Reactions of 2,4-Dinitrohalobenzenes with Nucleophiles. A New Correlation between Reactivities and Substrate Polarizability

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Abstract: We have investigated the reactivity of the four 2,4-dinitrohalobenzenes in methanol at 25 °C with seven nucleophiles chosen to provide a wide range of polarizability and basicity. The results strengthen Edwards' hypothesis that nucleophilicity can be accounted for by two factors, one linearly related to basicity, the other to polarizability. We are able to find a relationship linking reactivity to substrate polarizability (R_{sub}). The magnitudes of R_{sub} values and polarizability parameters of nucleophiles indicate that only atoms and bonds at or near the reaction center are involved in producing polarizability effects. A method to predict R_{sub} values is proposed.

It is known that rates of nucleophilic substitution do not follow the basicities of nucleophiles toward protons.[2] Swain and Scott[3a] set up a scale of nucleophilic strengths with data from displacements on methyl bromide. Edwards' equation[3b] represented nucleophilic reactivity as linearly depending both on basicity and polarizability of nucleophilic reagent. This relationship was satisfactorily applied to fit a wide range of kinetic data including data for displacement at saturated carbon and for H_2O_2 oxidation. In 1957 Bunnett[4] observed that in nucleophilic aromatic substitution, nucleophiles of high polarizability were found to be especially reactive, relative to nucleophiles of low polarizability, with substrates carrying a highly polarizable nucleofugic group.

Following Bunnett's suggestions, we[5] proposed

$$\log k_p/k_o = A + B \log R_x \tag{1}$$

to correlate the ratios of reactivity of two nucleophiles (N_p and N_o) of different degrees of polarizability with the polarizability properties of the nucleofugic group, expressed by bond refractivity values. The term B is proportional to the difference in polarizability between N_p and N_o. Although the fitting of experimental data by eq 1 is satisfactory for displacements of monatomic (halogens)[6] and polyatomic (NO_2, SO_2-Ph)[7] nucleofugic groups, bound to a large variety of substrates, this approach does not account for the important kinetic effects of substrate framework polarizability and the difference in basicity between N_p and N_o. The present study reports additional experiments designed to revise eq 1 so as to deal with variables previously not taken into account and thereby provide a more comprehensive view of all phonomena involved.

For these purposes we have measured reaction rates in methanol at 25 °C between 2,4-dinitrohalobenzenes and nucleophiles of different degrees of polarizability and basicity.

Results

We have investigated the reactivities of 2,4-dinitrohalobenzenes in methanol at 25 °C toward seven nucleophiles (MeO^-, PhO^-, piperidine, MeS^-, $PhCH_2S^-$, PhS^-, and N_3^-) chosen to provide a wide range of polarizability and basicity. Rate data are listed in Table III together with some taken from the literature.

Reactions with MeS^- and $PhCH_2S^-$. All kinetic experiments with $PhCH_2S^-$ and MeS^- were carried out in the presence of high concentrations of the corresponding thiols. These experimental conditions were necessary, because acid-base interaction of a nucleophile (N^-) with methanol yields free methoxide ion,

$$CH_3OH + N^- \rightleftarrows CH_3O^- + NH \tag{2}$$

which would compete for nucleophilic substitution. Concentrations of $PhCH_2SH$ and MeSH above 2×10^{-1} M were required to minimize this competitive reaction. No influence on rate due to the presence of free mercaptans was observed when their concentrations were in the range 2×10^{-1} to 1 M.

Our data are at variance with those reported by Miller and co-workers[8,9] for reactions with MeS^-. However, working under the same experimental conditions adopted by Miller, we did detect an appreciable amount of methoxy dehalogenation product. Arrhenius' parameters were recalculated for these reactions; results are listed in Table I.

Reactions with PhO^-. In experiments with phenoxide ion, which exhibits a very low reactivity, a large amount of free phenol is required and this changes the actual nucleophilicity of PhO^- by changing the nature of the medium. Liotta and Karelits[10] reported that the actual second-order rate constants (k_{PhO^-}) can be calculated from the observed rate constants (k_{obsd}) by means of the following equation

$$k_{obsd} = k_{PhO^-} + k_{MeO^-} K([MeOH]/[PhOH])$$

where K is the equilibrium constant of reaction 2. k_{obsd} values for all of the four 2,4-dinitrohalobenzenes are listed in Table II. Plots of k_{obsd} vs. [MeOH]/[PhOH] ratios yield values for k_{PhO^-} that are reported at the bottom of Table II.

Reactions with Piperidine and PhS^-. Kinetic experiments on reactions of 2,4-dinitrofluorobenzene with piperidine and of chloro, bromo, and iodo derivatives with PhS^- were performed under the experimental conditions reported by Bunnett.[11,12]

Reactions with N_3^-. In the case of reaction of 2,4-dinitrobromobenzene with N_3^- the same experimental conditions reported by Parker[13] were adopted.

Discussion

Since the main object of this work is to derive a correlation between basicity and polarizability from homogeneous experimental data, we must establish that all the reactions shown in Table III follow a uniform mechanistic pattern. We have good grounds for assuming that reaction rates for all nucleophiles depend on factors governing carbon-nucleophile bond ($C-N_p$) formation, according to the two-stage mechanism proposed by Bunnett.[17] While this assumption is generally accepted for piperidine and methoxide ion, in recent years an opposite theory concerning the reactivity of sulfur nucleophiles was advanced by Miller;[18] he interpreted the relative reactivities of halogen nucleofugic groups in reactions with PhS^- in terms of the step in which halide ion is expelled from the anionic intermediate being limiting. This interpretation was

Table I. Second-Order Rate Constants for Reactions of 2,4-Dinitrohalobenzenes with MeS^- in Methanol at Different Temperatures

t, °C	F	Cl	Br	I
15	6.6×10^2	9.4	1.1×10^1	8.8
25	1.0×10^3	1.7×10^1	2.0×10^1	1.7×10^1
35	1.7×10^3	3.2×10^1	3.8×10^1	3.0×10^1
E_a, kcal mol^{-1}	8.5	10.8	11.1	10.9
Log A	9.2	9.2	9.4	9.2

ruled out by Bunnett's finding[16] that no acid catalysis can be observed with the fluoro derivative. Since the step involving expulsion of nucleofugic group from the intermediate is most likely to be rate limiting when the nucleofugic group is the most difficult to expel, Bunnett's data indicate that for all the reactions listed in Table III the step in which the nucleophile attacks is rate limiting; this follows from the fact that the C–F bond has the highest breaking energy among halogen nucleofugic groups, while the C–SPh bond has the lowest one among C–N_p bonds.

Furthermore our present data are in sharp contrast with Miller's interpretation, which predicts[18] that nucleophiles capable of forming with carbon bonds weaker than C–OCH_3, but stronger than C–SPh, should behave like borderline nucleophiles; by consequence then, they should exhibit an intermediate order of nucleofugicity. On the contrary the actual reactivity order for PhO^- is very similar to that for MeO^-. The same similarity also holds for MeS^- and $PhCH_2S^-$, with respect to PhS^-. Miller's conclusions concerning MeS^- reactivity rest upon disputable experimental evidence. The present work indicates that other factors, such as polarizability, are involved in determining the relative reactivities of halogen nucleofugic groups.

Factors Affecting Reactivity. The reactivities of six nucleophiles relative to that of methoxide ion are reported in Table IV. As shown, while k_p/k_{MeO^-} ratios markedly increase from fluoro to iodo nucleofugic group when N_p is a sulfur nucleophile, no appreciable variation can be found when N_p is phenoxide ion; piperidine and azide ions show an intermediate behavior. This is in agreement with Bunnett's hypothesis;[4] some years ago he attributed the observed variation in reactivity ratios of any given pair of nucleophiles mainly to their difference in polarizability when rates are governed by bond making.

Close inspection of the data in Table IV contributes additional information of interest; when the polarizability of the nucleofugic group is very low, there is no convincing overall correlation between the reactivity order for nucleophiles and their basicities. This correlation is absent only for highly polarizable nucleophiles (PhS^-, $PhCH_2S^-$, MeS^-) more reactive than MeO^-; for scarcely polarizable nucleophiles the observed sequence is MeO^- > piperidine > PhO^- > N_3 in agreement with the basicity sequence. However, even in this circumstance there is no close proportionality between reactivity and basicity.

These results can be explained if we assume that the polarizability of the substrate framework also has an important effect on reactivity by conferring extra reactivity on highly polarizable nucleophiles, while its effect on less polarizable ones is substantially reduced. This interpretation requires a close correlation between reactivity and basicity for nucleophiles exhibiting a similar degree of polarizability. This is actually borne out by our data. We can assume on the one hand that MeS^- shows a polarizability character similar to that of $PhCH_2S^-$ and on the other that MeO^- is similar in polarizability to PhO^-; both the $k_{MeS^-}/k_{PhCH_2S^-}$ and the k_{MeO^-}/k_{PhO^-} are nearly constant in going from fluoro to iodo nucleofugic groups. Also, the ratios $k_{MeS^-}/k_{PhCH_2S^-}$ and k_{MeO^-}/k_{PhO^-} are proportional to the differences in respective pK_a values.

In conclusion, nucleophilic reactivity can be accounted for by basicity of nucleophile and electrophilicity of substrate on the one side and by the polarizability of both nucleophile and substrate on the other side. Although Edwards' equation[3b] contained these same suggestions, its derivation proceeded from polarizability properties of nucleophile. From our data the problem can be approached in a different way; we can attempt to evaluate substrate polarizability properties as a combination of properties of the nucleofugic group and the substrate framework.

Relationship between Reactivity and Substrate Polarizability. By using the same line of reasoning that led to eq 1, we propose

Table II. k_{obsd} Values for Reactions between 2,4-Dinitrohalobenzenes and Phenoxide Ion in Methanol at 25 °C in the Presence of an Excess of PhOH

F		Cl		Br		I	
k_{obsd}, s^{-1} mol^{-1}	[MeOH]/[PhOH]	k_{obsd}, s^{-1} mol^{-1}	[MeOH]/[PhOH]	k_{obsd}, s^{-1} mol^{-1}	[MeOH]/[PhOH]	k_{obsd}, s^{-1} mol^{-1}	[MeOH]/[PhOH]
9.5×10^{-1}	103	1.20×10^{-3}	79	1.00×10^{-3}	79	2.3×10^{-4}	79
9.9×10^{-1}	124	1.30×10^{-3}	110	1.07×10^{-3}	100	2.6×10^{-4}	100
1.10	150	1.45×10^{-3}	150	1.28×10^{-3}	135	2.8×10^{-4}	140
1.22	190	1.50×10^{-3}	200	1.52×10^{-3}	180	3.2×10^{-4}	200
1.35	227	1.68×10^{-3}	250	1.68×10^{-3}	230	3.7×10^{-4}	250
k_{PhO^-} 5.4×10^{-1}		1.0×10^{-3}		7.2×10^{-4}		1.8×10^{-4}	

Table III. Second-Order Rate Constants of Reactions between 2,4-Dinitrohalobenzenes and Nucleophiles (N) in Methanol at 25 °C

	k, s^{-1} mol^{-1} L, N =						
	MeO^-	PhO^-	$C_5H_{11}N$	N_3^-	MeS^-	$PhCH_2S^-$	PhS^-
F	1.8×10^{1}[a]	5.4×10^{-1}[a]	5.6[a]	2.4×10^{-1}[d]	1.0×10^{3}[a]	5.8×10^{2}[a]	7.8×10^{2}[f]
Cl	3.0×10^{-2}[b]	1.0×10^{-3}[a]	1.2×10^{-2}[c]	5.9×10^{-4}[e]	1.7×10^{1}[a]	9.7[a]	2.1×10^{1}[a]
Br	2.0×10^{-2}[b]	7.2×10^{-4}[a]	1.2×10^{-2}[c]	6.6×10^{-4}[a]	2.0×10^{1}[a]	1.3×10^{1}[a]	4.3×10^{1}[a]
I	5.8×10^{-3}[b]	1.8×10^{-4}[a]	3.0×10^{-3}[c]	3.0×10^{-4}[e]	1.7×10^{1}[a]	1.2×10^{1}[a]	2.9×10^{1}[a]

[a] This work. [b] See ref 14. [c] See ref 11. [d] See ref 15. [e] See ref 13. [f] See ref 16.

Table IV. Log k_p/k_{MeO^-} Values of Reactions between 2,4-Dinitrohalobenzenes and Nucleophiles in Methanol at 25 °C

	N_p =					
	PhO^-	$C_5H_{11}N$	N_3^-	MeS^-	$PhCH_2S^-$	PhS^-
F	−1.52	−0.50	−1.87	1.75	1.52	1.64
Cl	−1.47	−0.40	−1.70	2.76	2.51	2.85
Br	−1.43	−0.22	−1.47	3.01	2.83	3.35
I	−1.50	−0.28	−1.20	3.46	3.31	3.70

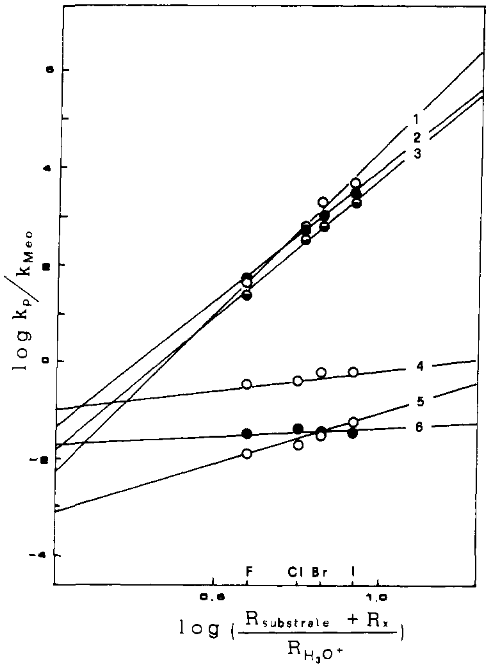

Figure 1. Plots of log k_p/k_{MeO^-} vs. log $[(R_{sub} + R_x)/R_{H_3O^+}]$ when a R_{sub} value of 10.5 cm^3 is given: N_p = (1) PhS^-; (2) MeS^-; (3) $PhCH_2S^-$; (4) $C_5H_{11}N$; (5) N_3^-; (6) PhO^-.

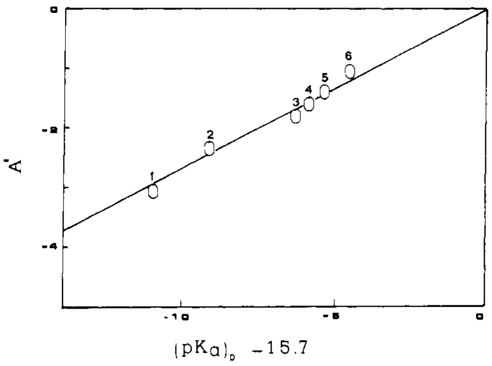

Figure 2. Plot of A' values vs. $[(pK_a)_p - 15.7]$ where 15.7 is the pK_a value of methoxide ion in water: N_p = (1) N_3^- (pK_a = 4.7); (2) PhS^- (6.5); (3) $PhCH_2S^-$ (9.4); (4) PhO^- (9.9); (5) MeS^- (10.3); (6) $C_5H_{11}N$ (11.2).

the following equation:

$$\log k_p/k_o = A_x' + B' \log \left(\frac{R_{sub} + R_x}{R_{H_3O^+}}\right) \qquad (3)$$

where

$$A_x' = \alpha_x[(pK_a)_p - (pK_a)_o]$$

k_p and k_o are the second-order rate constants for a highly polarizable nucleophile (N_p) and a poorly polarizable nucleophile (N_o), respectively; $(pK_a)_p$ and $(pK_a)_o$ refer to acid dissociation of their conjugate acids in water; and R_{sub}, R_x, and $R_{H_3O^+}$ (3.04 cm^3) are refractivities at the sodium D line of the substrate framework, nucleofugic group, and protonated water, respectively. The α_x parameter is characteristic for a substrate carrying an x nucleofugic group and it is proportional to the electrophilicity of the substrate. The B parameter depends on the differences in polarizability between N_p and N_o; $(R_{sub} + R_x)$ represents the overall polarizability of a substrate and its formulation takes into account the principle of additivity of bond refractivities. The term $R_{H_3O^+}$ was introduced as reference term for substrate polarizabilities; this means that, when polarizability becomes close to that of the electrophilic substrate H_3O^+, the differences in reactivity between two nucleophiles will tend to become exclusively dependent upon differences in basicity. We believe that this is justified by the fact that, if electrophilicity of a substrate is compared in eq 3 to that of protonated water by using the parameter α, it seems appropriate to compare polarizability properties by using the term $(R_{sub} + R_x)/R_{H_3O^+}$.

Although from electrostatic principles, it is to be expected that log k_p/k_o should be linearly dependent on polarizability rather than on log of polarizability, the use of the logarithmic function seems to be more appropriate. An analagous discrepancy was found by Edwards in the formulation of his relationship.[19]

R_x values are available from Le Fevre's tabulation.[20] For halogens the values are as follows: F, 1.48; Cl, 6.62; Br, 9.49; I, 14.61 cm^3. R_{sub} should be deduced from the values listed in Table IV. If we make the assumption that on changing the nucleofugic group progressively from fluorine to iodine the rise in k_p/k_o ratios is mainly due to the increase in polarizability, then the α_x parameter can be considered almost invariant for all of the 2,4-dinitrohalobenzenes.[21]

Under the above assumption log k_p/k_o yields a straight line when plotted vs. log $(R_{sub} + R_x/R_{H_3O^+})$; the intercept A' must be proportional to the pK_a value. Thus, under this constraint R_{sub} values can be obtained through iterative calculations. For the 2,4-dinitrophenyl substrate framework a value of about 10.5 cm^3 is found. Figure 1 shows excellent fits for six nucleophiles, whose reactivities are compared to that of MeO^- as reference nucleophile N_o. Values of A' and B' and statistical parameters are reported in Table V. Figure 2 represents a plot of A' vs. pK_a values; as shown, the excellent fit of data strongly supports the validity of eq 3. The magnitude of the experimental value for R_{sub} excludes the possibility that all the bonds and atoms of the substrate framework can be involved in producing polarizability phenomena. Preliminary work,[7] performed by us a few years ago to evaluate the influence of these factors on activated substrates carrying a polyatomic nucleofugic group, indicated that only the first atom of the nucleofugic group and the bonds connected with it contribute to polarizability effects.

Experimental averaged values for nitro and sulfonic groups were 6.9 and 9.1 cm^3, respectively, quite close to 7.3 and 9.6 cm^3 calculated from Le Fevre's data of bond refractivity values. Reinheimer and Bunnett[22] examined the influence on reactivity of highly polarizable substituents in a benzene substrate framework and found that only ortho substituents are involved in polarizability effects. Therefore it seems de-

Table V. A' and B' Parameters from Eq 3 for Nucleophilic Dehalogenation on 2,4-Dinitrohalobenzenes[a]

N_p	A'	B'	S
PhO^-	−1.6	0.1	0.1
$C_6H_{11}N$	−1.0	0.8	0.1
N_3^-	−3.1	2.1	0.1
MeS^-	−1.4	5.3	0.1
$PhCH_2S^-$	−1.8	5.6	0.1
PhS^-	−2.3	6.6	0.2

[a] S is the standard error[b] for linear plots of log k_p/k_{MeO^-} vs. log $[(R_{sub} + R_x)/R_{H_3O^+}]$. [b] See ref 25.

Table VI. Comparison between R_{sub} Values Obtained from Eq 3 and Those ($[R_{sub}]_{calcd}$) Calculated from Bond Refractivities[20]

	R_{sub}, cm^3	$[R_{sub}]_{calcd}$, cm^3
2,4-Dinitrohalogenobenzenes (HDNB)	10.5	9.5[b]
4-Nitrohalogenobenzenes (HNB)	10[a]	8.8[b]
6-Nitro-2-halogenobenzothiazoles (HNBT)	8[a]	8.6[b]
2-Halogenobenzothiazoles (HBT)	8[a]	8.6[b]

[a] From experimental data of halogeno substitution with a limited number of nucleophiles: MeO^-, MeS^-, PhS^-, and N_3^- (see ref 23). [b] Calculated as follows: HDNB, 2 × 2.69(2 C_{Ar}–C_{Ar}) + 2.44(1 C_{Ar}–N) + 1.69(1 C–H) = 9.5; HNB, 2 × 2.69(2 C_{Ar}–C_{Ar}) + 2 × 1.69(2 C–H) = 8.8; HNBT, 4.61(1 C–S) + 3.78(1 C=N) = 8.6; HBT, 4.61(1 C–S) + 3.78(1 C=N) = 8.6.

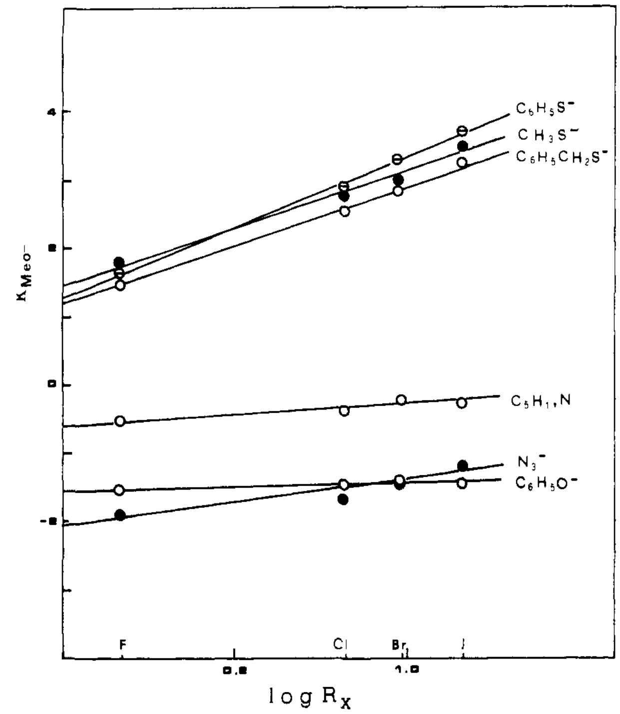

Figure 3. Plots of log k_p/k_{MeO^-} versus log R_x·B values are: PhS^-, 2.1; MeS^-, 1.6; $PhCH_2S^-$, 1.7; $C_5H_{11}N$, 0.3; N_3^-, 0.6; PhO^-, 0.1.

sirable, in order to be able to predict the polarizability of the 2,4-dinitrophenyl framework, to take into account C_1–C_2, C_1–C_6, C_2–N, and C_6–H bonds. We think that C_2–C_3 and C_6–C_5 aromatic bonds must be excluded from computation, since the cyclic structure of the benzene ring keeps them always outside the critical space within which polarizability forces operate during the reaction. Calculations based on the additivity of bond refractivity yield a value of 9.5 cm^3 for the 2,4-dinitrophenyl framework, very close to the value obtained from eq 3. Preliminary results[23] on reactions between *p*-nitrohalobenzenes, 2-halobenzothiazoles, and 6-nitro-2-halobenzothiazoles and a limited number of nucleophiles confirm the wide range of applicability of eq 3. Table VI shows R_{sub} values calculated from Le Fevre's[20] data as compared to those obtained from eq 3.

In conclusion, as far as the substrate is concerned, only atoms and bonds at or near the reaction center can be involved in producing poralizability effects. The same conclusions can be reached concerning the polarizability of nucleophiles. As shown in Table V, values for B' follow the expected sequence, if we assume that polarizability properties depend upon the nature of the nucleophilic atom and the bonds connected with it. In fact, sulfur nucleophiles show high B' values. The polarizability of thiophenoxide ion is somewhat higher than that of $PhCH_2S^-$ and MeS^-, in good agreement with the fact that the S^- moiety in thiophenoxide ion is connected to an aromatic framework. The polarizabilities of piperidine and phenoxide ion are very low and close to that of methoxide ion. Azide ion shows intermediate behavior.

In conclusion, we think that eq 3 represents useful advance over eq 1 for understanding reactivity in nucleophilic aromatic substitution, although eq 1 too can be satisfactorily applied to fit the rate data of Table III as shown in Figure 3. In fact while eq 1 only illustrates the influences of nucleofugic group polarizability on the relative reactivities of nucleophiles, eq 3 properly points out the influence of the global polarizability of a substrate.

A close connection exists between eq 3 and Edwards' equation.[19] In fact, when the second equation is applied to compare reactivities of two nucleophiles N_p and N_o, we obtain:

$$\log \frac{k_p}{k_o} = b[(pK_a)_p - (pK_a)_o] + a \log \frac{R_p}{R_o} \qquad (4)$$

If we assume that the first and second term of eq 4 are equal to the first and the second terms of eq 3, the b parameter becomes equal to the α_x parameter of our equation.

Log R_p/R_o and the a parameter are proportional to the terms B' and log $[(R_{sub} + R_x)/R_{H_3O^+}]$, respectively.

Experimental Section

Methanol (reagent grade) was purified by distillation over magnesium. 2,4-Dinitrohalobenzenes are commercial products. UV spectra are recorded by a Zeiss DMR 21 spectrophotometer. Mathematical calculations were performed by a Hewlett Packard 4100 B calculator.

Rate Measurements. Reactions of 2,4-Dinitrohalobenzenes with MeS^-, $PhCH_2S^-$. Kinetic experiments were performed under pseudo-first-order conditions using an excess of the base (1–2 × 10^{-2} M) and in the presence of a large excess of the corresponding conjugated acid, concentration of which ranged from 2 × 10^{-1} to 1 M. Kinetic runs were carried out by following the appearance of the corresponding sulfides at appropriate wavelengths in the mixing cell of a Durrum Gibson Flow apparatus.

Reactions of 2,4-Dinitrohalobenzenes with PhS^-. Experiments were performed under pseudo-first-order conditions using an excess of the base (1–2 × 10^{-2} M) and in the presence of a slight excess of free thiophenol (1.1–2.1 × 10^{-2} M). Kinetic runs were carried out by following the appearance of 2,4-diphenyl sulfide at the appropriate wavelength in the mixing cell of a stopped flow apparatus.

Reaction of 2,4-Dinitrofluorobenzene with MeO^-. Pseudo-first-order conditions with an excess of MeO^- were adopted. A stopped flow apparatus was used, following the appearance of methoxy derivative at the appropriate wavelength.

Reactions of 2,4-Dinitrohalobenzenes with PhO^-. Kinetic experiments with 2,4-dinitrofluorobenzene were performed under pseudo-first-order conditions with an excess of PhO^- (1–5 × 10^{-2} M) and in the presence of free phenol, the concentration of which was varied from 1 × 10^{-1} to 2.5 × 10^{-1} M. The reactions were run in the thermostatic cells of a Zeiss DMR 21 spectrophotometric apparatus by following the appearance of developed 2,4-dinitrodiphenyl ether at the appropriate wavelength. In the case of the other halogen derivatives kinetic experiments (second-order conditions) were carried out in the presence of an excess of free phenol, concentration of which ranged from 7×10^{-2} to 3.0×10^{-1} M. The same experimental procedure describe by Liotta and Karelits[10] was adopted.

Reaction of 2,4-Dinitrobromobenzene with N_3^-. Kinetic experiments were carried out exactly following the experimental procedure described by Parker.[13]

Reactions of 2,4-Dinitrofluorobenzene with Piperidine. Kinetic runs were carried out by following the appearance of the substitution product at appropriate wavelength. Pseudo-first-order conditions in the presence of an appropriate excess of the corresponding ammonium salt were adopted.

All experimental rate constants reported from the work represent averaged values of 3–4 single determinations.

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(21) Electronic properties of nucleofugic groups can show a strong influence[24] on α_x parameter of eq 3, when they markedly influence the magnitude of a positive charge at reaction center.[26] Since in the 2,4-dinitrobenzene series this positive charge is mainly induced by the presence of nitro groups in ortho and para positions with respect to the electrophilic atom, the above assumption seems to be correct. This assumption is also supported by the finding that when the electron-withdrawing character only of the nucleofugic group is being varied in a sequence of 2,4-dinitrophenyl z'-phenyl ethers, the Hammett's values for the more basic MeO$^-$ and the less basic MeS$^-$ are almost the same.

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Selective Deuteration in Neutron-Scattering Spectroscopy: Formic Acid and Deuterated Derivatives

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Abstract: The usefulness of selective deuteration as a technique for clarifying vibrational assignments in hydrogenous molecules is demonstrated by contrasting the inelastic neutron-scattering spectra of solid formic acid (HCOOH) and the deuterated derivatives HCOOD and DCOOH. Since the intensity of observed peaks depends on the vibrational motion of ^1H nuclei, deuteration at a given site virtually eliminates corresponding spectral features, permitting their unambiguous assignment. In particular, an intense peak around 250 cm^{-1} in the HCOOH and HCOOD spectra is greatly weakened in the DCOOH spectrum, indicating C–H involvement. The peak is thus assigned as a librational motion about an axis approximating the molecular A axis. Other features are discussed, and detailed assignments are made in accordance with previous infrared and Raman measurements and with normal-coordinate calculations.

Introduction

Inelastic neutron scattering (INS) spectroscopy is a uniquely useful tool for studying the vibrations of hydrogen-containing molecules due to the fact that the proton has an incoherent neutron-scattering cross section larger than that of any other nucleus, and an order of magnitude larger than most.[2] The intensity of a given vibrational peak in an INS spectrum is proportional to the sum over all nuclei of the scattering cross section times the square of the vibrational amplitude. The combined effects of light mass and high cross section for ^1H mean that hydrogen motions will dominate the spectrum, producing intense peaks for vibrational modes directly involving ^1H nuclei. If deuterium is substituted for hydrogen at a specific site in the molecule, the corresponding vibrations will be greatly reduced in intensity; thus selective deuteration in neutron scattering offers a means of unambiguously assigning hydrogen vibrations.[3,4] Formic acid (HCOOH) has two chemically distinct hydrogen sites—the aldehydic (C–H) and the carboxylic (O–H)—and so is one of the simplest compounds on which selective deuteration may be practiced. For that reason, and because of the intrinsic interest of the dynamics of hydrogen-bonded systems, we have undertaken an INS study of solid formic acid and the deuterated species HCOOD and DCOOH.