concentrated by a stream of dry nitrogen. The product was crystallized by cooling the hexane solution to −80°. Four crystallizations normally produced material containing at least 99% of the theoretical amount of iodine.

Because the benzhydryl iodides were rapidly decomposed by light or oxygen, the entire preparation was carried out under a dim red light. The hexane solution was stored at −80° in complete darkness. Samples were analyzed for iodine by dissolving a known weight in carbon tetrachloride, irradiating the solution with a tungsten lamp until the iodine concentration reached a steady value, and measuring that concentration spectrophotometrically. The quantitative validity of this method was checked by hydrolyzing a sample and titrating the liberated iodide potentiometrically with silver nitrate.

Other Benzhydryl Iodides. Attempts were also made to prepare benzhydryl iodides with electron-withdrawing nitro[2] or cyano substituents. The attempts were unsuccessful, apparently because these compounds decomposed by radical mechanisms almost as rapidly as they were formed.

Hexane. The hexane solvent was stirred with concentrated sulfuric acid and then twice with 30% fuming acid, washed with sodium carbonate and water, and dried over calcium chloride. The middle fraction boiled 67.9–68.8° at 750 mm.

Procedure. Stock solutions of labeled iodine were prepared by adding a few drops of aqueous carrier-free iodine-131 to a solution of iodine in hexane and were dried over magnesium perchlorate. Concentrations of iodine were determined spectrophotometrically, and those of organic iodide were determined in the same way after quantitative photolysis.

Kinetic procedures were difficult because the organic iodide was decomposed by light and by oxygen and because the rate of exchange was sensitive to traces of moisture. All operations were conducted

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(1) R. M. Noyes and E. Körös, *Accounts Chem. Res.*, **4**, 233 (1971).

(2) W. J. Muizebelt and R. M. Noyes, *J. Amer. Chem. Soc.*, **92**, 6012 (1970).

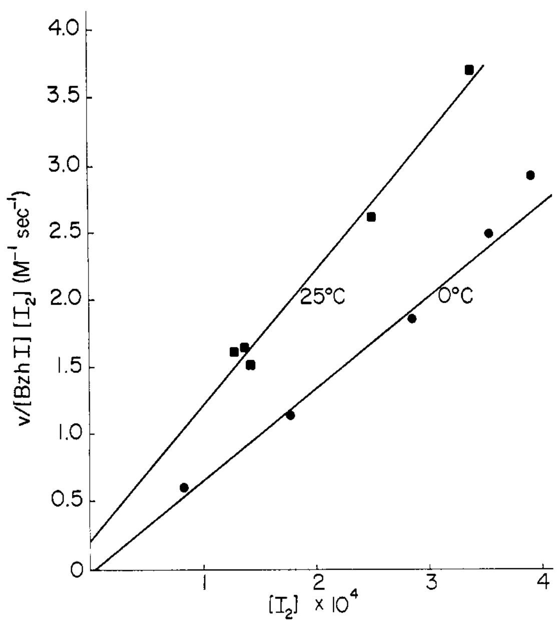

Figure 1. Rate data for exchange of *p*-methylbenzhydryl iodide with iodine in hexane.

in dim red light. Solutions of each reactant were stored over magnesium perchlorate for at least 3.5 hr and filtered immediately before use. Apparatus for handling the solutions was designed to minimize contact with atmospheric moisture. Each piece of glassware was cleaned by soaking it in a solution of 10% sodium hydroxide and 5% borax, traces of base were removed with dilute acetic acid, and the glassware was then dried for at least 24 hr at 180°. The inverted Y tubes in which the runs were carried out were cleaned and coated each time with "Desicote," a hydrophobic organosilicon material supplied by the Beckman Co.

Concentrations of methylbenzyhydryl iodide were in the neighborhood of 0.001 *M*, being somewhat less than this for the very reactive para compound and being up to 0.005 *M* for the meta compound. Concentrations of elementary iodine were almost always between 10^{-4} and 10^{-3} *M* and were always less than half the molar concentration of organic iodide.

The reactants were added to the arms of the Y; each tube was thermostated before the contents were mixed by shaking at zero time. At a subsequent time, reaction was quenched by pouring the contents of the Y tube into an ice-cold mixture of hexane and 0.05 *M* aqueous sodium sulfite. The iodine was reduced and extracted into the aqueous solution, and the residual radioactivity in the hexane solution was determined with a thin-walled Geiger counter. Completeness of exchange and absence of decomposition were established by radioactive and spectrophotometric measurements on solutions that had been mixed for about 14 half-lives.

Results

The first runs with *p*-methylbenzhydryl iodide were carried out in uncoated tubes. These runs exhibited large and variable amounts of initial exchange and considerable scatter in the dependence of the apparent rates of exchange on time and on the concentration of iodine. Drying glassware at higher temperatures reduced exchange rates. When the tubes were coated with "Desicote," apparent induced exchange was reduced to less than 10% of the theoretical maximum, variation of radioactivity with time obeyed the expression expected for a simple isotopic exchange, and the reduced rates varied consistently with the concentration of iodine.

Even in the dark, iodine catalyzes decomposition of benzhydryl iodides by what is probably a radical mechanism. The *m*-methyl compound is considerably more inert to decomposition than is the *p*-methyl one.

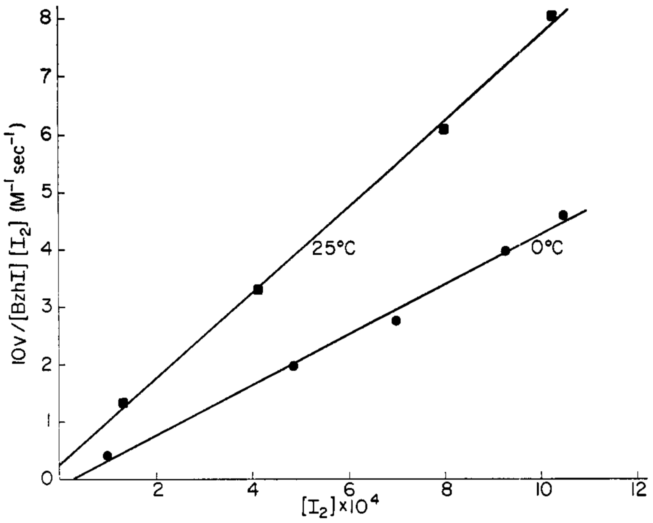

Figure 2. Rate data for exchange of *m*-methylbenzhydryl iodide with iodine in hexane.

However, this reaction was too slow to influence our exchange data with either compound. Thus reaction mixtures of each compound that had been left during 14 or more half-lives for exchange still contained 97% or more of the theoretical amount of radioactivity in the organically bound form. Decomposition clearly had a negligible effect on the apparent exchange rates.

As was anticipated from previous work,[2] the data for either compound at a specific temperature could be fitted reasonably well to an equation of the form of eq 1,

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

where v is the rate of isotopic exchange and BzhI is the substituted benzhydryl iodide. The rates of individual runs are presented in Figures 1 and 2 as plots of $v/[\mathrm{BzhI}][\mathrm{I_2}]$ *vs.* $[\mathrm{I_2}]$.

The data at 0° suggest a barely significant curvature in the direction to be expected if a term in $[\mathrm{I_2}]^3$ were contributing slightly to the rate. Other studies of polar exchange reactions[3,4] also detect contributions from higher order terms at low temperatures where the solubility of iodine is less. Such a high order contribution is particularly pronounced for *m*-chlorobenzhydryl iodide in hexane.[2] Chilling until solid iodine precipitates usually causes complete exchange in such systems.

An analysis of deviations from the least-squares lines in Figures 1 and 2 indicated that the intercepts were not significantly different from zero; therefore the k_1 term in eq 1 makes a negligible contribution to the rate. Runs with *p*-methylbenzhydryl iodide in tubes that had been dried, but not coated, were faster, and plots like Figure 1 seemed to fall on a line with a somewhat similar slope to that given by the coated tubes, but with a significant intercept. It therefore appears that the k_1 term in uncoated tubes is due either to heterogeneous reaction or to moisture initially present on the glass. These observations cast doubt on the mechanistic significance of the k_1 terms observed in hexane for other benzhydryl iodides[2] in dried but uncoated vessels.

The data plotted in Figures 1 and 2 were analyzed according to the two-parameter form of eq 1, and the

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[3] A. Goldman and R. M. Noyes, *J. Amer. Chem. Soc.*, **79**, 5370 (1957).

[4] J. E. Bujake, Jr., and R. M. Noyes, *ibid.*, **83**, 1555 (1961).

Table I. Rate Constants and Activation Parameters for k_2 Terms Involving Exchange of Benzhydryl Iodides in Hexane

Substituent	k_2, (mol/l.)$^{-2}$ sec^{-1} 0°	25°	E_2, kcal/mol	Log A_2	$\Delta S_2^{\ddagger}$, cal/(mol deg)
p-CH_3	6800 ± 500	10,100 ± 800	2.5 ± 1.0	5.9 ± 0.8	−34 ± 4
m-CH_3	440 ± 20	750 ± 20	3.5 ± 0.6	5.4 ± 0.5	−36 ± 2
Unsubstituted	90 ± 3	113 ± 5	1.3 ± 1.0	3.0 ± 0.7	−47 ± 3
p-Cl	57 ± 3	82 ± 3	2.6 ± 0.5	3.8 ± 0.3	−43 ± 2
m-Cl	1.3 ± 0.3				

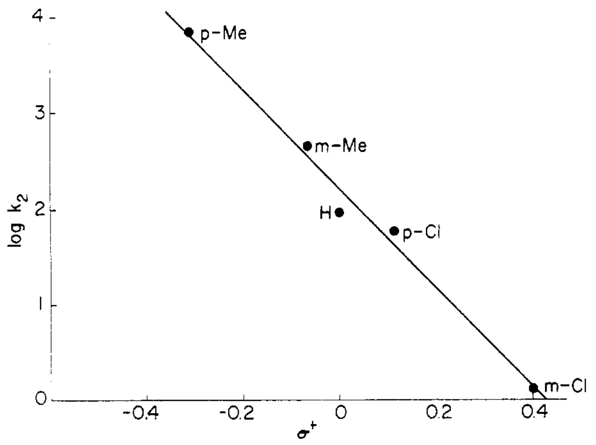

Figure 3. Hammett[5] plot for exchange of substituted benzhydryl iodides with iodine in hexane at 0°.

values of k_2 are presented in Table I along with the standard parameters for temperature dependence. They are also compared with the data[2] on other benzhydryl iodides in the same solvent. Although the scatter in activation parameters is large, the differences in rate of exchange seem to be due more to changes in the entropy than in the energy of activation.

Discussion

Figure 3 is a Hammett[5] plot of the data at 0°. The fit including the para substituents is very much better if σ^+ [6] is used instead of σ; such behavior is expected for a reaction such as this in which the transition state is expected to involve considerable carbonium ion character.

The plot in Figure 3 indicates a ρ of −5.2, which is an exceptionally large magnitude for a reaction between neutral species. Such a value, which corresponds to a factor of about 5000 in the rates of p-methyl and m-chloro compounds, is the kind of effect anticipated for the formation of an ion-pair transition state in a solvent of very low dielectric constant.

It will be difficult to extend the modest range of σ values studied here. Compounds having groups with more negative σ values, such as methoxy and dimethylamino, will be very susceptible to hydrolysis and will exchange so rapidly that rates will be difficult to measure. Rapid radical decomposition evidently frustrated our attempts to synthesize compounds having groups with more positive σ values, such as nitro and cyano.

The synthetic failure can be rationalized in hindsight. Because carbon and iodine differ so much in "hardness," equilibrium in the reaction $2RI \rightleftarrows R_2 + I_2$ will lie to the right for most organic iodides in spite of the opposite prediction of the electronegativity argument.[7] However, as long as the C–I bond in a compound is stronger than the I–I bond in the element, most of the radicals in any system will be iodine atoms. Decomposition of RI will then be slow in the absence of an irreversible scavenger for R radicals. If the strength of the C–I bond is less than or close to that of I–I, the reaction $RI + I \rightarrow R + I_2$ will take place easily and the resulting R radicals will react with each other with resulting decomposition of RI. Although the C–I bond strength in benzhydryl iodide is not known, extrapolation of values for alkyl and benzyl iodides[8] suggests that it is not much stronger than the 35.5 kcal/mol bond in I_2. Any substituents that tend to stabilize benzhydryl radicals will then make the iodides very susceptible to radical decomposition.

The k_1 term is of doubtful significance for the exchange in hexane of either *tert*-butyl[4] or benzhydryl[2] iodide. The reactive center in these compounds has sp^3 hybridization. It is tempting to suggest that the function of the second molecule of iodine is to interact with the backside of the incipient carbonium ion being formed in a solvent containing no other nucleophile. The transition state would then be of the form $I_2 \cdots R^+ I_3^-$. Exchange by such a mechanism would be accompanied by retention of configuration, although retention would not uniquely require this mechanism. It would be possible in principle to determine whether these monosubstituted benzhydryl iodides exchange with retention or with inversion of configuration, but the experiments have not been attempted. The k_1 and even k_0 terms are more important kinetically for the exchange of benzoyl iodides[3,9] where the carbon is hybridized differently, but the effects of coating glassware observed in the present study make mechanistic significance of these low order terms unsure.

Acknowledgment. This work was supported in part by a contract with the United States Atomic Energy Commission.

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