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Quantitative Study of Solvent Effects on Menshutkin Reaction between 1,4-Diazabicyclo[2.2.2]octane and (2-Chloroethyl)benzene, (2-Bromoethyl)benzene, and (2-Iodoethyl)benzene

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Received February 19, 1975

Abstract: By kinetic studies and product analysis, we have shown that the reaction between 1,4-diazabicyclo[2.2.2]octane on the one hand and (2-chloroethyl)benzene, (2-bromoethyl)benzene, and (2-iodoethyl)benzene on the other hand are Menshutkin quaternization reactions. By working in pure solvents and making use of the correlation method, the irregular behavior of protic solvents is shown. This is interpreted in terms of specific interactions between the protic solvents on the one hand and the halides on the other. There is a deactivation of the amine by formation of hydrogen bonded complexes with the protic solvents and a specific activation of the alkyl halides by these same protic solvents, all the more important as the halogen is more electronegative.

The influence of solvents on the rate of chemical reactions has been observed a long time ago. Attempts were made to express kinetic effects of the medium in terms of physical or thermodynamic properties of the solution.[1] Efforts which have been put forward to derive valid quantitative relationships are not satisfactory owing to oversimplifications. However, a "general" empirical solvent activity scale based on the results of a particular reaction has been put forward by some authors.[2] They deduced a relationship between ln k for a standard reaction in various solvents and ln k for the reaction under study in the same solvents. However, the activity scale shown was limited by the amplitude, e.g., the Ω values,[3] or mostly by specific influence of medium rather than physical effects, e.g., the Y values.[4] Nevertheless, under some conditions, it is possible to find with this activity scale a correlation which accounts fairly well for solvent effects.

The Menshutkin reaction has long been regarded as one of the best examples of solvent effects on the reaction rate. In this reaction, since ions are formed from neutral reactants, large increases in rate have been observed with increased polarity of the solvent.[5] So Drougard and Decroocq showed that it was possible to set up a solvent activity scale and chose as a standard reaction the quaternization of tripropylamine (TPA) by methyl iodide (MI) at 20°; the reaction was carried out in about a hundred solvents as well as in many binary mixtures.[6] In this scale, the solvent activity (S) was defined as

$$S = \log k_{2(\mathrm{TPA+MI})} \text{ at } (20°) \tag{1}$$

where k_2 was the second-order rate constant in l. mol^{-1} min^{-1} in a given solvent for the reaction between TPA and MI. The relationship between S and the reaction rate is given by eq 2:

$$\log k_2 = (\log k_2)_{S=0} + RS \tag{2}$$

where k_2 is the rate constant of a reaction in a solvent whose activity is S, R is a constant at a given temperature and is characteristic of the reaction. Thus, parameter R, which is supposed to be independent of the solvent, is a measure of the susceptibility of the reaction to the action of the solvent. There is a good linear correlation between the S values and solvent-sensitive absorption bands as well as kinetic data for various reactions.[6] In correlating a series of results, it became apparent that the solvent influenced the course of chemical reactions by nonspecific physical effects which depend on solvent polarity, polarizability, conjugated polarizability, and lastly on molecular structure and by specific chemical effects which depend on the solvation of the reactants.[7] Therefore, regular solvent effects must be distinguished from irregular ones. In some cases, reaction rates were only influenced by physical effects and gave perfect correlations; in others, there were specific reactant solvation effects. Protic solvents, for example, show an irregular behavior when they form hydrogen bonds with reactant species.

In this work, we analyze the solvent influence upon the Menshutkin reaction, particularly for protic solvents. The reactants chosen were 1,4-diazabicyclo[2.2.2]octane

Table I. Variation of the Rate Constant with the Nature of the Aprotic Solvent in the Reaction between 2CEB, 2BEB, 21EB, and Dabco at 54.5°

Solvent	Nr[a]	D at 20°[b]	S[b]	k_2, l. mol^{-1} min^{-1}		
				Dabco + 2CEB	Dabco + 2BEB	Dabco + 2IEB
Carbon tetrachloride	12	2.24	−2.85		9.38×10^{-4}	4.93×10^{-3}
Isopropyl ether	11				1.19×10^{-3}	6.78×10^{-3}
Ethylbenzene	Ar11	2.41	−2.14	2.48×10^{-5}	5.48×10^{-3}	2.52×10^{-2}
Toluene	Ar10	2.39	−2.00	3.63×10^{-5}	7.34×10^{-3}	3.27×10^{-2}
Benzene	Ar9	2.28	−1.69	6.98×10^{-5}	9.91×10^{-3}	4.73×10^{-2}
Ethyl acetate	10	6.20	−1.66	1.23×10^{-4}	2.08×10^{-2}	7.28×10^{-2}
Tetrahydrofuran	9	7.61	−1.54	1.31×10^{-4}	2.12×10^{-2}	9.68×10^{-2}
p-Dioxane	8	2.22	−1.43	1.70×10^{-4}	2.35×10^{-2}	1.24×10^{-1}
Chlorobenzene	Ar8	5.70	−1.15	1.89×10^{-4}	2.27×10^{-2}	9.37×10^{-2}
Styrene	Ar7	2.42	−1.28	2.15×10^{-4}	2.37×10^{-2}	1.03×10^{-1}
Bromobenzene	Ar6	5.46	−1.05	2.47×10^{-4}	2.85×10^{-2}	1.24×10^{-1}
3-Pentanone	7	16.90	−1.17	3.42×10^{-4}	5.29×10^{-2}	2.49×10^{-1}
Anisole	Ar5	4.39	−1.05	4.24×10^{-4}	4.98×10^{-2}	2.01×10^{-1}
1-Methylnaphthalene	Ar4	2.75	−0.73	6.09×10^{-4}	8.53×10^{-2}	4.14×10^{-1}
Acetone	6	20.70	−0.79	7.06×10^{-4}	1.19×10^{-1}	6.48×10^{-1}
Cyclohexanone	5	15.70	−0.81	7.70×10^{-4}	1.25×10^{-1}	7.73×10^{-1}
Benzonitrile	Ar3	25.65	−0.41	1.68×10^{-3}	2.09×10^{-1}	8.14×10^{-1}
Nitrobenzene	Ar2	35.75	−0.32	1.83×10^{-3}	2.16×10^{-1}	8.93×10^{-1}
Acetonitrile	4	36.80	−0.33	3.73×10^{-3}	3.70×10^{-1}	1.44
N,N-Dimethylformamide	3	38.42	−0.19	4.54×10^{-3}	6.70×10^{-1}	2.84
Phenylacetonitrile	Ar1	18.95	0.04	4.94×10^{-3}	4.36×10^{-1}	1.56
Nitromethane	2	37.45	0.04	6.88×10^{-3}	6.55×10^{-1}	1.61
Methyl sulfoxide	1	49.00	0.20	1.52×10^{-2}	1.55	6.04

[a] The numbers correspond to those of the plots. [b] References 6 and 7.

Table II. Variation of the Rate Constant with the Nature of the Protic Solvent in the Reaction between 2CEB, 2BEB, 21EB, and Dabco at 54.5°

Solvent	Nr[a]	D at 20°[b]	S[b]	k_2, l. mol^{-1} min^{-1}		
				Dabco + 2CEB	Dabco + 2BEB	Dabco + 21EB
Methanol	P1	33.60	−1.82	2.82×10^{-4}	1.35×10^{-2}	2.39×10^{-2}
Cyclohexanol	P2	17.05	−1.91	2.52×10^{-4}	1.16×10^{-2}	2.24×10^{-2}
Ethanol	P3	25.07	−1.98	2.27×10^{-4}	1.13×10^{-2}	2.07×10^{-2}
1-Propanol	P4	20.65	−2.14	1.87×10^{-4}	9.42×10^{-3}	1.39×10^{-2}
1-Butanol	P5	17.90	−2.19	1.69×10^{-4}	8.40×10^{-3}	1.24×10^{-2}
Isopropyl alcohol	P14			2.14×10^{-4}	9.98×10^{-3}	1.39×10^{-2}
Isobutyl alcohol	P17			1.64×10^{-4}	7.38×10^{-3}	1.02×10^{-2}
sec-Butyl alcohol	P7	16.80	−2.03	1.82×10^{-4}	8.09×10^{-3}	1.25×10^{-2}
tert-Butyl alcohol	P6	12.10	−1.87	1.98×10^{-4}	8.61×10^{-3}	1.38×10^{-2}
4-Methyl-2-pentanol	P16			1.47×10^{-4}	5.79×10^{-3}	9.32×10^{-3}
Benzyl alcohol	P8	13.62	−1.25	3.99×10^{-4}	1.76×10^{-2}	3.07×10^{-2}
Phenethyl alcohol	P12			2.81×10^{-4}	1.18×10^{-2}	2.17×10^{-2}
sec-Phenethyl alcohol	P13			2.47×10^{-4}	8.48×10^{-2}	2.05×10^{-2}
Allyl alcohol	P15			2.23×10^{-4}	8.25×10^{-3}	1.42×10^{-2}
Cinnamyl alcohol	P11			3.78×10^{-4}	2.18×10^{-3}	4.19×10^{-2}
m-Cresol	P10	11.80	−3.82	1.26×10^{-4}	2.44×10^{-3}	1.82×10^{-3}
Chloroform	P9	4.80	−0.92	2.81×10^{-4}	1.55×10^{-2}	2.31×10^{-2}

[a] The numbers correspond to those of the plots. [b] References 6 and 7.

(Dabco), and (2-chloroethyl)benzene (2CEB), (2-bromoethyl)benzene (2BEB), and (2-iodoethyl)benzene (2IEB).

Results and Discussion

First and foremost, it was ascertained that the chosen reactants gave rise to a true Menshutkin reaction. In solvents of weak polarity, the monoalkylated quaternary salt was isolated in almost quantitative yields. In no case did these reactants yield styrene. This fact was verified by uv spectroscopy and gas chromatography. The kinetics for all various conditions gave second-order constant, the initial and running rates being both proportional to the product of the amine and halide concentrations. It was also verified that the salt precipitation in solvents of weak polarity had no influence on the rate of the reactions. It was, therefore, concluded that the reactions studied were Menshutkin quaternization reactions.

The aprotic and protic solvent effect upon reaction rates can be seen respectively in Tables I and II. The dielectric constants and the *S* values are also listed in these tables. The reactivity sequence in the aprotic aliphatic solvents is the same for the three pairs studied and the reference pair TPA/MI. However, inversions are observed with aprotic aromatic solvents, becoming more important in going from 2CEB to 2BEB and 2IEB. From the results obtained for the three pairs studied, it was found that the dielectric constant alone can not account for medium effects. Indeed, the reaction rate in 1-methylnaphthalene ($D = 2.75$) is a hundred times faster than in carbon tetrachloride ($D = 2.24$) where the dielectric constant are similar, and inversely the reaction rate is practically the same in 1-methylnaphthalene and in acetone ($D = 20.70$), as can be seen in Table I. However, classification of solvent groups can be outlined in a log k_2 vs. D graph (Figure 1). The aprotic aliphatic solvents define a curve, called a basic curve.[6,8] For these solvents, the

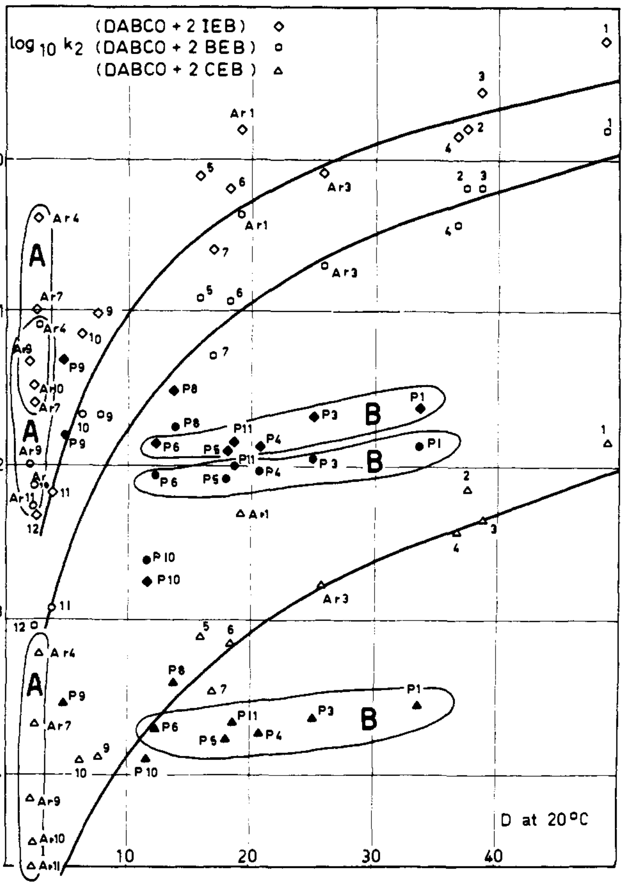

Figure. 1. Variation of the rate constant with the dielectric constant of the solvent.

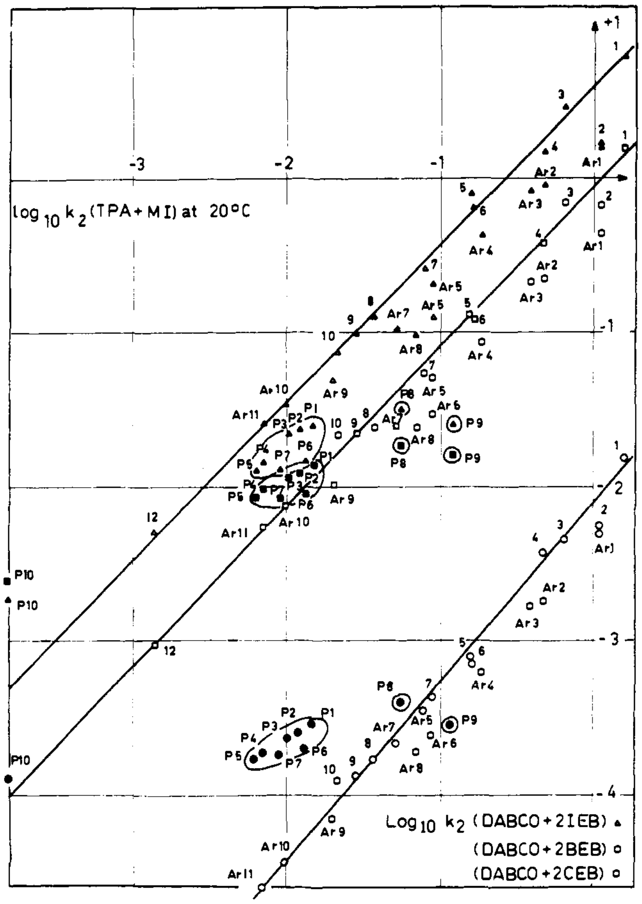

Figure 2. Correlation with the coefficient of solvent activity defined by Drougard and Decroocq.

variations in the rate constant are related to their polarity. It can also be seen that aromatic hydrocarbons show an effect greater than aliphatic ones (Figure 1, zone A). Their activity varies in the same direction as the number of unsaturated bonds. Thus, the solvent activity is also related to its polarizability. The great activity of phenylacetonitrile may be explained by the effect of polarity and conjugated polarizability. Protic solvents are found in the region of great dielectric constants and low reaction rates (Figure 1, zone B). The gap between the basic curve and the protic solvents zone increases when one goes from the Dabco/2CEB pair to the Dabco/2BEB pair and the Dabco/2IEB pair. These qualitative investigations of the influence of the dielectric constant showed the particular behavior of protic solvents. Their irregularity in comparison to the other solvents becomes more evident when the halide is varied.

Figure 2 illustrates the relationship between the solvent S values determined from the reference pair TPA/MI and the reaction rates of the three pairs studied. The correlation is good for the aprotic aliphatic solvents, but the points for the aprotic aromatic solvents all lie below the correlation lines defined by the aprotic aliphatic solvents. In going from 2CEB to 2BEB and to 2IEB, the gap between this points and the lines increases. An examination of the correlation parameters included in Table III confirms this fact.

The deviations of aprotic aromatic solvents disappear when the rates of the Dabco/2CEB and Dabco/2BEB pairs are correlated with the rate of the Dabco/2IEB pair, as shown in Figure 3 and Table IV.

The halides used include a polarizable aromatic ring, and furthermore the halide polarizability increases strongly in going from chlorine to iodine. It must be accepted that, the more polarizable are the reactants, the less are the catalytic effects of solvent polarizability. Although the reaction conditions are favorable, the solvent activity is small. This fact must relate to the slope variations of the correlations for the various pairs. It can be seen that R increases in going from the Dabco/2IEB pair to the Dabco/2BEB pair and to the Dabco/2CEB pair (Table III). This sequence is the same as that for the slopes obtained in the internal correlation (Table IV). Thus, the less reactive is the pair, the more sensitive is it to the solvent effects.

Table III. Correlation with the TPA/MI Pair

	Dabco/2CER		Dabco/2BEB		Dabco/2IEB	
Aprotic solvents	Aliph	Aliph + Ar	Aliph	Aliph + Ar	Aliph	Aliph +'Ar
Correlation coefficients	0.994	0.987	0.998	0.982	0.998	0.976
R	1.16	1.11	1.05	0.99	1.02	0.96

With regard to the protic solvents, there is no correlation. However, in Figure 2, it can be seen that the protic solvent zone lies far above the correlation line for the Dabco/2CEB pair, just above that for the Dabco/2BEB pair, and below that for the Dabco/2IEB pair. The same fact can be noticed in the internal correlation (Figure 3). This special effect of protic solvents can not be attributed only to a smaller activity of the amine from formation by hydrogen bond of a complex amine-alcohol. Such complexes have long been known to exist, and many association constants have been determined by various physical methods.[9] In the three pairs studied, the same amine is used and in the absence of other effects, the degree of activity of this amine should influence the rates by a constant factor. Since the

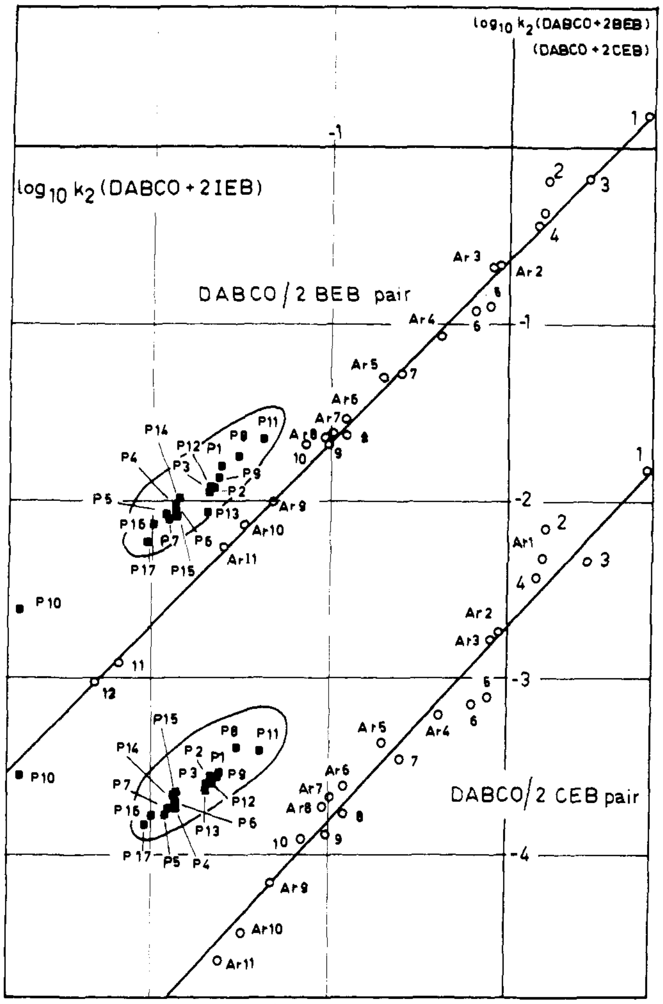

Figure 3. Internal correlation.

Table IV. Correlation with the Dabco/2IEB Pair

	Dabco/2CEB		Dabco/2BEB	
Aprotic solvents	Aliph	Aliph + Ar	Aliph	Aliph + Ar
Correlation coefficients	0.987	0.986	0.997	0.997
R	1.11	1.11	1.03	1.03

solvent effects vary with the nature of the halide, any explanation must, therefore, be linked to this fact. One must accept that there is a specific catalytic effect of protic compounds on the halide. Thus, there could be a specific solvation of the halide anions formed in the reaction by the protic solvent, through hydrogen bonding between the anion and the solvent. These interactions are known, and association constants have been determined by ir spectroscopy.[10] Formation of such a hydrogen bond facilitates the halide departure. Parker has already discussed, in qualitative manner, the variables affecting the solvation of anions.[11] A negative charge on small atoms produces anions, e.g., Cl^-, which are strong hydrogen bond acceptors. Such anions have strong hydrogen bonding interactions with protic solvents. This interaction does not occur in dipolar aprotic solvents. Localization of charge on large atoms produces an anion, e.g., I^-, which is a weak hydrogen bond acceptor. Such anions are not significantly more solvated by protic than dipolar aprotic solvents. The hypothesis of anion specific solvation by protic compounds is also confirmed by a comparison of the solubility of the quaternary salt. It should be noted that, although these salts precipitate right from the start in aprotic solvent of weak polarity, they are very soluble in all alcohols in spite of their weak dielectric constant. Thus in going from the Dabco/2CEB pair to the Dabco/2IEB pair, one would expect a decrease of the specific effect due to the halide and the amine complexation effect should become predominant. This fact may explain the inhibition of the reaction in the protic solvents for the Dabco/2IEB pair and its activation for the Dabco/2CEB pair and also the reactivity inversion for the Dabco/2BEB and Dabco/2IEB pairs in *m*-cresol as solvent (Table II).

Another explanation is that a weak hydrogen bond forms between the alkyl halide and the protic solvent before the reaction. Some authors have shown the existence of such bonds through thermodynamic measurements and ir spectroscopy.[12] Although they do not agree with the intensity value of this interactions, a searcher group comes to the conclusion that bond increases are: $I < Br < Cl < F$.[11,13] For example, the association constants between the cyclohexyl halides and phenol at 25° in carbon tetrachloride increases from the iodide ($K = 3.99$ l. mol^{-1}) to the bromide ($K = 4.18$ l. mol^{-1}), the chloride ($K = 4.83$ l. mol^{-1}), and the fluoride ($K = 9.12$ l. mol^{-1}).[14] Although this effect is weak, this sequence is the same as that found by kinetic studies. The catalytic effects of protic solvents in the quaternization reactions have already been reported by Swain and Eddy under a particular set of conditions; working at 100°, they could neglect the inhibitory effect of the protic solvent on the amine.[15]

Conclusions

The empirical parameter S constitutes a more comprehensive measure of the effect of a solvent than the dielectric constant or any other single physical characteristic since it reflects more faithfully the complete picture of almost all physical intermolecular forces acting in solutions. This parameter makes possible the semiquantitative estimation of the effect of solvents on the rate of reactions and so leads to conclusions regarding the reaction mechanism. Hence, with these values, we are able to interpret, though only qualitatively, the behavior of the solvents on the basis of two influences subject to the nature of the reaction partners. The physical influences, resulting from polarity and polarizability of various species present in the medium, have noticeable effects on the reaction rate. The specific influences appear by formation of complexes between protic compounds and the various species in the medium. If the protic compounds form hydrogen bonded complexes with the amine, its nucleophilic character becomes weaker, and thus we observe a specific inhibitory effect. On the other hand by association with the halide, the protic compounds will have a specific catalytic effect all the more important as the halogen is more electronegative. These two effects are always in competition, and the result is a function of the chemical nature of the reactants. Finally we have shown that a lesser reactivity leads to a greater susceptibility to the solvent influence.

Experimental Section

Materials. 1,4-Diazabicyclo[2.2.2]octane, (2-chloroethyl)benzene, (2-bromoethyl)benzene, and (2-iodoethyl)benzene were Fluka AG, purum grade. Solvents puriss grade were dried on molecular sieve, and the others were purified as described by Weisberger[16] and then dried on molecular sieve.

The products were isolated by precipitation in weak dielectric constant solvents. They were washed with carbon tetrachloride and dried in vacuo, giving crystals.

Phenethyl-1,4-diazabicyclo[2.2.2]octane Ammonium Chloride. Anal. Calcd for $C_{14}H_{21}N_2Cl$: C, 66.55; H, 8.32; N, 11.10; Cl, 14.13. Found: C, 64.60; H, 8.50; N, 10.74; Cl, 16.16.

Phenethyl-1,4-diazabicyclo[2.2.2]octane Ammonium Bromide. Anal. Calcd for $C_{14}H_{21}N_2Br$: C, 56.58; H, 7.12; N, 9.42; Br, 26.88. Found: C, 56.13; H, 7.09; N, 9.46; Br, 27.32.

Phenethyl-1,4-diazabicyclo[2.2.2]octane Ammonium Iodide. Anal. Calcd for $C_{14}H_{21}N_2I$: C, 48.85; H, 6.10; N, 8.15; I, 36.90. Found: C, 48.30; H, 6.10; N, 8.37; I, 37.32. NMR spectra in deuteriowater showed the two expected aromatic (δ 7.9) and aliphatic (δ 3.9) peaks, all signals integrating correctly.

Gas chromatographic analyses were performed on the gas chromatograph Varian Model 1840-1, equipped with a flame ionization detector. The stainless steel column (3 × ⅛ in.) was filled with Porapak Q (150–200 mesh). Uv spectra were performed on a Perkin-Elmer spectrophotometer Model 350.

Kinetic. Equal volumes of a halide solution (ca. 0.580 mol $l.^{-1}$) and an amine solution (ca. 0.200 mol $l.^{-1}$) were placed in a thermostat bath at 54.5° ± 0.2 for 30 min and then were mixed rapidly. The reactions were carried out in stoppered flasks, aliquots of reaction mixture being withdrawn at intervals and titrated.

Rates were determined by following the disappearance of base or the appearance of halide ion. In some instances, both methods were employed for the same reaction to provide an added check. In each case, the two rate constants were identical within the limits of experimental error. The base concentration was determined by titration with hydrochloric acid 0.1 mol $l.^{-1}$ in ethanol solvent using Bromophenol Blue as indicator. The halide ion concentration was determined by the Volhard method.

Second-order rate constants k_2 were calculated by using the integrated form of the rate equation as applied to nonequimolecular concentration, $k_2t = (a - b)^{-1}$ [ln $((a - x)/(b - x))$ − ln (a/b)], where a and b are respectively the initial concentration of the halide and the amine, and x is the concentration of the amine at time t.

Rate constants, correlations, and precision of each were obtained in the usual manner by a linear least-squares analysis. The computations were carried out by an IBM 1440 computer and appropriate Fortran programs.

Acknowledgments. We are grateful to Professor D. Decroocq for many suggestions and helpful discussions regarding the interpretation of the experimental results.

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Polar Effects in Radical Reactions. IV. The Reaction of Hydrogen Atoms with Substituted Toluenes[1]

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Abstract: Hydrogen atoms, produced by the photolysis (3500 Å) of *tert*-butyl peroxyformate (BUP) at 35°, were allowed to react with a series of substituted toluenes (QH) in the presence of 2-methyl-2-propanethiol-d_1 (RSD) as a standard reactant. As controls, a similar series of substituted benzenes also was studied. An equation is derived which shows that the relative reactivity of a hydrogen donor QH with the H atom is proportional to the slope of a plot of the ratio of the yields of H_2 to HD as the QH/RSD ratio is varied in the solvent mixture. All of the toluenes studied have about the same relative reactivity (per methyl group), 0.056. The benzenes have a similar but slightly lower relative reactivity, 0.028. Since the reactivity of the benzenes is so close to that of the toluenes, it is clear that some of the H_2 produced from toluenes arises from abstraction of ring hydrogens. Four possible mechanisms by which this might occur are considered, and it is concluded that the most likely is the reaction of an H atom with a cyclohexadienyl radical (eq 9). Despite this complication, an inspection of the data (Table I) makes it clear that the ρ value for the H atom is approximately zero. An empirical treatment of the data in which the reactivity of C_6H_5X is subtracted from that of $X\text{-}C_6H_4\text{-}CH_3$ gives a ρ of −0.1. Thus, it is clear that the H atom, like the methyl and phenyl radicals, shows little polar character in its attack on the benzylic position of substituted toluenes.

Reactions of the hydrogen atom in the gas phase have been extensively studied,[3,4] but the solution chemistry of this radical has come under intensive investigation only relatively recently.[5-8] The hydrogen atom is of great theoretical interest; for example, data on its reactions are necessary to test calculations of absolute rate theory.[3] In addition, it is desirable to compare the behavior of the H atom with that of other, larger free radicals.

A considerable effort has been expended toward understanding the role of the H atom in radiation chemistry and biology.[6-8] In the radiolysis of aqueous solutions, the H atom is produced along with various other species, e.g., the solvated electron, the hydroxyl radical, and excited molecules.[9] In order to interpret the chemical effects resulting from radiation, it is essential that the reactions of the different transient species be isolated and studied independently.