Cation–Anion Combination Reactions. IX.[1] A Remarkable Correlation of Nucleophilic Reactions with Cations

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Abstract: The reactions of a series of aryldiazonium ions with azide and cyanide ions in dimethyl sulfoxide solution have been studied by stop-flow spectrophotometry. The rate constants obtained in this study along with extensive data previously reported for aryldiazonium, triarylmethyl, and aryltropylium ions reacting with a range of nucleophiles in several solvents may all be correlated by the remarkably simple equation: $\log k_N = \log k_{H_2O} + N_+$, where k_N is the rate constant for reaction of a particular cation with a given nucleophile in a given solvent, k_{H_2O} is the rate constant for reaction of the same cation with water in pure water, and N_+ is a constant characteristic of the given nucleophile and solvent. A range of reactivities with any given cation of ten powers of ten, and with any given nucleophile of six powers of ten, is accommodated by the equation. The equilibrium constants for the reactions show no comparably simple correlation. It is suggested that the N_+ values are directly related to the solvation energies of the nucleophiles.

In the previous papers of this series[1a] we have reported rate and equilibrium constants for the reactions of three classes of stable cations with several nucleophiles in several solvents. In the present paper we report some additional data for reactions of aryldiazonium ions in dimethyl sulfoxide and proceed to an interpretation of the considerable body of data now available.

Our recent papers have repeatedly called attention to the remarkable invariance in the selectivities of the different cations toward various nucleophiles, but have been quite cautious in making generalizations or attempting interpretation. We now feel that enough data have been accumulated to support a general statement concerning invariance in selectivities for the cation–anion combination reactions considered.

Results

The new rate and equilibrium constants which we have determined are reported in Table I.

Because of the strong absorption of dimethyl sulfoxide at wavelengths much lower than 285 nm, several reactions could not be followed at the wavelengths of maximum absorbance of either reactant or product. This limitation was not severe in the cases of the azide ion reactions. For all compounds except H, *m*-Cl, and *p*-CN substituted benzenediazonium ions, either the azide product or the diazonium ion has maximum absorbance above *ca.* 285 nm. Even in the other three cases, large changes in absorbance at higher wavelengths are observed as the reaction proceeds. For the cyanide reactions, however, the limitation is quite severe. Not only are the changes in absorbance much smaller for these reactions than for the azide reactions, but side reactions are much more bothersome.

For the more reactive diazonium ions, there also appears to be a complication due to the buffer necessary for the study of the cyanide reactions. For example, the absorbance at 320 nm for *p*-nitrobenzenediazonium ion in a buffer solution prepared by the addition of *p*-toluenesulfonic acid to triethylamine in DMSO is considerably lower than that in a dilute solution of *p*-toluenesulfonic acid alone. The rate constants observed for the change in absorbance on addition of cyanide ion to the buffered solutions appear to depend on buffer concentration as well as on cyanide ion concentration, but the dependence is not simple.

Because of these difficulties, we have been able to determine reliable data on the cyanide ion reactions only with the *p*-Br, *p*-Cl, *p*-CH_3, and *p*-CH_3O substituted benzenediazonium ions. In these cases the reactions could be followed at or near the wavelength of maximum absorbance of the diazonium ion, and runs at various cyanide ion and buffer concentrations gave consistent values for equilibrium and rate constants. We assume that the reactions observed are analogous to those observed in aqueous solution,[2] producing the *syn*-diazocyanides.

The reactions of the diazonium ions with azide ion show the same characteristics which we have previously reported for these reactions in aqueous[3] and methanol[4] solutions. A rapid initial change in absorbance is followed by a much slower change which does not depend on azide ion concentration. The rapid reaction produces aryl azide and arylpentazole, while the slow reaction is the decomposition of the arylpentazole to aryl azide. The slow reaction causes a large enough change in absorbance for reliable calculation of the first-order decomposition rate constants only for the first four entries in Table I. In these cases, the slow change in absorbance amounts to 10–13% of the total change in absorbance. The decomposition rate constants are not very solvent dependent. For *p*-benzoylphenylpentazole, the rate constant is 1.9×10^{-2} sec^{-1} in water, 7.9×10^{-2} sec^{-1} in methanol, and 4.2×10^{-2} sec^{-1} in DMSO.

The rapid reaction of azide ion with aryldiazonium ions to form aryl azide and arylpentazole is believed to be a two-step reaction proceeding through a diazoazide intermediate. For the reactions in water, we have argued that the rate-determining step is the conversion of the intermediate to products, while in methanol the

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[1] (a) Previous paper in this series: C. D. Ritchie and P. O. I. Virtanen, *J. Amer. Chem. Soc.* **94**, 4963 (1972). (b) This work was supported by Grant No. GP-29164 from National Science Foundation, and Grant No. GM-12832 from NIH–PHS.

[2] C. D. Ritchie and D. J. Wright, *ibid.*, **93**, 6574 (1971).

[3] C. D. Ritchie and D. J. Wright, *ibid.*, **93**, 2429 (1971).

[4] C. D. Ritchie and P. O. I. Virtanen, *ibid.*, **94**, 1589 (1972).

Table I. Rate and Equilibrium Constants for Reactions of Aryldiazonium Ions, X–$C_6H_4N_2^+$, in DMSO Solution at 23 ± 1°

X	λ^a	$k_{N_3^-}{}^b$	$k_{dec}{}^c$	$k_{CN^-}{}^d$	$K_{CN^-}{}^e$
p-NO_2	320	1.0×10^{10}	7.6×10^{-2}		
p-CN	285	1.0×10^{10}	5.0×10^{-2}		
p-C_6H_5CO	298	6.7×10^{9}	4.2×10^{-2}		
p-COOH	298	5.9×10^{9}	3.1×10^{-2}		
m-Cl	310	7.0×10^{9}			
p-Br	290	4.0×10^{9}		1.6×10^{8}	3.2×10^{9}
p-Cl	285	4.1×10^{9}		1.5×10^{8}	2.5×10^{9}
H	296	1.4×10^{9}			
p-CH_3	285	4.3×10^{8}		3.8×10^{7}	1.4×10^{8}
p-CH_3O	314	7.1×10^{7}		1.6×10^{7}	8.5×10^{7}

[a] Wavelength at which reactions were followed in nm. [b] Second-order rate constant for reaction with azide ion in units of M^{-1} sec^{-1}. [c] First-order rate constant for decomposition of arylpentazole in units of sec^{-1}. [d] Second-order rate constant for reaction with cyanide ion in units of M^{-1} sec^{-1}. [e] Equilibrium constant for formation of the *syn*-diazocyanides in units of M^{-1}.

rate-determining step is believed to be the formation of the intermediate. Since the rate constants found for the more reactive diazonium ions in DMSO are either diffusion controlled, or quite close to it, the rate-determining step must be the formation of the intermediate diazoazide. For those cases where the rate constant is well below diffusion controlled, the second step might be rate determining, but we see no reason to assume that a change in rate-determining step has occurred.

Discussion

An examination of all of the data for reactions of cations with nucleophiles which we have accumulated reveals that the relative rates of reaction of a cation with any two combinations of nucleophile and solvent are quite insensitive to the structure of the cation. Because of the large amount of data involved, the most efficient method of illustrating this observation is by means of a graphical presentation.

For this purpose, we define a parameter, N_+, for a given nucleophile in a given solvent by eq 1

$$N_+ = \log k_N{}^{PNMG} - \log k_{H_2O}{}^{PNMG} \qquad (1)$$

where $k_N{}^{PNMG}$ is the rate constant for reaction of *p*-nitro(Malachite Green) (bis(*p*-dimethylaminophenyl)-*p*-nitrophenylmethyl cation) with the given nucleophile in the given solvent, and $k_{H_2O}{}^{PNMG}$ is the pseudo-first-order rate constant for reaction of *p*-nitro(Malachite Green) with water in pure water. The data and resulting N_+ values are shown in Table II.

Table II. Nucleophilic Parameters Defined by Eq 1

Nucleophile (solvent)	Log k^a	N_+
H_2O (H_2O)	−3.75	0.00
MeOH (MeOH)	−3.27	0.5
CN^- (H_2O)	0.05	3.8
OH^- (H_2O)	0.75	4.5
CH_3O^- (MeOH)	3.78	7.5
N_3^- (MeOH)	4.79	8.5
CN^- (DMSO)	4.87	8.6
CN^- (DMF)^b	5.63	9.4
$C_6H_5S^-$ (MeOH)	6.97	10.7
$C_6H_5S^-$ (DMSO)	9.4	13.1

[a] Rate constants for reactions of *p*-nitro(Malachite Green) all taken from previous papers in this series; see ref 1a. [b] Dimethylformamide.

We find that the data for reactions of all of the systems which we have studied can be correlated by eq 2

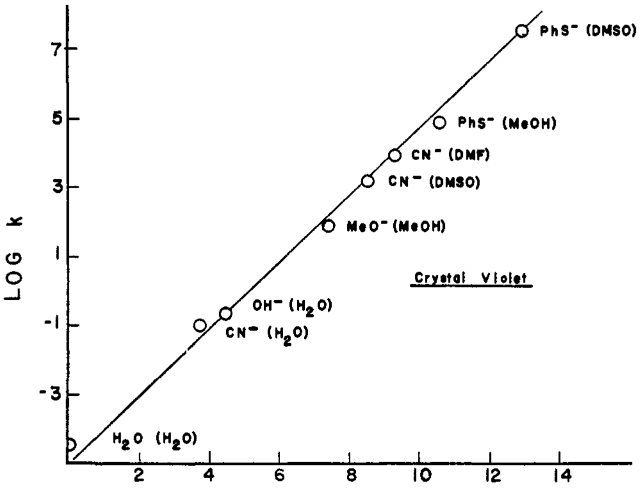

Figure 1. Correlation of the reactions of Crystal Violet by eq 2.

$$\log k_N{}^R = \log k_{H_2O}{}^R + N_+ \qquad (2)$$

where $k_N{}^R$ is the rate constant for reaction of a particular cation with a given nucleophilic system (*i.e.*, nucleophile and solvent), and $k_{H_2O}{}^R$ is the pseudo-first-order rate constant for reaction of the same cation with water in water. Some N_+ values which could not be obtained from *p*-nitro(Malachite Green) reactions can be obtained from eq 2 using data for other cations. A few such values are reported in Table III.

Table III. "Secondary" Nucleophilic Parameters Defined by Eq 2

Nucleophile (solvent)	N_+	Cation, R
CN^- (MeOH)	5.9	p-$NO_2C_6H_4N_2^+$
N_3^- (DMSO)	10.7	$C_6H_5N_2^+$
$C_6H_5SO_2^-$ (MeOH)	3.8	p-$NO_2C_6H_4N_2^{+a}$
N_3^- (H_2O)	5.4	(p-$CH_3OC_6H_4)_3C^{+b}$

[a] C. D. Ritchie, J. D. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961). [b] Reference 8. We are grateful to Professor Bunton for allowing us to read this manuscript before publication.

Figures 1–7 graphically present the correlations obtained for several triarylmethyl cations, aryldiazonium ions, and aryltropylium ions reacting with the various nucleophiles. Not all of our accumulated data are presented in the figures, but the systems shown are representative. The solid lines shown in the figures

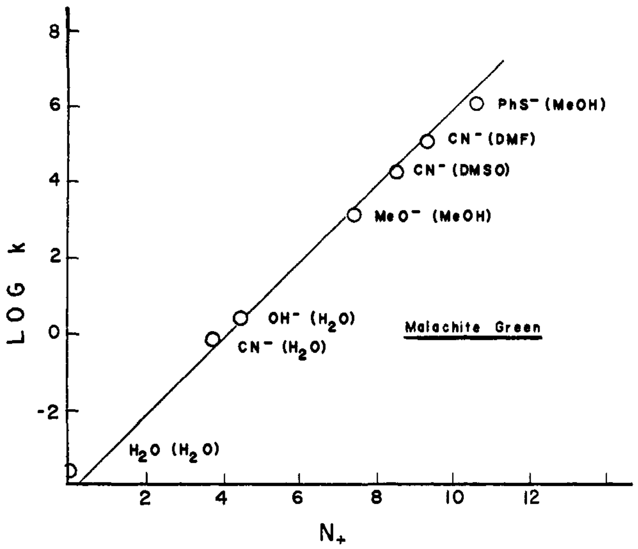

Figure 2. Correlation of the reactions of Malachite Green by eq 2.

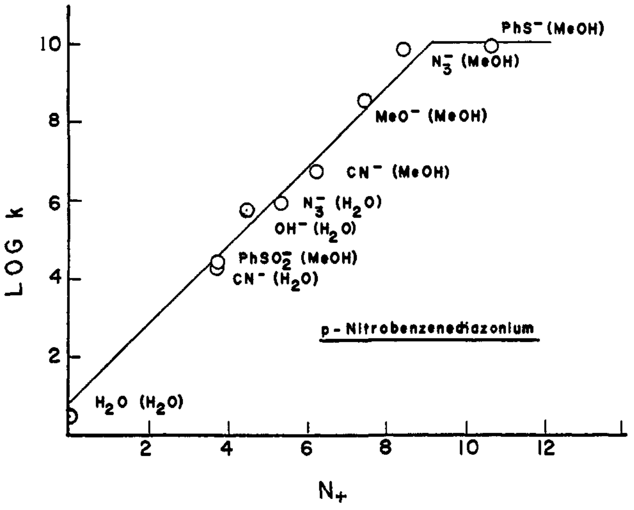

Figure 3. Correlation of the reactions of p-nitrobenzenediazonium ion by eq 2.

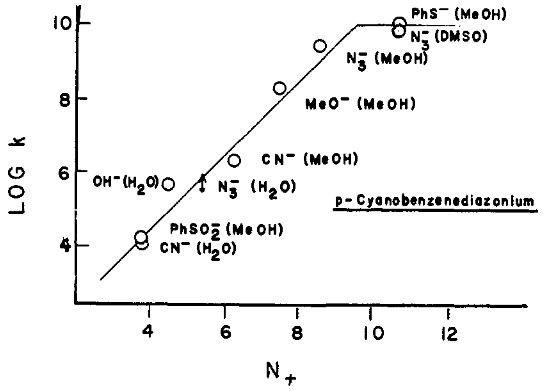

Figure 4. Correlation of the reactions of p-cyanobenzenediazonium ion by eq 2.

have unit slope, as required by eq 2, up to $k_N{}^R$ values of 10^{10} M^{-1} sec^{-1}, and then have zero slope since the rates are diffusion controlled.

The different vertical scales in the figures illustrate the fact that the reactivities of the various cations toward a constant nucleophile span a considerable range. For example, the reaction of Crystal Violet (tris(p-dimethylaminophenyl)methyl cation) with hydroxide ion in water has a rate constant of 2.0 × 10^{-1}

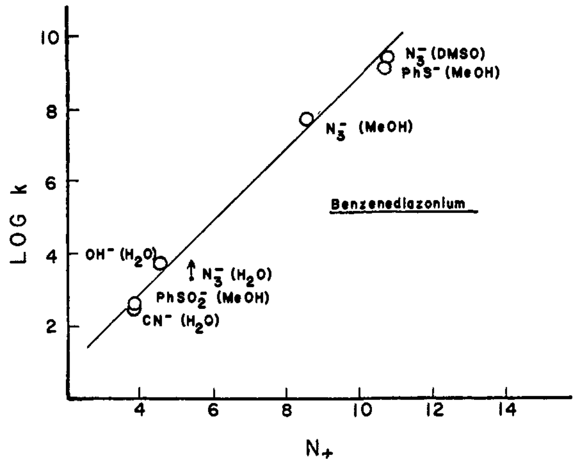

Figure 5. Correlation of the reactions of benzenediazonium ion by eq 2.

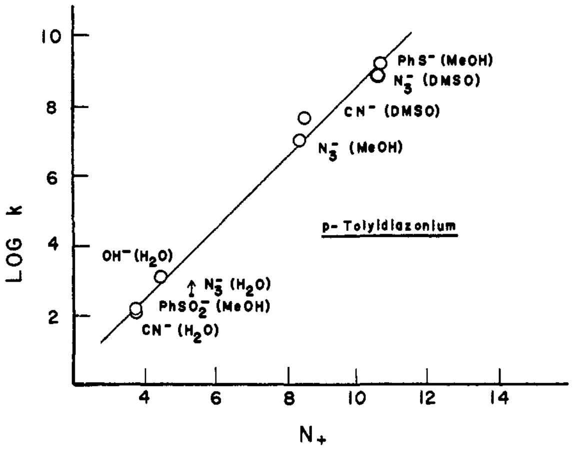

Figure 6. Correlation of the reactions of p-tolyldiazonium ion by eq 2.

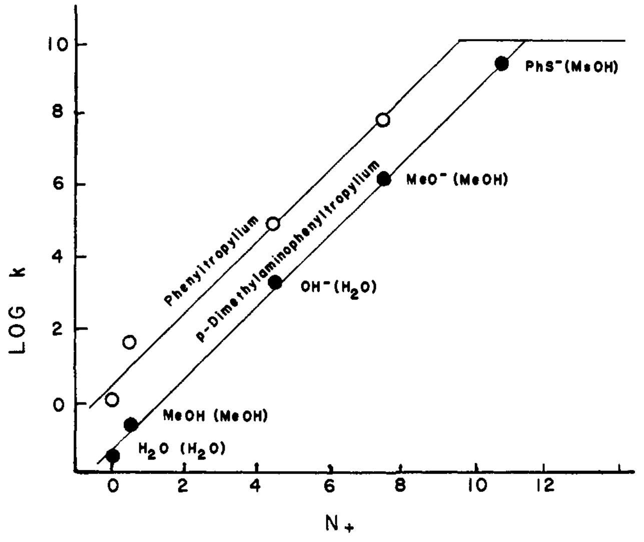

Figure 7. Correlation of the reactions of phenyltropylium ion and of p-dimethylaminophenyltropylium ion by eq 2.

M^{-1} sec^{-1}, while *p*-nitrobenzenediazonium ion has a rate constant of 5.4×10^5 M^{-1} sec^{-1} for the same reaction. The range of reactivities of different nucleophiles with the same cation is even larger, covering more than ten powers of ten in rate constants for several of the cations.

The simplicity of eq 2 is no less than astounding. Previous equations[5] proposed for correlating nucleophilic reactivities have required at least one adjustable parameter for each different electrophile. Even with this flexibility, a change in the element at the electrophilic center could generally[5] not be accommodated.

The N_+ parameters do not seem to be related in any way to previous scales of nucleophilicity. In particular, we have called attention to the unique order of reactivity $N_3^- > CH_3O^- > CN^-$ for the cation–anion combination reactions several times in earlier papers. Some data concerning nucleophilic attack on methyl iodide are compared to the N_+ values in Table IV.

Table IV. Comparison of Nucleophilic Reactivities toward Methyl Iodide and toward Cations

Nucleophile (solvent)	Log k_{MeI}[a]	N_+
N_3^- (MeOH)	−4.1	8.5
CH_3O^- (MeOH)	−3.6	7.5
CN^- (MeOH)	−3.2	5.9
$C_6H_5S^-$ (MeOH)	−1.3	10.7
CN^- (DMF)	2.5	9.4

[a] Rate constants for reactions of methyl iodide in methanol at 25° taken from R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, **90**, 5049 (1968).

The more surprising facet of the data for the cation–anion combination reactions is that there is no correlation of equilibrium constants even though the rate constants are correlated so well by eq 2. Some of the data illustrating this point are shown in Table V. In the immediately preceding paper of this series,[1a] we presented arguments that some of the differences in relative equilibrium constants for the several cations resulted from different steric requirements of the cationic moieties in the products and different solvation energies of the reactant cations. It also seems likely that the relative bond strengths in the diazonium ion products would be different from those in the carbonium ion products. Since these various factors do not influence the relative rates of the reactions, the solvation of the cationic moiety at the transition state must be very close to that of the reactant cation, and the separation of cation and nucleophile at the transition state must be fairly great. The fact that the relative reactivities of two anions vary with solvent indicates that the solvation of the anionic moiety at the transition state is different from that of the reactant anion.

Table V. Equilibrium Constants for Cation–Anion Combination Reactions[a]

	Cation			
Anion (solvent)	MG[b]	PNMG[b]	*p*-$NO_2PhN_2^+$[b]	DMATr[b]
OH^- (H_2O)	1.4×10^7	3.1×10^8		4.5×10^6
CH_3O^- (MeOH)	1.3×10^8	1.3×10^{10}	5.6×10^7	1.7×10^{10}
PhS^- (MeOH)	1.0×10^6	2.6×10^6	1.9×10^{10}	9.1×10^8
N_3^- (MeOH)		1.6×10^3		1.9×10^3

[a] Equilibrium constants in units of M^{-1}. All data from previous papers in this series; see ref 1a. [b] The abbreviations for the cations are MG = Malachite Green, bis(*p*-dimethylaminophenyl)–phenylmethyl cation; PNMG = *p*-nitro(Malachite Green); *p*-$NO_2PhN_2^+$ = *p*-nitrobenzenediazonium ion; DMATr = *p*-dimethylaminophenyltropylium ion.

A very "reactant-like" transition state would show some of the characteristics just discussed. The postulation of such a transition state, however, is not consistent with the observed great differences in absolute rate constants for the various cations with a single nucleophile or various nucleophiles with a single cation.

The data are consistent with the postulation that the transition states for these reactions are reached at the point where the last molecule of solvent between cation and nucleophile is in the process of being eliminated, with nucleophilic desolvation well ahead of cation desolvation. This postulate leads us to expect two factors to be important in determining the rate constants for the reactions: (1) the desolvation energy of the anion; and (2) the effective ionic radii of the cation and ion, which will determine the coulombic attraction of the two moieties. We therefore expect that the N_+ values will be directly related to the anion solvation energies.

Parker[6] has argued that the changes in rate of reaction of methyl iodide with a nucleophile on changing solvent from methanol to dimethylformamide are measures of the hydrogen bonding solvation of the nucleophiles in methanol solution. Thus, we might expect that the N_+ values for nucleophiles in methanol will parallel the changes in rates of the nucleophiles found by Parker. This is a particularly interesting test since we have already discussed the fact that the N_+ values for nucleophiles in methanol do not show any relationship to the rates of reactions of the nucleophiles with methyl iodide. The limited amount of data available are shown in Table VI. The expected relationship does appear to hold.

The postulated nature of the transition state also leads us to expect that water and hydroxide ion in water and methanol and methoxide ion in methanol will behave as unusual nucleophiles. In the cases of hydroxide ion in water and methoxide ion in methanol, a proton transfer can accomplish what must be accomplished by desolvation for other nucleophiles.

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(5) The two most popular equations are the Swain–Scott equation, and the Edwards–Pearson equation. See: C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953); J. O. Edwards and R. G. Pearson, *ibid.*, **84**, 16 (1962). A more recent discussion of nucleophilic reactivity with good references to the earlier literature, and particularly aimed at the limitations of the correlations of nucleophilic reactivity, will be found in: R. G. Pearson, H. Sobel, and J. Songstad, *ibid.*, **90**, 319 (1968).

(6) R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *ibid.*, **90**, 5049 (1968), and earlier references cited there.

Table VI. Comparison of N_+ Values with Solvent Effects on Rates of Reaction of Methyl Iodide with Nucleophiles

Nucleophile	Δ Log k_{MeI}[a]	N_+[b]
$C_6H_5S^-$	4.0	10.7
N_3^-	4.6	8.5
CN^-	5.7	5.9

[a] $\Delta \log k = \log k(\mathrm{DMF}) - \log k(\mathrm{MeOH})$; all data from ref 6. [b] The N_+ values are for the anions in methanol solution.

These ions, in their respective solvents, are far more strongly solvated than any of the other ions considered, and if solvation were to play the same role as for other nucleophiles, they would be expected to react much more slowly than is actually observed.

The problem of treating solvent as a nucleophile is an interesting one, but we can offer no enlightenment at this time. The major problem, we believe, is the distinction between a solvated cation and the corresponding protonated product of reaction with solvent. The remarkable fact which we have observed in all of our studies[1a] is that the reactions of cations with water or methanol do not appear to involve general base catalysis. Other workers have also commented on their failures to observe general base catalysis for such reactions.[7,8] We have initiated a study of the reactions of neutral nucleophiles with the various cations in an attempt to throw some light on this subject.[8a]

With the exception of the solvent reactions just discussed, we feel that the relative reactivities of the various nucleophiles are understandable in terms of the solvation energies of the anions in the various solvents. We now turn our attention to the relative reactivities of the cations.

The conclusions already listed concerning the absence of specific cation–nucleophile interactions and of any serious disturbance of the cation solvation at the transition states seem to eliminate most of the sources of variations in cation reactivity which are commonly postulated for other types of reactions. With only a single solvent molecule separating cation and anion, as our postulate supposes, however, the effective dielectric constant for coulombic interaction of cation and anion is quite small, and such interactions should be quite large. Thus, variation of the effective ionic radius of the cation should have large effects on the energy of the transition state. By the term "effective ionic radius," we mean to include all those factors of ionic structure which would influence the interaction with a counterion, such as substituents, charge distribution, etc. Unfortunately, we have no measures of the "effective ionic radii" of the various cations employed in the present studies, but it does not seem qualitatively unreasonable to suppose that the cationic reactivities could be explained in terms of this concept.

We believe that the most important point emerging from the present studies is that of the independence of the N_+ parameters on cation structure. If our supposition that these parameters are directly related to solvation energies is correct, the parameters should be useful in understanding the general problem of nucleophilic reactivity. Certainly, in all nucleophilic reactions desolvation of the nucleophile is an important factor. The difficult question has been the identification of other important factors. It may be that the use of the N_+ parameters will allow the separation of solvation factors from others so that they may be identified. At the present time, there is not enough data to allow the assignment of N_+ values to many of the nucleophiles commonly studied in SN2 or carbonyl addition reactions, and the cations which we have studied thus far do not react with many of these nucleophiles.

Experimental Section

Materials. The aryldiazonium fluoroborates were available from our earlier studies.[1a] Dimethyl sulfoxide was purified as described in earlier work[9] and was stored and handled under an argon atmosphere. Karl-Fischer titration showed less than 10 ppm of water.

Triethylenediamine, DABCO, was a commercial product recrystallized from heptane. Triethylamine was purified by distillation at atmospheric pressure. Sodium azide, potassium cyanide, and *p*-toluenesulfonic acid monohydrate were commercial products used without further purification.

Equipment. The stop-flow spectrophotometer used in this work has been described in earlier papers.[9] Kinetic and equilibrium measurements were carried out in an air conditioned room maintained at 23 ± 1°.

Azide Ion Reactions. Solutions of sodium azide in DMSO containing *ca.* 10^{-2} *M* *p*-toluenesulfonic acid were prepared and handled under an argon atmosphere. The concentrations of free azide ion in the solutions were calculated from the accurately known concentrations of *p*-toluenesulfonic acid and sodium azide added, assuming complete dissociation of the *p*-toluenesulfonic acid,[10] using the pK_a of 7.9 for hydrazoic acid in DMSO.[9]

Azide ion concentration was varied by varying the total concentration of sodium azide added to the solutions. Observation of the pseudo-first-order rate constants for reaction with diazonium ion at different azide ion concentrations established that the reactions are first order with respect to azide ion concentration.

For *p*-nitro-, *p*-cyano-, *p*-benzoyl-, and *p*-carboxybenzenediazonium ions reactions, a slow change in absorbance occurred after an initial rapid reaction, as we have previously observed for the reactions in water and methanol.[3,4] Rate constants for the slow reaction are reported in Table I as the decomposition rates of the arylpentazoles, the identification being based on analogy with the previous studies. For the other diazonium ions, the slow second reaction could be observed, but the changes in absorbance were too small to allow calculation of a rate constant.

The results are reported in Table I.

Cyanide Ion Reactions. The reactions of the diazonium ions with cyanide ion were carried out in solutions of potassium cyanide buffered with either triethylamine or DABCO partially neutralized with *p*-toluenesulfonic acid. The determination of the equilibrium constants also utilized unbuffered solutions of potassium cyanide. Secondary reactions of the products of the initial cyanide ion reactions were observed in several cases, but these reactions were slow enough for the cases in which we have been able to obtain rate constants for the initial reaction that they caused little trouble. Runs at different buffer concentrations and ratios established the expected first-order dependence of the rates on cyanide ion concentration and the independence of the rates on buffer concentration for those cases reported in Table I. Second-order rate constants were calculated by the use of pK_a values of 12.9 for hydrocyanic acid,[10] 9.0 for triethylammonium ion,[11] and 8.8 for protonated DABCO. The

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(7) E. A. Hill and W. J. Mueller, *Tetrahedron Lett.*, 2565 (1968).

(8) C. A. Bunton and S. K. Huang, *J. Amer. Chem. Soc.*, **94**, 3536 (1972).

(8a) NOTE ADDED IN PROOF. Since the preparation of the original manuscript, we have obtained conclusive evidence that the reaction of Malachite Green with water involves general base catalysis. See: C. D. Ritchie, *ibid.*, **94**, 3275 (1972).

(9) C. D. Ritchie, G. A. Skinner, and V. G. Badding, *ibid.*, **89**, 2063 (1967).

(10) C. D. Ritchie and R. E. Uschold, *ibid.*, **89**, 1721 (1967).

(11) I. M. Kolthoff, M. K. Chantooni, Jr., and S. Bhowmik, *ibid.*, **90**, 23 (1968).

latter pK value was calculated from the observed rates of reactions of p-chlorobenzenediazonium ion in triethylamine and DABCO buffers. The value obtained in this experiment was in agreement with a similar experiment using p-methoxybenzenediazonium ion as reactant.

In the cases for which no data are reported in Table I, either the strong absorbance of solvent prevented us from following the reactions at the wavelengths of maximum absorption of reactants or products, or, in the case of p-nitrobenzenediazonium ion, there were complications which may be due to buffer reaction.

Carbanions. XII. *p*-Biphenylyl Migration in Reactions of 1-Chloro-2-*p*-biphenylylethane-*1,1*-d_2 with Alkali Metals[1]

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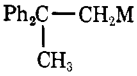
Abstract: The question of whether or not simple 2-arylethyl anions will undergo 1,2 migration of aryl is explored for the *p*-biphenylylethyl system. Reaction of 1-chloro-2-*p*-biphenylylethane-*1,1*-d_2 with excess lithium metal in tetrahydrofuran (THF) solution at −70° gave a good yield of 2-*p*-biphenylylethyllithium-*1,1*-d_2. On warming to 0° this organolithium reagent failed to undergo appreciable rearrangement as judged by the position of the deuterium label in the products of carbonation and protonation even though the conditions were so severe that most of the reagent had decomposed. In contrast, reaction of the same chloride with cesium or potassium metal in THF at reflux temperature gave an essentially 50/50 mixture of 1-*p*-biphenylylethane-*2,2*-d_2 and 1-*p*-biphenylylethane-*1,1*-d_2; in reaction of the chloride at −65° with Cs–K–Na alloy, scrambling of the label in the *p*-biphenylylethane was only partial. Repetition of the reaction with potassium in presence of a small amount of *tert*-butyl alcohol resulted in a greatly reduced amount of rearrangement in the product *p*-biphenylylethane. It is concluded that *p*-biphenylylethylcesium and potassium rearrange readily provided that protonation by solvent or solvent component does not intervene. The present work provides no evidence for participation of neighboring biphenylyl radical anions (or dianions) in a concerted reductive–rearrangement step.

While a 1,2 shift of a vinyl group in simple organometallic compounds is known, *e.g.*, rearrangement of allylcarbinylmagnesium halide,[2] corresponding 1,2 shifts of a phenyl or aryl group are known to occur only from a quaternary carbon having attached to it one or more additional phenyl or vinyl groups, *e.g.*, in 2,2,2-triphenylethyl,[3] 2,2-diphenylpropyl,[4] and 6-methyl-6-phenylcyclohexadienyl[5] alkali metal compounds, **1**, **2**, and **3**, respectively. The effects of the additional unsaturation in these substances are manifold. The extra unsaturation stabilizes the product of rearrangement and ensures that the product is more stable than (or as stable as) the reactant. It also accelerates the reaction by providing additional delocalization of electrons in the bridged transition state for rearrangement, as has been confirmed by molecular orbital calculations.[4] The unsaturated group along with the other groups present at the quaternary carbon of **1**–**3** probably produces some steric compression in these reactants which is likely reduced in the transition state for rearrangement (steric acceleration).[6] Finally the unsaturated groups help to stabilize the anion toward protonation by the solvent. The net effect of the additional unsaturation is evidently to increase the rate of rearrangement relative to the rate of destruction of the carbanion by solvent.

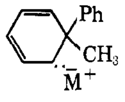
Ph_3CCH_2M

1



$Ph_2C(CH_3)—CH_2M$

2



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Cram and Dalton[7] have examined the question of aryl migration for reaction of alkali metal with four substrates in which additional unsaturation is absent in the organic moiety of interest. Reduction of 1,1-dideuterio-1-methoxy-2-(1-naphthyl)ethane and of 1,1-dideuterio-2-(1-naphthyl)ethyl methanesulfonate with potassium in 1,2-dimethoxyethane at 0° gave 1-ethylnaphthalene deuterated only in the methyl group; no detectable rearrangement (less than 5%) accompanied reduction. Reaction of *threo*-2-phenyl-3-pentyl methanesulfonate with potassium in 1,2-dimethoxyethane at 25° gave 94.5% of 2-phenylpentane and 5.5% of 3-phenylpentane (product of phenyl migration); reaction of *threo*-3-phenyl-2-pentyl methanesulfonate with sodium in liquid ammonia gave 75% of 3-phenylpentane and 3.1% of 2-phenylpentane. The most plausible mechanism for rearrangement was thought to be one-electron transfer from the alkali metal to the phenyl group, whose radical anion, as a powerful nucleophile, displaced the methanesulfonate group to give a phenyl-bridged radical. Further reaction with a second metal atom gave an organometallic compound which abstracted a proton from the solvent to give the observed

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[1] (a) Presented in part at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Massachusetts, July, 1971. (b) Abstracted in large part from the Ph.D. thesis of Y.-M. Cheng, Georgia Institute of Technology, 1970.

[2] M. S. Silver, P. R. Shafer, J. E. Norlander, C. Rüchardt, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960); D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965).

[3] (a) E. Grovenstein, Jr., *ibid.*, **79**, 4985 (1957); (b) H. E. Zimmerman and F. J. Smentowski, *ibid.*, **79**, 5455 (1957); (c) E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 412 (1961).

[4] H. E. Zimmerman and A. Zweig, *ibid.*, **83**, 1196 (1961).

[5] S. W. Staley and J. P. Erdman, *ibid.*, **92**, 3832 (1970).

[6] E. Grovenstein, Jr., and L. P. Williams, Jr., *ibid.*, **83**, 2537 (1961).

[7] D. J. Cram and C. K. Dalton, *ibid.*, **85**, 1268 (1963).