Cation–Anion Combination Reactions. 15.[1] Rates of Nucleophilic Aromatic Substitution Reactions in Water and Methanol Solutions

Calvin D. Ritchie* and Masami Sawada

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received December 22, 1976*

Abstract: Rate constants for the reactions of a wide range of nucleophiles with the four 2,4-dinitrohalobenzenes in water and methanol solutions at low ionic strengths and 25 °C have been determined. The values are compared with those for reactions of the same nucleophiles with organic cations under closely similar conditions. We find, as in previous work, that selectivity and reactivity are unrelated and that the nucleophilic aromatic substitution reactions are generally correlated by the N_+ scale of nucleophilicities. Several specific features of the present reactions, however, contrast with reactions of organic cations. First, azide ion, relative to other nucleophiles, reacts much more slowly with neutral electrophiles than with charged electrophiles. Second, the reactivities of the aryl halides relative to organic cations are solvent dependent. Third, as originally observed by Bunnett, sulfur nucleophiles, relative to oxygen and nitrogen nucleophiles, react more rapidly with the aryl iodide than with the aryl fluoride. With the exception of the azide ion behavior, it appears that the N_+ scale of nucleophilicities incorporates the major factors determining reactivity in electrophile–nucleophile reactions, with other factors, such as the latter two mentioned above, causing scatter in the correlations.

The results which have been presented in previous papers of this series[1] document an unprecedented regularity in the patterns of rate constants for reactions of nucleophiles with organic cations. In these simple bond-forming reactions, the relative reactivities of quite diverse nucleophiles are nearly invariant with respect to the identity and reactivity of the cation. It appears that this regularity of behavior also extends to the reactions of nucleophiles with some esters[1] and, at least approximately, to reactions of nucleophiles at sulfur in various oxidation states.[2] The observed invariances are expressed in

$$\log k = \log k_0 + N_+ \qquad (1)$$

where $\log k_0$ is independent of nucleophile and solvent, and N_+ is independent of electrophile.

At present, it is becoming obvious that eq 1 has some severe limitations which affect its precision. In addition to the early examples of S_N2 reactions[3] and reactions of ion pairs[4] which show behaviors strongly at variance with eq 1, in our most recent work[1] we have begun to see evidence of factors such as steric effects which cause moderate deviations from the averaged N_+ scale. A substantial part of our current research effort is aimed at the exploration and understanding of these limitations.

The reactions of nucleophiles with 2,4-dinitrohalobenzenes appeared to us to be of particular interest in this latter regard. In protic solvents, the reactions appear to be mechanistically uncomplicated, with attack of nucleophile being the rate-determining step.[5] Moreover, variation of the halogen leaving group furnishes an opportunity to study the effects of reasonably systematic changes in the immediate environment of the electrophilic center.

Although these reactions have been studied extensively in the past, there are surprisingly little data which can be compared directly with those for reactions of cations. In the present paper, we report an extensive set of rate constants for reactions of a diverse set of nucleophiles with the four 2,4-dinitrohalobenzenes under conditions closely similar to those used in our previous studies of cations.

Experimental Section

Materials. Acetonitrile, potassium cyanide, sodium thioglycollate, aqueous hydrogen peroxide, and aqueous perchloric acid were high purity commercial materials used without further purification. All other commercial materials were recrystallized, distilled under argon, or sublimed under argon, as appropriate. Melting points and boiling points of all organic compounds agreed closely with those reported in the literature.

The preparation of 2,4-dinitrocyanobenzene was accomplished by standard thionyl chloride dehydration of the corresponding amide. The product was recrystallized from ethanol (mp 105–106 °C, lit. 103–104 °C[6]).

Preparations of 2,4-dinitrophenyl phenyl ether (mp 69.5–70.0 °C, lit. 68.2–69.8 °C[7]), 2,4-dinitrophenyl 2′,2′,2′-trifluoroethyl ether (mp 78.0–78.5 °C, lit. 78.0 °C[8]), 2,4-dinitrophenyl thiophenyl ether (mp 122–123 °C, lit. 121 °C[9]), *N*-(2,2,2-trifluoroethyl)-2,4-dinitroaniline (mp 117–118 °C, lit. 115–116 °C[10]), *N*-methoxy-2,4-dinitroaniline (mp 110.5–111.0 °C, lit. 110 °C[10]), 2,4-dinitromorpholinobenzene (mp 120.5–121.5 °C, lit. 118 °C[11]), 2,4-dinitropiperidinobenzene (mp 92–93 °C, lit. 92–93 °C[12]), 2,4-dinitroazidobenzene (mp 61 °C dec, lit. 66–67 °C[13]), and 5-nitrobenzofuroxan (mp 70–71 °C, lit. 71 °C[13]) followed methods given in the cited references.

Water was distilled from potassium permanganate under nitrogen and was stored under nitrogen. Methanol was dried by molecular sieves and purified by ion exchange as previously described.[14] The purified solvent was stored under nitrogen. Sodium methoxide and perchloric acid solutions in methanol were prepared as previously described.[14]

Sodium hydroxide solutions were standardized periodically with potassium hydrogen phthalate, and were used for standardization of the aqueous hydrochloric and perchloric acid solutions.

Aqueous hydrogen peroxide solution was standardized by titration with potassium permanganate solution which, in turn, was standardized with sodium oxalate.

Apparatus. Ultraviolet and visible spectra were recorded with a Cary Model 14 spectrophotometer. For reactions with half-lives greater than ca. 2 min, kinetic studies utilized either the Cary Model 14 or a Gilford Model 140 spectrophotometer. Both spectrophotometers were equipped with thermostated cell holders for 1–10-cm cells which maintained constant temperature of the solutions to ±0.1 °C.

Reactions with half-lives of less than 2 min were studied by use of a small-scale stop-flow spectrophotometer connected to a digital oscilloscope interfaced to a programmable calculator. The entire working part of the stop-flow apparatus is enclosed in a thermostated jacket capable of maintaining constant temperature within ±0.1 °C.

A Beckman Model 1019 pH meter with glass and saturated calomel electrodes standardized with phosphate buffer at pH 6.863 was used for all pH measurements.

Kinetic Measurements. Preliminary studies of Beer's law behavior of the 2,4-dinitrohalobenzenes and of all expected products of the reactions were made to determine solubility limitations in aqueous solutions. All runs were then made with initial concentrations such that concentrations of reactants and products would be within the range of Beer's law adherence.

For the reactions in aqueous solutions, two routine checks were performed on each run: (1) the "infinity time" absorbance at the wavelength of maximum absorption of product was verified to be within 3% of that calculated from the initial concentration of aryl halide and the independently determined molar absorptivity of product; (2) the pH of the reaction solution was verified to be within 0.02 units of that at the start of the run. If either of these checks failed, the results of the run were discarded. For reactions in methanol, only the first check was performed.

The reactions of thioglycollate and thiophenoxide ions were studied by stop-flow spectrophotometry. In these, the solutions of nucleophile, buffer, and salt were mixed with equal volume of a solution of the aryl halide in the stop-flow apparatus after sufficient time had been allowed for thermal equilibration of both solutions.

All other reactions were studied by conventional spectrophotometry. For these, a measured volume of the solution containing nucleophile, buffer, and salt (either KCl or $KClO_4$) was placed in a spectrophotometer cell, the cell placed in the spectrophotometer, and 15-20 min allowed for thermal equilibration. A 50-μL portion of a master solution of the aryl halide in acetonitrile was injected into the spectrophotometer cell to start the reaction.

Absorbance at the wavelength of maximum absorbance of product was followed for 8-10 half-lives of reaction except for a few cases where side reactions became bothersome at long times. In those reactions in which hydroxide ion competed with another nucleophile (i.e., cyanide, phenoxide) the 2,4-dinitrophenoxide ion absorbance at 360 nm was followed.

All reactions were run under pseudo-first-order conditions with nucleophile in large excess. For the simple reactions (i.e., all reactions other than cyanide, azide, and phenoxide) the absorbance vs. time data were treated by straightforward nonlinear least-squares methods to obtain pseudo-first-order rate constants. The root mean square deviations from first-order behavior were always less than the possible error in spectrophotometric readings.

For the reaction of cyanide ion with 2,4-dinitrofluorobenzene, side reactions were apparent from the appearance of long wavelength absorption at long times, or even rather short times when high concentrations of cyanide were used. For these reactions, a three-point spectral analysis for aryl fluoride, cyanide, and oxide was carried out on solutions up to 4 half-lives. These analyses utilized absorbances at 282 nm, the isosbestic point for the cyano and phenoxide products, 303 nm, the absorbance maximum for the cyano product, and 360 nm, the absorbance maximum of the aryl oxide. Good material balance was obtained, and the results were in good agreement with product ratios which could be calculated from separate measurements of overall pseudo-first-order rate constants and the known rate constant for reaction of hydroxide ion with the aryl fluoride.

The reactions of phenoxide ion with aryl chloride, bromide, and iodide were complicated by the further reaction of the product ether with hydroxide ion. In order to obtain the rate constant for the phenoxide reaction, we used Murto's[8] value for the rate constant for reaction of hydroxide ion with 2,4-dinitrophenyl phenyl ether.

Similarly, the reactions of aryl halides with azide ion are complicated by the further reaction of the azide product to form 5-nitrobenzofuroxan.[13] Independent measurements of the rate constant for this latter reaction were carried out.

The experimental conditions for the kinetic measurements are summarized in Table I.

Results

Reactions of Hydroxide Ion. The reactions of hydroxide ion with 2,4-dinitrofluorobenzene were studied in both buffered and unbuffered solutions. In the unbuffered solutions, the known concentrations of hydroxide ion together with the measured **pH** gave a value of 0.78 for the apparent activity coefficient of hydroxide ion in 0.1 M ionic strength solutions at 25.0 °C. This value is in good agreement with that tabulated by Albert and Serjeant[20] for comparable conditions. With both Dabco and quinuclidine buffers, the measured pH values were in excellent agreement with values calculated from the known p*K*s of the conjugate acids[15b] and the concentrations of base and conjugate acid added to the solutions.

In both buffered and unbuffered solutions, the pseudo-first-order rate constants for reactions of 2,4-dinitrofluorobenzene were directly proportional to hydroxide ion concentrations. No buffer catalysis nor water reaction could be detected. These experiments were particularly carefully done and we believe that the second-order rate constant reported in Table I is accurate to ±2%.

For the other three 2,4-dinitrohalobenzenes, only unbuffered sodium hydroxide solutions were studied. No water reaction was detectable and the measured pseudo-first-order rate constants divided by hydroxide ion concentrations gave the second-order rate constants reported in Table I with a precision of better than ±5%.

Both Bunton[21] and Murto[8] have reported rate constants for the reaction of hydroxide ion with 2,4-dinitrofluorobenzene (1.2×10^{-1} and 1.3×10^{-1} $M^{-1}\ s^{-1}$) and with 2,4-dinitrochlorobenzene (1.4×10^{-4} and 1.9×10^{-4} $M^{-1}\ s^{-1}$), under conditions similar to ours, which are in reasonable agreement with the values in Table I.

Reaction of Cyanide Ion. Cyanide ion is known to react with aromatic nitro compounds to give reduction and displacement of nitro groups.[22] These reactions are apparently fast enough to prevent observation of any appreciable product from displacement of halogen from 2,4-dinitrohalobenzenes when the halogen is chloro, bromo, or iodo. In the case of 2,4-dinitrofluorobenzene, spectral analysis of the reaction solution shows clearly that 2,4-dinitrocyanobenzene is formed simultaneously with 2,4-dinitrophenoxide ion when the reaction is run at high (i.e., greater than the p*K* of HCN) pH. These are the only appreciable products of reaction during the first 4 half-lives.

Side reactions of cyanide ion with the 2,4-dinitrocyanobenzene and with 2,4-dinitrophenoxide apparently produce products which absorb in the visible spectrum, and which interfere with the simple reaction when high concentrations of cyanide or long observation times are used.

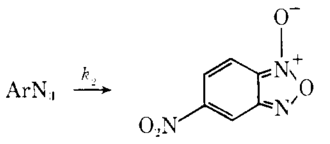
Our studies utilized conditions such that hydroxide ion accounts for 60-90% of the total observed pseudo-first-order rate constant. This, plus the limitation of following the reactions for only 4 half-lives, makes the second-order rate constant reported in Table I for this reaction considerably less precise than for most of the other reactions studied. On the basis of a large number of measurements, we are confident that the value is accurate to ±50%, which is adequate for the present purposes.

Reactions of Azide Ion. The reaction of azide ion with 2,4-dinitrofluorobenzene under the conditions shown in Table I gave good pseudo-first-order kinetics to ca. 5-6 half-lives. The deviations at longer times are due to the conversion of the 2,4-dinitroazidobenzene product to 5-nitrobenzofuroxan.[23] For the aryl fluoride reaction, this complication can be avoided by calculating rate constants based only on the first 5 half-lives of the reaction. The calculated second-order rate constant reported in Table I is estimated to be accurate to better than ±5% on the basis of repetitive measurements over a range of azide ion concentrations.

In the cases of the other three 2,4-dinitrohalobenzenes, the rate of decomposition of the azide product is comparable to the rate of attack of azide ion on the aryl halide. In order to obtain accurate values for the rate constant of attack of azide ion on the aryl halides, we carried out independent measurements of the rate constant for conversion of 2,4-dinitroazidobenzene to 5-nitrobenzofuroxan under the same experimental conditions. The values obtained for this latter rate constant were $5.3 \times 10^{-4}\ s^{-1}$ at 68.4 °C and $5.5 \times 10^{-5}\ s^{-1}$ at 47.5 °C. As expected, these values in aqueous solution are not far different from the value of $6.5 \times 10^{-5}\ s^{-1}$ at 50 °C in diethyl phthalate solution.[23]

In order to obtain the rate constant for attack of azide ion on aryl halide, we used the reaction scheme

$$\mathrm{ArX} + \mathrm{N_3^-} \xrightarrow{k_1} \mathrm{ArN_3} + \mathrm{X^-}$$



which gives the differential equations

$$\frac{\mathrm{d(ArX)}}{\mathrm{d}t} = -k_1(\mathrm{N_3^-})(\mathrm{ArX})$$

$$\frac{\mathrm{d(ArN_3)}}{\mathrm{d}t} = k_1(\mathrm{N_3^-})(\mathrm{ArX}) - k_2(\mathrm{ArN_3})$$

$$\frac{\mathrm{d(5\text{-}NBF)}}{\mathrm{d}t} = k_2(\mathrm{ArN_3})$$

$$\frac{\mathrm{d}A_{310}}{\mathrm{d}t} = \epsilon_1\frac{\mathrm{d(ArX)}}{\mathrm{d}t} + \epsilon_2\frac{\mathrm{d(ArN_3)}}{\mathrm{d}t} + \epsilon_3\frac{\mathrm{d(5\text{-}NBF)}}{\mathrm{d}t}$$

where ϵ_1, ϵ_2, and ϵ_3 are the molar absorptivities, at 310 nm, of the aryl halide, aryl azide, and 5-nitrobenzofuroxan (5-NBF), and A_{310} is the observed absorbance at 310 nm. Values for the molar absorptivities were obtained in independent experiments. The first three equations can be integrated simultaneously[50] to give A_{310} in terms of the ks, ϵs, and initial concentration, as a function of time. Since k_2 is known from independent experiments, the only unknown in the integrated expression is k_1.

The data for absorbance vs. time for the reaction of azide ion with each of the aryl halides, for each concentration of azide ion, were fitted by least-squares selection of the pseudo-first-order rate constant, $k_1(\mathrm{N_3^-})$. The values obtained in each case were directly proportional to azide ion concentration within the estimated experimental error of ±5%. The derived second-order rate constants are shown in Table I.

Standard treatment of the data reported in Table I leads to the rate constants at 25 °C, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values reported in Table II.

Reactions of Phenoxide Ion. The reactions of phenoxide ion with the 2,4-dinitrohalobenzenes are accompanied by the simultaneous reaction of hydroxide ion with both the initial aryl halide and with the product phenyl ether. In the case of the aryl fluoride, the reaction of hydroxide ion with the aryl phenyl ether is slow in comparison to the reactions of the aryl fluoride, and simple first-order kinetics are observed under the conditions shown in Table I. Since the rate constants for the reactions of hydroxide ion with the aryl halides are known from independent experiments, the contribution of the hydroxide ion reaction to the observed pseudo-first-order rate constants can be calculated. For the aryl fluoride reaction, the "corrected" pseudo-first-order rate constants were proportional to the phenoxide ion concentrations, and lead to the second-order rate constants reported in Table I. In each run, the product ratio which could be calculated from the rate constants was in excellent agreement with the ratio calculated from the spectra at "infinite" time. From the observed precision of rate constants, we estimate that the second-order rate constant for reaction of phenoxide ion with aryl fluoride is accurate to ca. ±2%.

In order to handle the simultaneous and consecutive kinetics of the reaction of phenoxide ion solutions with aryl chloride, bromide, and iodide, we made use of the reported[8] value of the rate constant for reaction of hydroxide ion with the aryl phenyl ether under conditions quite similar to the present study. The kinetic scheme in this case is similar to that for the azide ion reactions discussed above, and leads to an expression for the absorbance vs. time in which the only unknown is the rate constant for attack of phenoxide ion on the aryl halide. As with the azide ion reactions, the unknown rate constant was selected by least-squares fitting of data. The pseudo-first-order rate constant obtained from each run was directly proportional to the concentration of phenoxide ion within the estimated experimental error of ±5%. The values obtained lead to the second-order rate constants reported in Table I.

Reactions of Hydroperoxide Ion. The reactions of the aryl halides with peroxide ion followed pseudo-first-order kinetics to better than 8 half-lives in each run. The addition of EDTA to the solutions had no observable effect.

There is apparently a slow decomposition of the initial product of these reactions to form 2,4-dinitrophenoxide ion, since it was observed that the spectra of the reaction solutions showed a slow change from a maximum absorbance at 345 nm to one at 360 nm. In a few runs utilizing borate buffers, this change from 345 to 360 nm appeared to be much faster than in the absence of borate.

The pseudo-first-order rate constants for these reactions are directly proportional to peroxide ion concentration, and lead to the second-order rate constants reported in Table I. The precision in values obtained indicates an accuracy of better than ±5% in the second-order rate constants.

Our value of the rate constant for the reaction of hydroperoxide ion with 2,4-dinitrochlorobenzene (2.3×10^{-1} $\mathrm{M^{-1}\,s^{-1}}$) is in good agreement with the value (2.1×10^{-1} $\mathrm{M^{-1}\,s^{-1}}$) reported by Behrman[24] for similar conditions, but is unreasonably different from the value at 30 °C and 1 M ionic strength (23 $\mathrm{M^{-1}\,s^{-1}}$) reported by Bruice.[25] The present value for the rate constant for reaction of hydroperoxide ion with 2,4-dinitrofluorobenzene (66 $\mathrm{M^{-1}\,s^{-1}}$) is also much lower than the one reported by Bruice[25] (1.4×10^4 $\mathrm{M^{-1}\,s^{-1}}$) for reaction at 30 °C and 1 M ionic strength. It seems most likely that the values reported by Bruice are grossly in error, perhaps due to an error in units or an error in transcription.

Reaction of Trifluoroethoxide Ion. Under the conditions shown in Table I, the reactions of trifluoroethoxide ion and hydroxide ion with 2,4-dinitrofluorobenzene are competitive, with the trifluoroethoxide ion reaction accounting for 40–95% of the total rates in the various runs. The known rate constant for reaction of hydroxide ion with the aryl halide was used to "correct" the observed pseudo-first-order rate constants, and these corrected values lead to the second-order rate constants reported in Table I. The reactions are not complicated by further reaction of hydroxide ion with the ether product, which is negligibly slow ($k_2 = 1.5 \times 10^{-3}$ $\mathrm{M^{-1}\,s^{-1}}$)[8] in comparison to the reaction of the aryl fluoride. The observed precision of the measurements of the second-order rate constant for reaction of trifluoroethoxide ion at various concentrations lead to an estimated accuracy of ±3% for the value reported. Our present value is in excellent agreement with that reported by Bunton.[21c]

Reactions of Thioglycollate and Thiophenoxide Ions. Reactions of these two nucleophiles were fast enough that the stop-flow technique was most conveniently used for the kinetic studies. The reactions showed simple pseudo-first-order kinetics and were not complicated by any observable side reactions. Rate constants for the reactions of thiophenoxide ion in methanol solution are in good agreement with the values which have been reported by Bunnett,[5c,26,33] some of which were obtained by extrapolation from lower temperatures. We estimate the accuracies of the values reported in Table I to be better than ±10% as commonly found for such stop-flow studies.

Reactions of Amines. All of the reactions of amines studied were cleanly first order in amine concentration and independent of pH and concentration of ammonium ion. With the solutions buffered in each case close to the pK_a of the conjugate

Table I. Reaction Conditions and Rate Constants for Reactions of $2,4\text{-}(NO_2)_2C_6H_3X$ with Nucleophiles

X	Temp, °C	Nucleophile (solvent)	Buffer (concn)[a,b]	Nucleophile[b] concn range used	Ionic[b] strength	k_2, M^{-1} s^{-1}
F	25.0	OH^- (water)	None	0.001-0.005	0.10	1.20×10^{-1}
			Quinuclidine (1.8×10^{-2})	0.001-0.004	0.10	1.18×10^{-1}
			Dabco[c] (0.05)	1.2×10^{-4}	0.10	1.17×10^{-1}
Cl	25.0	OH^- (water)	None	0.03-0.10	0.10	1.2×10^{-4}
Br	25.0	OH^- (water)	None	0.03-0.10	0.10	9.9×10^{-5}
I	25.0	OH^- (water)	None	0.076-0.10	0.10	4.6×10^{-5}
F	25.0	CN^- (water)	Quinuclidine (4.0×10^{-3})	0.005-0.03	0.10	1.6×10^{-3}
F	25.0	N_3^- (water)[d]	None	0.01-0.05	0.10	1.9×10^{-2}
Cl	68.4	N_3^- (water)	None	0.06-0.10	0.10	2.9×10^{-3}
	47.5	N_3^- (water)	None	0.06-0.10	0.10	3.7×10^{-4}
Br	68.4	N_3^- (water)	None	0.06-0.10	0.10	4.5×10^{-3}
	59.9	N_3^- (water)	None	0.06-0.10	0.10	2.3×10^{-3}
	47.5	N_3^- (water)	None	0.06-0.10	0.10	6.4×10^{-4}
I	68.4	N_3^- (water)	None	0.06-0.10	0.10	3.9×10^{-3}
	47.5	N_3^- (water)	None	0.06-0.10	0.10	4.8×10^{-4}
F	25.0	$C_6H_5O^-$ (water)[e]	Quinuclidine (0.011)	$1.9\text{-}6.6 \times 10^{-4}$	0.10	5.9×10^{-1}
Cl	25.0	$C_6H_5O^-$ (water)	$C_6H_5O^-$	0.006-0.08	0.10	1.0×10^{-3}
Br	25.0	$C_6H_5O^-$ (water)	$C_6H_5O^-$	0.006-0.025	0.10	1.5×10^{-3}
I	25.0	$C_6H_5O^-$ (water)	$C_6H_5O^-$	0.013-0.05	0.10	5.0×10^{-4}
F	25.0	$CF_3CH_2O^-$ (water)	$CF_3CH_2O^-$	0.0003-0.003	0.10	1.1
F	25.0	HOO^- (water)	HOO^-	$0.67\text{-}2.6 \times 10^{-4}$	0.10	6.6×10
Cl	25.0	HOO^- (water)	HOO^-	0.006-0.05	0.10	2.3×10^{-1}
Br	25.0	HOO^- (water)	HOO^-	0.006-0.05	0.10	2.4×10^{-1}
F	25.0	$^-SCH_2COO^-$ (water)	$^-SCH_2COO^-$	$7.3 \times 10^{-5}\text{-}2.5 \times 10^{-2}$	0.10	1.7×10^2
Cl	25.0	$^-SCH_2COO^-$ (water)	$^-SCH_2COO^-$	0.004-0.025	0.10	3.7
Br	25.0	$^-SCH_2COO^-$ (water)	$^-SCH_2COO^-$	0.001-0.025	0.10	5.5
I	25.0	$^-SCH_2COO^-$ (water)	$^-SCH_2COO^-$	0.001-0.020	0.10	6.5
F	25.0	$CF_3CH_2NH_2$ (water)	$CF_3CH_2NH_2$	0.01-0.05	0.10	1.6×10^{-3}
F	25.0	$CF_3CH_2NH_2$ (MeOH)	$CF_3CH_2NH_2$	0.005-0.025	0.03	1.2×10^{-3}
F	25.0	CH_3ONH_2 (water)	CH_3ONH_2	0.01-0.05	0.10	2.6×10^{-3}
F	25.0	CH_3ONH_2 (water)	CH_3ONH_2	0.03	1.0	3.3×10^{-3}
F	25.0	CH_3ONH_2 (MeOH)	CH_3ONH_2	0.005-0.014	0.02	1.1×10^{-2}
F	25.0	CH_3ONH_2 (MeOH)	CH_3ONH_2	0.10	0.20	1.2×10^{-2}
Cl	45.2	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	3.3×10^{-5}
	37.1	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	1.5×10^{-5}
Br	45.2	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	4.0×10^{-5}
	37.1	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	1.9×10^{-5}
I	45.2	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	1.7×10^{-5}
	37.1	CH_3ONH_2 (water)	CH_3ONH_2	0.68	0.10	7.4×10^{-6}
F	25.0	H_2NCH_2COOEt (water)	H_2NCH_2COOEt	0.002-0.04	0.10	3.2×10^{-2}
F	25.0	H_2NCH_2COOEt (MeOH)	H_2NCH_2COOEt	0.005-0.012	0.02	4.8×10^{-2}
F	25.0	NH_2NH_2 (water)	NH_2NH_2	0.001-0.02	0.10	4.0×10^{-2}
F	25.0	Morpholine (water)	Morpholine	0.001-0.01	0.10	1.0
F	25.0	Morpholine (MeOH)	Morpholine	0.0001-0.02	0.01	6.2×10^{-1}
Cl	25.0	Morpholine (water)	Morpholine	0.08-0.56	0.10	3.3×10^{-3}
Cl	25.0	Morpholine (MeOH)	Morpholine	0.01-0.1	0.01	2.6×10^{-3}
Br	25.0	Morpholine (water)	Morpholine	0.08-0.56	0.10	4.1×10^{-3}
I	25.0	Morpholine (water)	Morpholine	0.08-0.56	0.10	1.4×10^{-3}
I	25.0	Morpholine (MeOH)	Morpholine	0.024-0.11	0.01	6.5×10^{-4}
F	25.0	Piperidine (water)	Piperidine	0.0001-0.0006	0.10	9.9
Cl	25.0	Piperidine (water)	Piperidine	0.0006-0.066	0.10	4.1×10^{-2}
Br	25.0	Piperidine (water)	Piperidine	0.008-0.02	0.10	4.7×10^{-2}
I	25.0	Piperidine (water)	Piperidine	0.008-0.02	0.10	1.8×10^{-2}
F	25.0	$C_6H_5S^-$ (MeOH)	$C_6H_5S^-$	0.0003-0.0005	0.01	5.9×10^2
Cl	25.0	$C_6H_5S^-$ (MeOH)	$C_6H_5S^-$	5.7×10^{-4}	0.001	22.
Br	25.0	$C_6H_5S^-$ (MeOH)	$C_6H_5S^-$	5.7×10^{-4}	0.001	40.
I	25.0	$C_6H_5S^-$ (MeOH)	$C_6H_5S^-$	5.7×10^{-4}	0.001	35.

[a] The conjugate base of the buffer and the maximum concentration used are shown. [b] Concentrations are in units of molarity. The following pK values were used in the calculations: HCN, 9.2;[15] C_6H_5OH, 9.9;[16] CF_3CH_2OH, 12.4;[17] HOOH, 11.65;[18] $HSCH_2COO^-$, 10.01.[19] [c] 1,4-Diazabicyclo[2.2.2]octane. [d] Independent measurements of the rate constants for conversion of 2,4-dinitroazidobenzene to 5-nitrobenzofuroxan gave values of 5.3×10^{-4} s^{-1} at 68.4 °C and 5.5×10^{-5} s^{-1} at 47.5 °C. [e] Under conditions similar to ours, the reported rate constant for reaction of OH^- with 2,4-dinitrophenyl phenyl ether is 2.0×10^{-4} M^{-1} s^{-1} (ref 8). [f] Addition of EDTA to the solutions had no effect. In the cases of aryl chloride and bromide, the decomposition of the initial product to ArO^- became appreciable after ca. 5 half-lives. Borate buffers appeared to increase the rate of this decomposition.

acid of the amine, there is no competing reaction of hydroxide ion observable.

For reactions of methoxylamine with the aryl chloride, bromide, and iodide, elevated temperatures facilitated the kinetic studies. The data shown in Table I were treated by standard methods to obtain the rate constants at 25 °C, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ values reported in Table II.

From the observed precisions of the measurements at

Table II. Reactions of Nucleophiles with 2,4-Dinitrohalobenzenes at 25 °C

		Log k_2, M^{-1} s^{-1} [$\Delta H^{\ddagger}$, kcal/mol; $\Delta S^{\ddagger}$, eu]			
No.	Nucleophile/solvent	ArF	ArCl	ArBr	ArI
1	OH^-/H_2O	−0.92 [16.; −9.][a]	−3.91 [20.; −10][a]	−4.01	−4.34
2	CN^-/H_2O	−2.8			
3	N_3^-/H_2O	−1.71	−4.5 [21.; −9.]	−4.2 [20.; −12.]	−4.4 [21; −8.]
4	$C_6H_5O^-/H_2O$	−0.23	−3.0	−2.8	−3.3
5	$CF_3CH_2O^-/H_2O$	0.03			
6	HOO^-/H_2O	1.82	−0.64	−0.62	
7	$^-O_2CCH_2S^-/H_2O$	2.24	0.57	0.74	0.81
8	N_3^-/MeOH[b]	−0.58 [16.; −7.]	−3.28 [17.; −16.]		−3.49 [18.; −13.]
9	CH_3O^-/MeOH[c]	1.1 [12.; −12.]	−1.5 [17.; −9.]	−1.7 [17.; −11.]	−2.2 [18.; −7.]
10	$C_6H_5S^-$/MeOH	2.8 [10.; −11][d]	1.3 [10.; −19.][d]	1.6 [9.; −21.][d]	1.5 [10.; −18.][d]
11	$CF_3CH_2NH_2/H_2O$	−2.81			
12	$CF_3CH_2NH_2$/MeOH	−2.91			
13	CH_3ONH_2/H_2O	−2.59	−5.35 [18.; −23.]	−5.25 [18.; −23.]	−5.69 [19.; −20.]
14	CH_3ONH_2/MeOH	−1.95			
15	$EtO_2CCH_2NH_2/H_2O$	−1.49			
16	$EtO_2CCH_2NH_2$/MeOH	−1.32			
17	Aniline/H_2O[e]	−1.52			
18	$^-O_2CCH_2NHCOCH_2NH_2/H_2O$	−1.48[e]	−4.2[f]		−4.5[f]
19	$^-O_2CCH_2NH_2/H_2O$	−0.78[e]	−3.4[f]		−3.7[f]
20	H_2NNH_2/H_2O	−0.39	−2.8[f]		−3.2[f]
21	Morpholine/H_2O	0.01	−2.48	−2.39	−2.85
22	Morpholine/MeOH	−0.21	−2.59		−3.19
23	Piperidine/H_2O	0.99	−1.39	−1.33	−1.74
24	Piperidine/MeOH	0.83[g]	−2.00[h] [12.; −30.]	−1.91[i] [11.; −30.]	−2.54[i] [12.; −32.]

[a] Average rounded values from ref 8 and 21. [b] Data for aryl chloride and aryl fluoride are from ref 27; those for aryl iodide are from ref 28. [c] Average rounded values from ref 27, 29, 30, 31, and 32. [d] Average rounded values from ref 26, 27, and 33. [e] Rate constants from ref 34. [f] The rate constants reported in ref 35, obtained at 30 °C and in 1 M ionic strength solutions, are "corrected" to 25 °C and 0.1 M ionic strength by subtraction of 0.4 log units. [g] Data are from ref 5c. [h] Average rounded values from ref 36 and 37. [i] Data from ref 37.

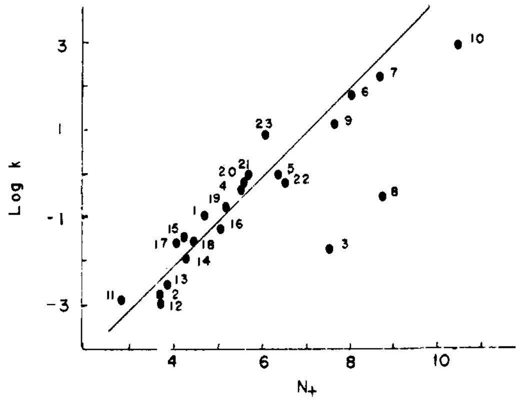


Figure 1. Plot of data from Table II for 2,4-dinitrofluorobenzene according to eq 1. Numbering corresponds to that in Table II.

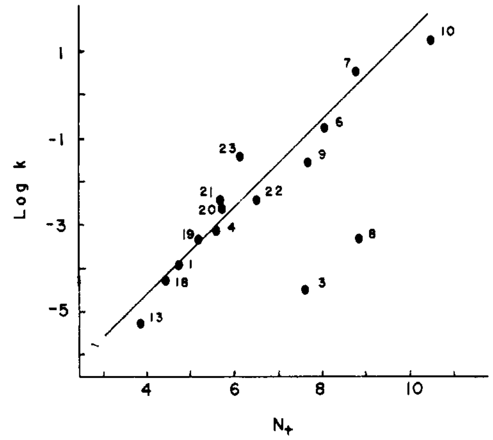


Figure 2. Plot of data from Table II for 2,4-dinitrochlorobenzene according to eq 1. Numbering corresponds to that in Table II.

varying amine concentrations, we estimate that all of the rate constants for reactions of amines are accurate to better than ±5%.

The data from the present study together with some pertinent data from the literature are summarized in Table II.

Discussion

General. The correlations of the data in Table II by eq 1 are shown in Figures 1–4. With exceptions of azide and thiolate ions, discussed further below, the correlations are quite satisfactory. The nucleophiles showing behavior in accord with eq 1 include anionic, neutral, "hard",[38] "soft",[38] and "α-effect"[39] nucleophiles. It is particularly worth emphasis that the N_+ values, which are based heavily on the reactions of nucleophiles with cationic centers, apply equally well to both anionic and neutral nucleophiles reacting with the aryl halides. The conclusion, reached in earlier studies,[40] that coulombic interactions of electrophile and nucleophile at the transition state for these combination reactions are unimportant, seems inescapable.

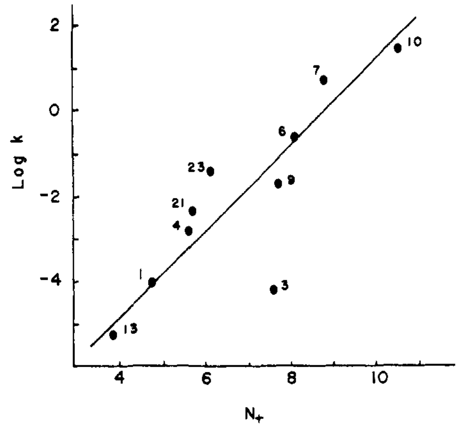


Figure 3. Plot of data from Table II for 2,4-dinitrobromobenzene according to eq 1. Numbering corresponds to that in Table II.

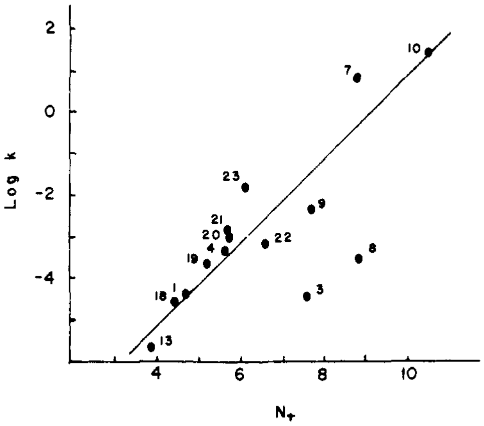


Figure 4. Plot of data from Table II for 2,4-dinitroiodobenzene according to eq 1. Numbering corresponds to that in Table II.

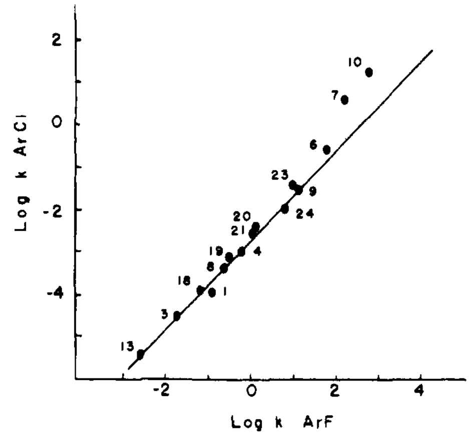


Figure 5. Linear free energy relation for reactions of 2,4-dinitrofluorobenzene and those of 2,4-dinitrochlorobenzene. Numbering corresponds to that in Table II.

Another surprising facet of the success of eq 1 is the absence of selectivity-reactivity relationships in all of the electrophile-nucleophile combination reactions studied thus far. The absence of such relationships in the present reactions is even more clearly demonstrated in Figures 5-9 in which direct comparisons of electrophiles remove much of the scatter resulting from averaged values of N_+. With the exception only of the thiolate ion nucleophiles, there are excellent unit-slope linear relationships between the log ks for any pair of aryl halides, even though the aryl fluoride reacts ca. 10^3 faster with any given nucleophile than the other corresponding aryl halides. From the standpoint of relative reactivities of nucleophiles, the data for reactions of methoxylamine and peroxide ion, believed to be sterically "unhindered" reagents,[1] seem particularly pertinent. The values of log $k_{\mathrm{HOO^-}}/k_{\mathrm{CH_3ONH_2}}$ are 4.41 for the aryl fluoride, 4.71 for the aryl chloride, and 4.63 for the aryl bromide, showing no appreciable variation with reactivity of the electrophile.

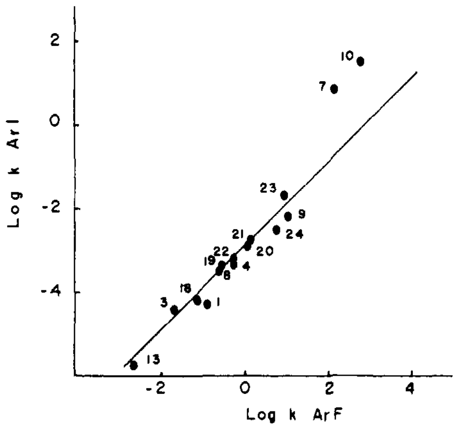


Figure 6. Linear free energy relation for reactions of 2,4-dinitrofluorobenzene and those of 2,4-dinitroiodobenzene. Numbering corresponds to that in Table II.

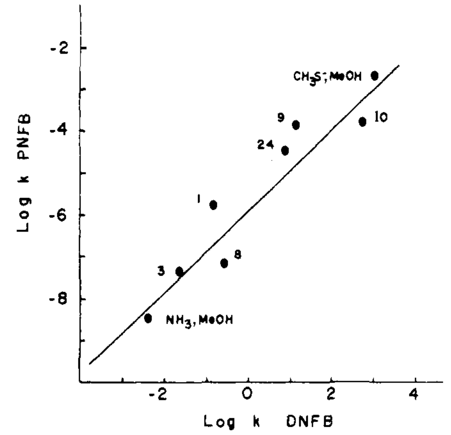


Figure 7. Linear free energy relation for reactions of 2,4-dinitrofluorobenzene and those of p-nitrofluorobenzene. Numbering corresponds to that in Table II. Data for NH_3 and CH_3S^- are from J. Miller and K. W. Wong, *J. Chem. Soc.*, 5454 (1965); D. E. Giles and A. J. Parker, *J. Am. Chem. Soc.*, **83,** 835 (1961); J. D. Reinheimer and J. F. Bunnett, *ibid.*, **81,** 315 (1959).

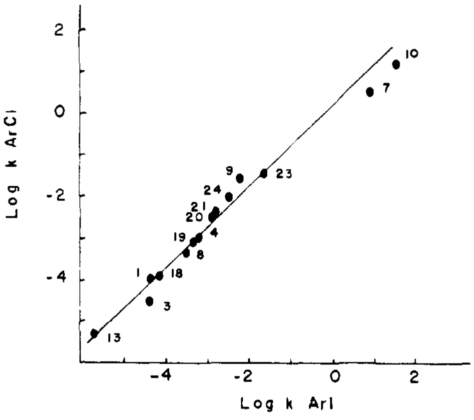


Figure 8. Linear free energy relation for reactions of 2,4-dinitrochlorobenzene and those of 2,4-dinitroiodobenzene. Numbering corresponds to that in Table II.

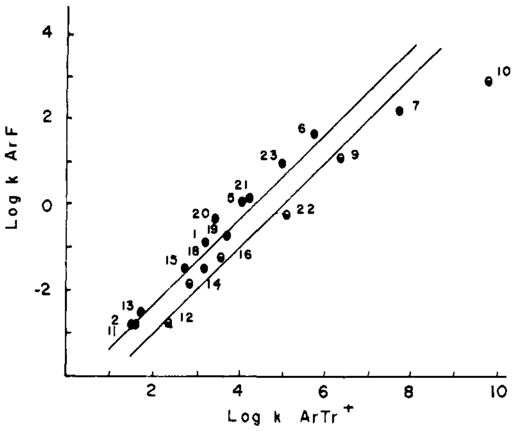


Figure 9. Linear free energy relation for reactions of 2,4-dinitrofluorobenzene and those of *p*-dimethylaminophenyltropylium ion in water and methanol. Data for the *p*-dimethylaminophenyltropylium ion are from ref 1. Numbering corresponds to that in Table II.

As indicated in Figure 7, even the behavior of the thiolate ions appears not to be attributable to selectivity-reactivity. The reactivity of thiolate ions, relative to other nucleophiles, is nearly the same toward *p*-nitrofluorobenzene and 2,4-dinitrofluorobenzene even though the dinitro compound reacts ca. 10^6 faster than the mononitro. The scatter in Figure 7 is more likely due to inaccuracies in rate constants, which were obtained for a common temperature by long extrapolations, than to any "chemical" cause.

Solvent Effects. Both the absence of coulombic effects and of selectivity relationships have been noted in our earlier studies.[41] Figure 9 demonstrates a feature of the electrophile-nucleophile reactions which we have not previously found: that the relative reactivities of the two electrophiles, *p*-dimethylaminophenyltropylium ion and 2,4-dinitrofluorobenzene, are solvent dependent. The effect clearly seen in Figure 9 is barely discernible in Figures 1-4 because of the averaging which has gone into the assignment of N_+ values.[1]

We have previously noted that the relative reactivities of cations are *not* solvent dependent[42] in spite of the fact that the free energies of transfers of the cations among solvents are strongly dependent on cation structure.[43] It is also true, as seen in Figures 5-8, that the relative reactivities of the aryl halides are not solvent dependent, at least in water and methanol solution.

The lines shown in Figure 9 are separated by 0.7 log units, corresponding to an energy difference of slightly less than 1 kcal/mol. We can evaluate the free energy of transfer from water to methanol of 2,4-dinitrofluorobenzene[44] and *p*-dimethylaminophenyltropylium ion[45] as −5.75 and −2.9 kcal/mol, respectively. Thus, of the 2.9 kcal/mol difference in free energies of transfer, 1.9 kcal/mol remains at the transition states for reactions with nucleophiles.

The failure to observe a solvent dependence of the relative reactivities of cations cannot be attributed to a small difference in the free energies of transfer of the cations. The free energies of transfer of crystal violet cation and phenyltropylium ion from water to methanol solution differ by at least 4 kcal/mol,[46] but the ratio of rate constants for reactions of methoxide ion in methanol and of hydroxide ion in water is virtually identical ($\log k_{\mathrm{MeO}}/k_{\mathrm{HO}} = 3.3$)[42] for both cations, but appreciably different from the ratio for 2,4-dinitrofluorobenzene ($\log k_{\mathrm{MeO}}/k_{\mathrm{HO}} = 2.1$).

In order to understand these facts, one would like to have information concerning the specific contribution of the reaction site solvation to the transfer free energies. In the absence of this information, we cannot decide between two possibilities: (1) that the solvation of the electrophilic center is very slightly disturbed on going from reactant to transition state, or (2) that the electrophilic centers of various electrophiles are very similarly solvated, with the differences in free energies of transfer due to solvation remote from the electrophilic center. A more complex explanation, involving a finely balanced set of compensating factors, has been suggested,[47] but is not to us very satisfying unless there were some way to evaluate the independent factors.

Azide Ion Reactions. The most serious deviations from eq 1 found in the present study are for the reactions of azide ion. The points for reactions with all four aryl halides in both water and methanol solutions fall ca. 3 log units below the correlation lines shown in Figures 1-4. The reactivity of azide ion relative to other nucleophiles is, however, constant for the four aryl halides as shown in Figures 5-8.

The N_+ value for azide ion in water is based on the single reaction with tri-*p*-anisylmethyl cation,[48] and could conceivably be incorrect. Since, however, the value in methanol solution is firmly established, being based on reactions of *p*-nitro malachite green and several aryldiazonium ions, and since the deviations in Figures 1-4 are identical for both water and methanol solution, we do not believe that the matter is that simple. We have also noted[1] that the reactions of azide ion with esters in water gave large deviations from eq 1.

On the basis of the present results, it appears that azide ion, uniquely among the nucleophiles studied, shows entirely different relative reactivities toward cationic and neutral centers. An N_+ value of 4.4 for azide ion in water, and of 5.8 for azide ion in methanol, would place the points in Figures 1-4 on the lines shown. This value for azide ion in water would also account better for azide ion reactions with esters than does the "cationic" value of 7.6. Both the reactions of azide ion with 4-methoxy-*N*-acetoxypyridinium ion and with phenyl α-disulfone would be assigned a rate-determining azide ion attack, and the calculated values for rate constants would be in nearly perfect agreement with the experimental values.[1] With the previously assigned N_+ value, these reactions could be correlated only if azide ion were assigned a very high leaving group ability, making the attack step non-rate-determining.

The behavior of azide ion does not appear to be explicable in terms of any of the extant theories of nucleophilicity. Thus, for example, azide ion is considered to be "borderline", while neither the "soft" cyanide ion nor the "hard" hydroxide ions show appreciable deviations from eq 1. For the same reasons which we give below for thiolate ion reactions, the fact that the points for azide ion fall on the lines of Figures 5-8 makes it most unlikely that the azide ion reactions have different rate-determining steps than for other nucleophiles in the reactions of the aryl halides.

Thiolate Ion Reactions. The deviant behaviors shown by thiolate ions in Figures 1-9 are quite different from those shown by azide ion, in that relative reactivity of the thiolates depends on the identity of the aryl halide. This behavior has been observed by Bunnett[5c,26,33] and was attributed to a favorable interaction of thiophenoxide ion with the polarizable halides. An alternate explanation, based on a change in rate-determining step, was disfavored since general acid catalysis of the reaction with 2,4-dinitrofluorobenzene could not be observed[26] and was expected if the leaving of fluoride ion were rate determining.

We believe that our observations of the reactions of thioglycollate ion with the aryl halides in water also argue against the possibility that the behavior is due to a change in rate-determining step. The leaving group ability of fluoride ion, relative to the other halides, should be enhanced in water over that in methanol solution. This should result in the thiolate ions having more nearly the same relative reactivities toward the different aryl halides in water than in methanol solutions. Figures 5-8 show that this is not the case.

Although we find it hard to understand why short-range interactions, such as polarizability-polarizability, but not long-range interactions, such as coulombic attractions, should be important, we tend to agree with Bunnett[5c,26] that this is the important factor. It is worth noting that Jencks[49] has observed that the reactivities of thiolate ions, relative to oxy anions, are greater toward thiol esters than toward oxy esers. Kice's data[2] also indicate a small, but significant, contribution of polarizability-polarizability interactions in the reactions of nucleophiles at sulfur in various oxidation states.

In both Kice's data and the present data, it appears that the N_+ scale includes the major factors accounting for nucleophilicities, with polarizability causing significant, but relatively minor, deviations in the plots according to eq 1.

Summary

The present study has provided further support for the general applicability of the N_+ scale of nucleophilicity to reactions involving simple bond formation between nucleophile and electrophile. Charge type of nucleophile or of electrophile does not appear to be important, and selectivity is not a function of reactivity, in such reactions. Polarizability-polarizability interactions, surprisingly, appear to give significant rate effects. The present data further indicate that the relative reactivities of electrophiles are significantly solvent dependent when cationic and neutral electrophiles are compared, but are solvent independent when cationic electrophiles alone, or neutral electrophiles alone, are compared. Azide ion, uniquely among the nucleophiles studied, is markedly less reactive toward neutral electrophiles than toward cationic electrophiles.

Acknowledgments. This work was supported by grants from the National Science Foundation (CHE 7400520) and from the National Institutes of Health, USPHS (GM-12832).

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