Stepwise versus Concerted Mechanisms at Trigonal Carbon: Transfer of the 1,3,5-Triazinyl Group between Aryl Oxide Ions in Aqueous Solution

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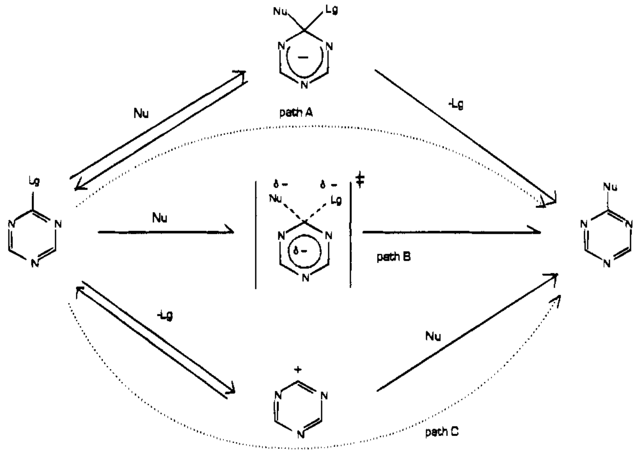
Abstract: Displacements of 4-nitrophenolate ions from 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine by substituted phenolate ions in aqueous solution obey a linear Brønsted-type equation, log $k_{\mathrm{ArO}} = 0.951\mathrm{p}K_a - 10.98$, over a range of p$K_a$ values greater than and less than the pK_a of the leaving phenol. The absence of curvature is consistent with a mechanism involving a single transition state. This conclusion is supported by the existence of cross-correlation effects ($p_{xy} = 0.0561$) on β_{nuc} of the pK_a of the leaving group and on β_{lg} of the pK_a of the nucleophile on β_{lg}. The value of β_{eq}, the Brønsted selectivity for transfer of the triazinyl function between phenolate ions, is calculated from the Brønsted data to be 1.48. The identity reaction of 3,4-dinitrophenolate ion with the (3,4-dinitrophenoxy)triazine is calculated to have a Kreevoy–Albery τ value of 1.04, indicating that in this case changes in effective charge on entering and leaving ligands are approximately balanced.

Introduction

Nucleophilic substitution at trigonal carbon often involves formation of an intermediate with tetrahedral carbon which collapses to yield the transferred product.[1] This mechanism has been challenged for reactions at the carbonyl center where, under certain conditions, the reaction proceeds through a single step.[2] There is some theoretical evidence that nucleophilic substitution at vinyl centers can involve a concerted path in addition to the more common stepwise mechanism.[3] Nucleophilic aromatic substitution classically involves the addition–elimination route (Scheme 1, path A).[4–6] It was thought not possible on theoretical grounds to involve a concerted pathway (Scheme 1, path B),[4] but the observation of aryne and aromatic carbocation intermediates (for example, path C in Scheme 1)[5] demonstrate the existence of two extremes of timing; this indicates that a concerted process could be possible under favorable intermediate conditions.

Scheme 1. Paths for Nucleophilic Aromatic Substitution



The technique of searching for a change in rate-limiting step at a predicted condition by use of quasi-symmetrical reactions was used to probe concertedness in acyl group transfer[2a,7] reactions. The technique is appropriate for nucleophilic aromatic substitution and is experimentally feasible if rate constants are accessible over a wide range of nucleophile structures with pK_a values above and below the predicted break point.[7] The rate constants need to be readily measured in aqueous solution. The 1,3,5-triazine system offers an excellent opportunity to search for, or exclude, intermediates in aromatic substitution because the endocyclic nitrogen atoms confer a suitable reactivity to displacement at two, four, or six centers.[6a,b] Unlike corresponding nitro-substituted species, the triazinyl system also possesses relatively weak electronic absorption in the ultra-violet and visible spectrum, making it suitable for study of the nucleophile or leaving group in this region of the spectrum. As far as we are aware no kinetic studies of potentially symmetrical reactions have been recorded although nucleophilic substitution at 1,3,5-triazines with halide and other good leaving groups has been investigated.[8]

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(1) March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley and Sons: New York, 1992.

(2) (a) Ba-Saif, S. A.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362. (b) Hengge, A. *J. Am. Chem. Soc.* **1992**, *114*, 6575. (c) For alternative views see: Buncel, E.; Um, I. H.; Hoz, S. *J. Am. Chem. Soc.* **1989**, *111*, 971.

(3) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961.

(4) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *51*, 273.

(5) Zoltewicz, J. A. *Top. Curr. Chem.* **1975**, *59*, 33.

(6) (a) Illuminati, G. *Adv. Heterocycl. Chem.* **1964**, *3*, 285. (b) Illuminati, G.; Stegel, F. *Adv. Heterocycl. Chem.* **1983**, *34*, 305. (c) Crampton, M. R. *Adv. Phys. Org. Chem.* **1969**, *7*, 211. (d) Bernasconi, C. F.; Muller, M. C. *Chem. Rev.* **1982**, *82*, 78. (e) Mandeville, R. A.; Buncel, E. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 1887; *J. Amer. Chem. Soc.* **1993**, *115*, 8985. (f) Terrier, F. *Nucleophilic Aromatic Displacement: Influence of the Nitro Group*; VCH: Weinheim, Germany, 1991. (g) Buncel, E.; Crampton, M. R.; Strauss, M. J.; Terrier, F. *Electron Deficient Aromatic and Heterocyclic-Base Interactions*; Elesevier: Amsterdam, 1984. (h) Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: Amsterdam, 1968.

(7) (a) Williams, A. *Chem. Soc. Rev.* 1994, 93. (b) Williams, A. *Acc. Chem. Res.* **1989**, *22*, 387.

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Table 1. Physical and Analytical Data for 2-(Substituted phenoxy)-4,6-dimethoxy-1,3,5-triazines

		calcd				found		
X	mp/°C	C	H	N	formula	C	H	N
3,4-$(NO_2)_2$	138−140	40.88	2.81	21.67	$C_{11}H_9N_5O_7$	40.79	2.62	21.93
3,5-$(NO_2)_2$	139−140	40.88	2.81	21.67	$C_{11}H_9N_5O_7$	40.67	2.50	21.82
4-NO_2-3-Cl	144−5	42.26	2.90	17.92	$C_{11}H_9N_4O_5Cl$	41.80	2.69	17.84
4-Cl-3-NO_2	136−8	42.26	2.90	17.92	$C_{11}H_9N_4O_5Cl$	41.89	2.52	17.87
2-Cl-4-NO_2	109−10	42.26	2.90	17.92	$C_{11}H_9N_4O_5Cl$	42.32	2.69	17.92
4-NO_2	136−7[a]	47.48	3.62	20.14	$C_{11}H_{10}N_4O_5$	47.53	3.44	20.23
3-NO_2	178−80[b]	47.48	3.62	20.14	$C_{11}H_{10}N_4O_5$	47.43	3.40	20.29
4-CHO	173−4[c]	55.17	4.24	16.09	$C_{12}H_{11}N_3O_4$	55.29	4.18	16.09
3-CHO	130−1	55.17	4.24	16.09	$C_{12}H_{11}N_3O_4$	55.11	4.08	16.08
2,4,5-Cl_3	157−9	39.26	2.40	12.49	$C_{11}H_8N_3O_3Cl_3$	38.91	2.17	12.37

[a] Lit.[10] mp 136.5−137.5 °C. [b] Lit.[10] mp 179−180 °C. [c] Lit. 173−174 °C (Ohto, Y.; Shizuka, H.; Sekiguchi, S.; Matsui, K. *Bull. Chem. Soc. Jpn*,**1974**, *47*, 209).

The linearity of a Brønsted plot for a symmetrical nucleophilic substitution reaction over a substantial range of pK_{nuc} spanning that of the leaving group is good evidence for the existence of a mechanism with a single transition state.[7] This technique has been applied extensively to nucleophilic substitution reactions in general[7] including those at trigonal-carbon.[9] This work involves a kinetic study of the attack of substituted phenolate ions on (4-nitrophenoxy)-1,3,5-triazine to elucidate the possibility of intermediates or a single transition state; it also includes studies of the effect of leaving group structure for attack at (aryloxy)triazines to determine the full effective charge structure of this reaction.

Experimental Section

Materials. Water used throughout was degassed, double distilled from glass. KCl, acetonitrile, and buffers were of AR grade, and phenols were either obtained commercially or prepared by known procedures and purified by recrystallization, redistillation, or sublimation. Dioxane was purified by its passage through active alumina and the filtrate tested for peroxides by use of KI solution. 2-(Substituted phenoxy)-4,6-dimethoxy-1,3,5-triazines were prepared from the reaction between 2-chloro-4,6-dimethoxy-1,3,5-triazine and the appropriate phenol by the method of Harayama.[10]

2-Chloro-4,6-dimethoxy-1,3,5-triazine.[11] Cyanuric chloride (18.5 g, 0.1 mol) was added in portions to a mixture of sodium bicarbonate (16.8 g, 0.2 mol), methanol (45 g), and water (5 g) over 30 min. Carbon dioxide was liberated, and the temperature of the reaction mixture rose to 35 °C. After gas evolution had subsided the mixture was refluxed for 30 min and then allowed to cool to room temperature and diluted with water (100 mL) and the precipitate collected at the pump. The product was washed with water until the washings were free of chloride ion and dried over silica *in vacuo*. The product was recrystallized from heptane and kept over wax turnings before storage. Mp 75−77 °C (lit.[11] mp 74−7 °C). Anal. Calcd for $C_5H_6N_3Cl$ C, 34.20, H, 3.44, N, 23.93. Found: C, 33.81; H, 3.13; N, 24.06.

2-(Substituted phenoxy)-4,6-dimethoxy-1,3,5-triazines. A solution of sodium hydroxide (10% w/v in water, 1 equiv) was added dropwise with stirring to a solution of 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.75 g, 0.003 mol) and the appropriate phenol (1 equiv) in acetone (40 mL), and the resulting mixture was refluxed for 4 h. The reaction mixture was allowed to cool to room temperature, added to a stirred mixture of ice−water (100 mL), and allowed to stir for 30 min. The resulting precipitate was collected at the pump and washed with water. The product was dried over silica *in vacuo*, recrystallized from ethanol, and kept over phosphorus pentoxide *in vacuo* before storage. Small samples were submitted for elemental analysis, and analytical data are recorded in Table 1. The IR and NMR spectra are in agreement with the proposed structures.

Kinetic Methods. Rates of phenolysis were measured at 25 °C in a solvent mixture of composition 10% dioxane−water (v/v). The ionic strength was maintained at 0.25 M with KCl. A series of solutions were prepared which had the same pH, ionic strength, and solvent composition but varying concentrations of the substituted phenol. Stock solutions of phenol containing buffers were prepared by adding the substituted phenol, dioxane, buffer (where necessary, 0.05 M total concentration), KOH (1.0 M, stock solution), and water to produce solutions of the appropriate pH and 10% in dioxane. Stock solutions of the substrates were prepared in acetonitrile at a concentration of between 20 and 30 mg in 5 mL.

The kinetics of the reactions were monitored at a suitable wavelength corresponding to the absorption of the released phenolate, and reactions were initiated by adding an aliquot (0.02 mL) of the substrate solution to a silica cuvette containing sample solution (2.5 mL) contained within the thermostated cell compartment of a spectrophotometer (Unicam SP-800 or Perkin-Elmer Lambda 5 instrument). Each wavelength was determined in a separate trial experiment involving repetitive scanning of the spectrum. The method of initial rates was employed[2a] for the less basic phenolate nucleophiles where the reactions were too slow to be followed to completion. The rate constants obtained from initial rate studies are derived from the rate of change of absorbance at the wavelength in use divided by the total absorbance change expected for the complete release of the phenol under the conditions of the kinetic experiment.

Data were fit directly to theoretical equations to derive the associated parameters by grid-search programs written in BASIC and using a BBC Master-128 computer or an Opus VII desk top PC.

Product Analyses. Product analyses were carried out by HPLC assay of the reaction mixtures resulting from the attack of 4-formylphenolate and 2,4,5-trichlorophenolate ions upon (4-nitrophenoxy)-1,3,5-triazine under conditions similar to those for the kinetic runs. The following chromatographic conditions were employed to analyze products of the reaction of 4-formylphenolate ion with (4-nitrophenoxy)-1,3,5-triazine: column, Beckman Ultrasphere ODS, 5 μm, 4.6 mm × 25 cm; eluent, 60:40 methanol−water, v/v, pH 7.0; wavelength, 275 nm; flow rate, 1.0 mL/min. The conditions were modified to reduce the retention time in the case of the reaction of the 2,4,5-trichlorophenolate ion: eluent, 25:45:30 acetonitrile−methanol−water, v/v, pH 8.00; wavelength, 235 nm; flow rate, 1.25 mL/min. These conditions achieved a good resolution of the product peak from those of the substrate. Products were identified by peak coincidence of the eluted compounds with those of authentic samples of the phenoxytriazines.

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(8) (a) Renfrew, A. H. M.; Taylor, J. A.; Whitmore, J. M. J.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2389. (b) Chakrabarti, J. K.; Cockerill, A. F.; Davies, G. L. O.; Hotten, T. M.; Rackham, D. M.; Tupper, D. E. *J. Chem. Soc., Perkin Trans. 2* **1974**, 861. (c) Cockerill, A. F.; Davies, G. L. O.; Rackham, D. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 723.

(9) (a) Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040. (b) Stephanidis, D.; Cho, S.; Dhe-Paganon, S.; Jencks, W. P. *J. Am. Chem. Soc.* **1993**, *115*, 1650. (c) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1989**, *111*, 2649.

(10) Harayama, T.; Okado, K.; Sekiguchi, S.; Matsui, K. *J. Heterocycl. Chem.* **1970**, *7*, 981.

(11) Dudley, J. R.; Thurston, J. T.; Schaeffer, F. C.; Holm-Hansen, D.; Hull, C. J.; Adams, P. *J. Am. Chem. Soc.* **1951**, *73*, 2986.

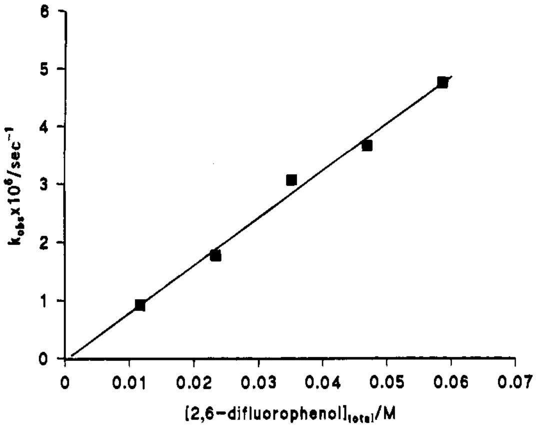

Figure 1. Reaction of 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine in buffers containing increasing amounts of 2,6-difluorophenol. Details of the conditions are given in Table 2; the line is from eq 1 with parameters from Table 2.

Product analysis was checked in each kinetic experiment by comparison of the total change in absorbance at the kinetic wavelength with that calculated from the known extinction coefficients and substrate concentration for the complete release of phenol. The extinction coefficients were determined under the conditions of the kinetic experiments in separate experiments.

Values of pK_a were determined by standard UV−pH−titration techniques under the conditions of 1 M ionic strength (made up with KCl) and 25 °C.

Results

The principal products of the reactions in phenol-containing buffers, determined by HPLC assay, were the substituted phenoxytriazines. Liberation of phenolate ion from the substrates in the presence of buffers containing aryl oxide nucleophiles obeyed excellent pseudo-first-order kinetics up to about 90% of their total reaction, and the rate constants were linearly dependent on the phenol concentration. Initial rates were determined for the slow reactions of phenolate ions with phenoxytriazines; they were linearly dependent on phenol concentration, and the rate law was assumed to be first-order in substrate and phenol concentrations.

The data from both methods were fit to eq 1. k_w = composite pseudo-first-order rate constant for hydrolysis of the substrate

$$k_{obs} = k_w + k'_2[\mathrm{ArOH}]_{total} \qquad (1)$$

at the recorded pH and was negligible compared with the value k'_2[ArOH] in all the phenolate experiments; $[\mathrm{ArOH}]_{total}$ = the total concentration of the phenol in the sample solution. An example of a plot of k_{obs} vs substituted phenol concentration is shown in Figure 1 for the reaction of 2,6-difluorophenolate ion with 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine.

The second-order rate constants, k_{ArO}, were obtained by dividing the slope of k_{obs} vs $[\mathrm{ArOH}]_{total}$ (k'_2) by FB, the fraction of the phenol present as the phenolate ion. The rate constants for 2,6-disubstituted phenols (except 2,6-difluoro) are much slower than expected on the basis of their pK_a values and set an upper limit to the incursion of base-catalyzed hydrolysis in k_{ArO}. Product analyses indicate that the triazine is all converted to the substituted phenoxytriazine products in the reaction mixtures analyzed. That tris(hydroxymethyl)aminomethane buffer does not act as a nucleophile is excluded by product analyses and because the second-order rate constant, k_{ArO}, is the same in the presence and absence of the buffer component in the case of phenolysis of the 2-(4-nitrophenoxy)triazine.

Table 2. Kinetic Data for the Reactions of Phenolate Ions with 2-(4-Nitrophenoxy-1,3,5-triazine[h]

X[a]	pK_a[b]	k_{ArO}[c]/ (10^{-4} M^{-1} s^{-1})	pH[d]	[XArOH][e]/ (10^2 M)	k_{obs}[f]/ (10^{-5} s^{-1})	N[g]
2,6-Me$_2$	10.63	27.10[i]	10.10	1.11−3.33	1.2−2.5	5
4-CH$_3$	10.09	310[j]	10.15	0.87−4.36	14.5−65.5	4
4-H	9.81	160[j]	9.90	1.56−7.94	12.4−64.2	5
4-Cl	9.26	126[j]	9.85	0.83−4.16	9.0−43.9	4
3-Cl	8.87	47.5[j]	9.25	0.84−4.21	2.9−13.1	5
2-Cl	8.32	8.68[j]	9.05	1.56−7.78	1.44−5.83	5
4-COMe	7.91	2.72[i]	8.52	0.81−4.03	0.23−0.90	5
4-CN	7.80	3.02[i]	8.60	0.81−4.05	0.24−1.05	5
4-CHO	7.66	0.97[i]	7.68	1.25−6.26	0.07−0.33	5
2,3-Cl$_2$	7.51	1.33[i]	7.81	0.54−2.69	0.04−0.22	5
2,6-F$_2$	7.12	0.93[i]	8.08	1.17−5.86	0.09−0.48	5
2,6-Cl$_2$	6.78	0.005[i]	8.45	1.41−4.70	0.04−0.05	4
2,4,5-Cl$_3$	6.98	0.56[i]	8.41	0.73−3.64	0.07−0.23	5
2,3,5-Cl$_3$	6.58	0.20[i]	8.25	0.42−2.16	0.01−0.05	4
2,3,4,5-Cl$_4$	5.64	0.022[i]	8.48	1.21−3.02	0.02−0.03	4
F$_5$	5.33	0.012[i]	8.37	1.34−6.68	0.003−0.009	4

[a] Substituent(s) in the nucleophilic phenolate ion. [b] Values of pK_a are from ref 9b except for those of 2,6-Me$_2$, 4-CHO, 2,6-Cl$_2$ and 2,3,4,5-Cl$_4$ phenolate ions which are measured under the conditions of ref 9b. [c] Error range not more than 10% of the quoted figure except for the reactions of 2,4,5-Cl$_3$, 2,3,4,5-Cl$_4$, and F$_5$ where the error is no greater than 20%. [d] Average pH for all the runs. The pH was maintained with each substituted phenolate acting as its own buffer except for the reactions of F$_5$, 2,3,4,5-Cl$_4$, and 2,3,5- and 2,4,5-Cl$_3$ ions where 0.05 M Tris was employed. [e] Concentration range of the phenol. [f] Range of the observed pseudo-first-order rate constants. [g] Number of data points not including duplicates. [h] General conditions: 25 °C, ionic strength 0.25 M, 10% dioxane/water (v/v)—except for the reactions of F$_5$ and 4-COMe where 15% dioxane was employed—wavelength for kinetic study 400 nm. [i] Rate constants determined by the method of initial rates. [j] Rate constants determined from kinetic studies of the full reaction.

Reaction of Phenolate Ions with 2-(4-Nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine. These results have, in part, been communicated,[12a] and the data were processed using pK_a values taken from a "best set" which was compiled from a number of sources; since then a set of pK_a values have become available which were determined under constant conditions. Using these values Stefanadis and co-workers[9b] have shown that 2-halo-substituted phenolates are subject to slight steric hindrance in their reactions with phenyl acetates, and may interact differently from other phenolates in their reactions with phenyl formates. This suggests that it may be necessary to use a set of pK_a values which are determined under standard conditions, especially when 2-halo-substituted phenols are included in a Brønsted correlation.

We decided to use a set of pK_a values determined at 25 °C and 1 M ionic strength in water as a basis for processing our kinetic data. The pK_a of 4-nitrophenol determined in 10% dioxane-water at 25 °C with ionic strength 0.25 M is 7.22, and in water at 1 M ionic strength it is 7.15; it is assumed that the pK_a values under our kinetic conditions will be very close to those for the standard conditions.

The second-order rate constants for the reactions of phenolate ions with the 2-(4-nitrophenoxy)triazine (with the exception of the 2,6-dimethyl- and 2,6-dichlorophenolates) are shown in Table 2; they are force fit to a theoretical Brönsted-type equation[12b]

$$k_{ArO} = k_H \times 10^{\beta_1 \Delta pK_a}/(1 + 10^{\Delta\beta\Delta pK_a}) \qquad (2)$$

for a stepwise mechanism to yield parameters $\beta_1 = 0.950 \pm 0.047$, $\Delta\beta = -0.016 \pm 0.097$, and $\log k_H = -3.88 \pm 0.07$ with $r = 0.9934$. $\Delta pK_a = pK_a(\mathrm{ArOH}) - pK_{lg}$. The value of $\Delta\beta$ is indistinguishable from zero because of the absence of

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(12) (a) Renfrew, A. H. M.; Taylor, J. A.; Whitmore, J. M. J.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1993**, 1703. (b) A derivation of this equation is given in ref 11d of Bourne, N.; Chrystiuk, E.; Davis, A. M.; Williams, A. *J. Am. Chem. Soc.* **1988**, *110*, 1890.

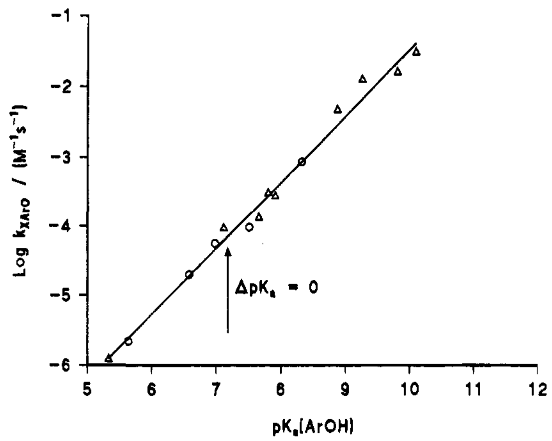

Figure 2. Brønsted plot for reaction of 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine with substituted phenolate ions. The open circles represent phenolate ions possessing 2-chloro substituents. The data are from Table 2, and the line is calculated from eq 3.

detectable curvature in the correlation Figure 2 and because $\Delta\beta$ is less than its uncertainty. The data best fit a linear Brønsted-type equation (3) which is analogous to eq 2 where $\Delta\beta$ is zero.

$$\log k_{\mathrm{Aro}} = (0.951 \pm 0.030)\mathrm{p}K_a - 10.98 \pm 0.23 \qquad (n = 14, r = 0.9942) \quad (3)$$

The fit of the experimental data to eq 3 is shown in Figure 2. The 2-halo-substituted phenolate ions do not show any significant deviations from the fit to either eq 2 or eq 3. In Figure 2 the two groups of phenolates are shown with different labels and appear to follow the same correlation: there is no evidence of steric hindrance or a break point at the pK_a of 4-nitrophenol for the 2-halophenolates studied.

Effect of a Change in Structure of the Leaving Phenolate Ion. Kinetics of the reactions of phenolate ions and substituted phenoxytriazines were measured and the data recorded in Table 3. The derived values of k_{ArO} fit linear Brønsted-type equations recorded in Table 4.

The values of β_{lg} for phenolate ion nucleophiles may be used to estimate the value of β_{lg} for the reaction of 4-nitrophenolate with substituted phenoxytriazines (for which kinetics would be difficult to measure). The parameters β_{lg} and β_{nuc} (Table 4) are globally fit to the general eqs 4 and 5.[13a] The resultant

$$\beta_{\mathrm{lg}} = p_{xy}(\mathrm{p}K_{\mathrm{nuc}}) + C_1 \qquad (4)$$

$$\beta_{\mathrm{nuc}} = p_{xy}(\mathrm{p}K_{\mathrm{lg}}) + C_2 \qquad (5)$$

parameters ($p_{xy} = 0.0561 \pm 0.001$; $C_1 = 0.976 \pm 0.12$; $C_2 = 0.439 \pm 0.098$) fit the data to the equations with a correlation coefficient of $r = 0.9979$.

The data for either β_{lg} or β_{nuc} may be fit *separately* to eq 4 or 5, respectively (Figure 3), and the separate equation for β_{lg} may be used to estimate β_{lg} for the reaction where 4-nitrophenolate ion is the nucleophile (-0.577 ± 0.11); since this is similar to the β_{lg} value for 4-cyanophenol (with pK_a close to that of 4-nitrophenol), we can be reasonably confident that it is fairly accurate. Hence, the value for β_{eq} may be estimated from eq 6 to be 1.53 ± 0.11.

$$\beta_{\mathrm{eq}} = \beta_{\mathrm{nuc}} - \beta_{\mathrm{lg}} = 0.951 \pm 0.03 - (-0.577 \pm 0.11) = 1.53 \pm 0.08 \quad (6)$$

Subtracting eq 4 from eq 5 should also give a value of β_{eq} (1.42 ± 0.022) which is close to the value from eq 6. The average of the two figures, 1.48, is taken as the value of β_{eq} for this reaction and differs slightly from that quoted previously[12a] because of the improved pK_a values employed in this paper.

Identity Rate Constants. The rate constants (k_{ii}) for the identity reaction where the displaced ligand is the same as the entering one may be calculated from the Brønsted relationships in Table 4. The values of k_{ii} are illustrated in Figure 4 as a function of pK_{ii}, the pK_a of the entering and leaving phenoxide ions. Equations 4 and 5 may be combined[9c] to give eq 7a which integrates to give eq 7b.

$$\beta_{ii} = 0.112\mathrm{p}K_{ii} - 0.537 \qquad (7a)$$

$$\log k_{ii} = 0.0561(\mathrm{p}K_{ii})^2 - 0.537\mathrm{p}K_{ii} + C \qquad (7b)$$

$$\log k_{ii} = p_{xy}(\mathrm{p}K_{ii})^2 + B(\mathrm{p}K_{ii}) + C \qquad (7c)$$

Fitting the data of Table 4 to eq 7b gives $C = -2.95 \pm 0.052$ ($r = 0.8881$). The data may also be fit, without using predicted values of p_{xy} and B (eq 7a), to the eq 7c; a much poorer fit is obtained, but p_{xy} and B (0.072 ± 0.03 and -0.79 ± 0.49, respectively) come reasonably close to the values in eq 7b, and the agreement is illustrated in Figure 4. The identity rate constants calculated from both types of correlations (variation of the entering ligand and variation of the leaving group) are in good agreement (Figure 4) with the common calculated line. Most of the calculations of k_{ii} do not require large extrapolations, and even when they do the agreement is quite good on a logarithmic scale.

Alkaline Fission of the Substituted Phenoxytriazines. Most of the pH values employed in the reactions with phenolate ions were such that negligible background hydrolysis occurs due to hydroxide ion or added buffer; in these pH regions full release of the phenol is observed. Reactions at relatively high pH did not result in the full release of the leaving phenol group as judged from the spectral analysis of the products. This is considered to be due to incursion of hydroxide ion attack at the methyl group of the methoxy substituent in the triazine (Scheme 2). The overall second-order rate constant for reaction of hydroxide ion with the triazine may be dissected into components according to eq 8 by use of the ratio of the observed

$$k_{\mathrm{OH}}(\mathrm{overall}) = k_{\mathrm{OH}}(\mathrm{OMe}) + k_{\mathrm{OH}} \qquad (8)$$

phenolate product yield to the theoretical yield. Values of k_{OH}(OMe) and k_{OH} are recorded in Table 5, and the parameters obey Hammett eqs 9 and 10.

$$\log k_{\mathrm{OH}}(\mathrm{OMe}) = (0.74 \pm 0.08)\sigma - 2.13 \pm 0.09 \qquad (r = 0.9762) \quad (9)$$

$$\log k_{\mathrm{OH}} = (0.61 \pm 0.11)\sigma - 2.06 \pm 0.12 \; (r = 0.9445) \quad (10)$$

Discussion

Reaction of Substituted Phenolate Ions with the 2-(4-Nitrophenoxy)triazine. The kinetics of reaction of 2-(4-nitrophenoxy)-4,6-dimethoxy-1,3,5-triazine in phenolate ion buffers are reasonably interpreted as displacement of the 4-nitrophenolate ion. Evidence consistent with this stoichiometry includes product analysis results and the observation that

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(13) (a) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. (b) Microscopic medium effects in Brønsted plots have been discussed in ref 9a and in Bruice, T. C.; Benkovic, S. T., *Bio-organic Mechanisms*; Benjamin: New York, 1966; Part 1, p 153.

Table 3. Data for the Attack of Phenolate Ions upon Substituted Phenoxytriazines[a]

Phenolate Ion, $\mathrm{p}K_a = 9.81$

X^d	$\mathrm{p}K_a{}^e$	$k_{\mathrm{ArO}}{}^f/(10^{-2}\ \mathrm{M^{-1}\ s^{-1}})$	pH^g	$[\mathrm{ArOH}]^h/(10^{-2}\ \mathrm{M})$	$k_{\mathrm{obs}}{}^j/(10^{-3}\ \mathrm{s^{-1}})$	N^i	$\lambda_{\max}{}^k/\mathrm{nm}$
3,4-$(NO_2)_2$	5.28	7.93	9.93	1.59−7.94	0.81−3.39	5	400
3,5-$(NO_2)_2$	6.68	6.34	9.88	1.70−8.52	0.64−2.74	5	400
2Cl-4NO_2	5.45	1.07	9.93	1.62−8.08	0.1−0.45	5	400
3-Cl-4-NO_2	6.80	2.58	9.75	1.61−8.05	0.2−0.9	5	400
4-NO_2	7.15	1.60	9.90	1.56−7.94	0.12−0.64	5	400
4-CHO	7.66	0.57	9.86	1.72−8.58	0.07−0.25	5	365
4-Cl-3-NO_2	7.75	1.30	9.75	1.74−8.70	0.16−0.48	5	400
3-NO_2	8.19	0.64	10.30	2.66−13.32	0.05−0.24	5	400
3-CHO	8.99	0.25	9.93	1.62−8.08	0.01−0.54	5	360

3-Chlorophenolate Ion, $\mathrm{p}K_a = 8.87$

X	$\mathrm{p}K_a$	$k_{\mathrm{ArO}}/(10^{-3}\ \mathrm{M^{-1}\ s^{-1}})$	pH	$[\mathrm{ArOH}]/(10^{-2}\ \mathrm{M})$	$k_{\mathrm{obs}}/(10^{-4}\ \mathrm{s^{-1}})$	N	$\lambda_{\max}/\mathrm{nm}$
3,4-$(NO_2)_2$	5.28	42.8	9.43	1.27−6.32	4.44−20.6	5	400
3-Cl-4-NO_2	6.80	9.53	9.37	1.52−7.62	1.3−5.4	5	400
4-NO_2	7.15	4.75	9.25	0.84−4.21	0.3−1.3	5	400
4-Cl-3-NO_2	7.75	4.97	9.52	1.51−7.53	0.7−3.0	5	400
3-NO_2	8.19	$1.68^{b,c}$	9.38	1.54−3.09	0.15−0.46	4	400
3-CHO	8.99	$0.43^{b,c}$	9.45	1.62−8.10	0.09−0.30	5	360

2-Chlorophenolate Ion, $\mathrm{p}K_a = 8.32$

X	$\mathrm{p}K_a$	$k_{\mathrm{ArO}}/(10^{-4}\ \mathrm{M^{-1}\ s^{-1}})$	pH	$[\mathrm{ArOH}]/(10^{-2}\ \mathrm{M})$	$k_{\mathrm{obs}}/(10^{-5}\ \mathrm{s^{-1}})$	N	$\lambda_{\max}/\mathrm{nm}$
3,4-$(NO_2)_2$	5.28	100.5	9.00	1.6−8.0	16.4−69.2	5	400
3-Cl-4-NO_2	6.80	26.6	9.08	1.8−9.0	4.6−20.4	5	400
4-NO_2	7.15	8.68	9.05	1.56−7.78	1.44−5.83	5	400
4-Cl-3-NO_2	7.75	7.76	8.97	3.98−9.94	2.55−6.17	4	400
3-NO_2	8.19	$3.55^{b,c}$	9.42	1.88−9.38	0.62−2.98	5	400
3-CHO	8.99	$1.13^{b,c}$	9.48	2.2−11.0	0.25−1.20	4	360

4-Cyanophenolate Ion, $\mathrm{p}K_a = 7.80$

X	$\mathrm{p}K_a$	$k_{\mathrm{ArO}}/(10^{-4}\ \mathrm{M^{-1}\ s^{-1}})$	pH	$[\mathrm{ArOH}]/(10^{-2}\ \mathrm{M})$	$k_{\mathrm{obs}}/(10^{-5}\ \mathrm{s^{-1}})$	N	$\lambda_{\max}/\mathrm{nm}$
3,4-$(NO_2)_2$	5.28	30.5	8.55	0.9−4.51	2.6−11.1	5	400
3,5-$(NO_2)_2$	6.68	14.0^{c}	8.43	0.63−3.16	0.81−3.49	5	400
3-Cl-4-NO_2	6.80	7.18^{c}	8.46	0.91−4.56	6.1−26.1	4	400
4-NO_2	7.15	3.02	8.60	0.81−4.05	0.24−1.05	5	400
4-CHO	7.66	1.23	8.71	0.87−4.36	0.13−0.49	5	365
4-Cl-3-NO_2	7.75	2.78	8.70	1.46−7.31	0.42−1.75	5	400
3-NO_2	8.19	$0.97^{b,c}$	10.29	2.02−10.1	0.49−1.29	4	400
3-CHO	8.99	$0.33^{b,c}$	9.98	2.35−11.77	0.30−0.60	5	360

[a] Conditions as in footnote *h* of Table 2. [b] Carbonate buffer (0.05 M) employed. [c] Rate constants determined by the method of initial rates. [d] Substituents on the leaving phenol. [e] See footnote *b* in Table 2. [f] Error range is not more than ±10% of the quoted figure. [g] The pH is maintained with the substituted phenolate nucleophile acting as its own buffer except where stated. [h] Range of total phenol concentrations. [i] Number of data points not including duplicates. [j] Range of observed pseudo-first-order rate constants. [k] Wavelength of the kinetic study.

Table 4. Brønsted Dependencies for the Reaction of Substituted Phenoxide Ion with 2-(Substituted phenoxy)-4,6-dimethoxy-1,3,5-triazines[a]

nucleophile	leaving group	$\mathrm{p}K_{ii}{}^f$	β_{nuc} or $\beta_{\mathrm{lg}}{}^b$	intercept^b	r	N^c	τ^d	$\log k_{ii}{}^e$
4-$CNC_6H_4O^-$	ArO^-	7.80	-0.534 ± 0.04	0.41 ± 0.30	0.9887	6	1.28	-3.76 ± 0.03
2-$ClC_6H_4O^-$	ArO^-	8.32	-0.537 ± 0.04	0.96 ± 0.30	0.9887	6	1.27	-3.51 ± 0.03
3-$ClC_6H_4O^-$	ArO^-	8.87	-0.527 ± 0.06	1.54 ± 0.42	0.9778	6	1.29	-3.13 ± 0.11
4-$CH(O)C_6H_4O^-$	ArO^-	7.66	-0.503 ± 0.1	-0.21 ± 0.65	0.9709	4	1.32	-4.06 ± 0.12
$C_6H_5O^-$	ArO^-	9.81	-0.405 ± 0.03	1.13 ± 0.23	0.9890	6	1.45	-2.84 ± 0.06
ArO^-	4-$NO_2C_6H_4O^{-\,h}$	7.15	0.951	−10.98			1.29	-4.21 ± 0.02
ArO^-	4-Cl-3-$NO_2C_6H_4O^-$	7.75	0.860 ± 0.15	-10.16 ± 1.28	0.9719	5	1.16	-3.50 ± 0.12
ArO^-	3-$NO_2C_6H_4O^-$	8.19	0.910 ± 0.10	-11.02 ± 0.91	0.9870	4	1.23	-3.57 ± 0.09
ArO^-	3-$CH(O)C_6H_4O^-$	8.99	0.936 ± 0.04	-11.74 ± 0.39	0.9977	4	1.26	-3.33 ± 0.03
ArO^-	3,4-$(NO_2)_2C_6H_3O^-$	5.28	0.708 ± 0.15	-7.90 ± 1.34	0.9563	5	0.957	-4.16 ± 0.45
ArO^-	3-Cl-4-$NO_2C_6H_3O^-$	6.80	0.768 ± 0.12	-9.01 ± 1.03	0.9773	5	1.04	-3.79 ± 0.21
ArO^-	3,5-$(NO_2)_2C_6H_3O^-$	6.68	0.82^g	-9.28^g		2	1.11	-3.80^g
ArO^-	4-$CH(O)C_6H_4O^-$	7.66	0.83^g	-10.38^g		2	1.12	-4.02^g

[a] Conditions as in footnote *h* of Table 2. [b] From $\log k_{\mathrm{ArO}} = \beta(\mathrm{p}K_a) +$ intercept. [c] Number of data points. [d] Value of τ obtained from α_{nuc} or α_{lg} as explained in the text and in ref 17a. [e] Value of $k_{ii}/(\mathrm{M^{-1}\ s^{-1}})$ calculated from the Brønsted equation (see footnote *b* using $\mathrm{p}K_{ii}$). [f] Value of the $\mathrm{p}K_a$ of the ligand in the identity reaction (see footnote *b* in Table 2). [g] Since there are only two data points for this relationship, no tolerances can be given. [h] Parameters from eq 3.

the highly hindered di-ortho-substituted phenolate ions (2,6-dichloro and 2,6-dimethyl) have markedly low rate constants compared with those of the regular phenolate ions. The attack of the substituted phenolate ions follows a good linear Brønsted relationship over a wide $\mathrm{p}K_a$ range (Figure 2).

A two-step mechanism with two transition states predicts a break in the Brønsted plot at the $\mathrm{p}K_a$ of 4-nitrophenol (7.15). Linearity over a range of $\mathrm{p}K_a$ values above and below the predicted break point is *prima-facie* evidence for a mechanism with only one transition state and thus for a concerted process.[7,8]

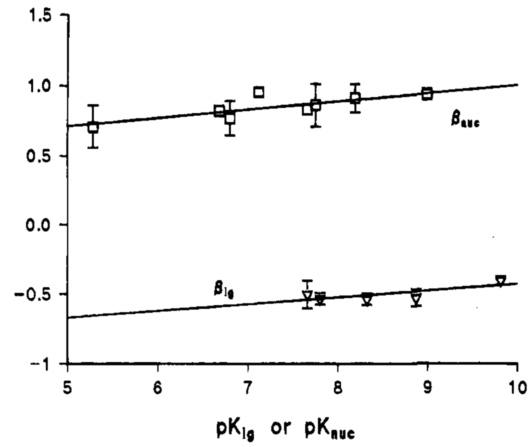


Figure 3. Dependence of β_{nuc} and β_{lg} on pK_{lg} and pK_{nuc}, respectively. The data are from Table 4, and the lines are calculated from eqs 4 and 5.

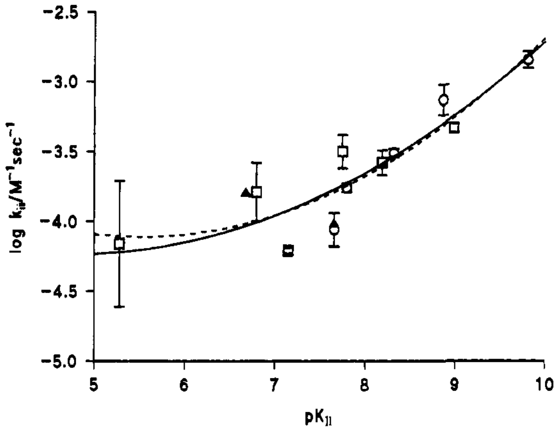
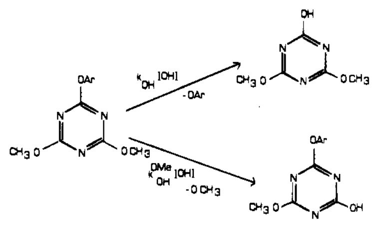


Figure 4. Dependence of the rate constants for the identity reactions (k_{ii}) on the pK_a of the ligand phenol (pK_{ii}). The data are from Table 4, and the solid line is calculated from eq 7b with $C = -2.95$. The dashed line is the best fit to eq 7c. The triangles are log k_{ii} values calculated from "two-point" Brønsted plots, open squares are from the β_{nuc} equations of Table 4, and open circles are from the β_{lg} equations from Table 4.

Scheme 2. Reaction of Alkali with Substituted Phenoxytriazines

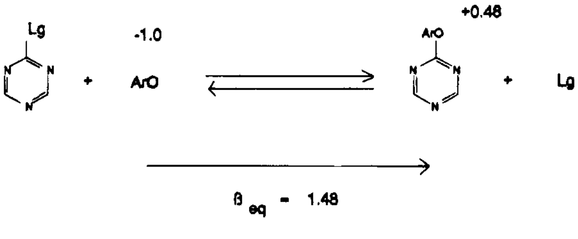


The slight scatter in Figure 2 is attributed to a microscopic medium effect due to substituent specific variation in solvent organization in the ionization standard compared with that in the preassociative complex required for the displacement reaction prior to the chemical reaction.[13b]

It is possible to estimate the value of β_{nuc} in the region of pK_a where the second step of a putative two-step process is rate limiting (i.e., below pK_a 7.15). The value of k_{ArO} under these conditions is k_1k_2/k_{-1}, and β'_{eq} for formation of the Meisenheimer adduct (Scheme 3) must be less than β_{nuc} (in this case <0.95). The overall β_{eq} for formation of product is 1.48 so that the β''_{eq} for formation of product from the Meisenheimer adduct will be greater than 1.48−0.95 (>0.53, Scheme 3). It is inconceivable for the putative, two-step mechanism that the change in effective charge for bond fission seen by the nucleophile is similar to that for bond formation. The analogous displacement of pyridines from triazinylpyridinium ions involves a two-step process,[14a] and there is a substantial difference between the changes in effective charge on the two steps seen by the nucleophile ($\beta'_{eq} = 1.14$ and $\beta''_{eq} = 0.1$ for attack of substituted pyridines with pyridine as the leaving group).[14a] The inequalities detailed for the phenoxy system indicate that the difference between β'_{eq} and β''_{eq} is less than 0.42. The two β values sum to 1.48 (Scheme 3); thus, β''_{eq} is large for a step where no substantial bonding change is expected. Such data are not consistent with the stepwise process.

The value of $\Delta\beta$ measures the difference in effective charge between the transition states in the putative two-step process (see Scheme 3). In the present case the difference can be no greater than 0.1 unit (see parameter tolerances for eq 2); this is 7% of the total possible change of 1.48 units. If the intermediate had any existence, it would have to support a change in effective charge on the attacking oxygen from the intermediate to one of the transition states (forward or reverse) which must be less than *half* of 7% of the total change in effective charge in the overall reaction.[2a,9a,14b-d]

Effect of Substituents on β_{nuc} and β_{lg}. The effects of varying the leaving group and nucleophile structure on β_{nuc} and β_{lg}, respectively, are recorded in Table 4 and in eqs 4 and 5. These dependencies may be employed to determine the value of the overall β_{eq} as described in the Results. The various Brønsted plots are linear, and although they mostly do not have ranges significantly spanning a break point pK_a, the results for the 4-nitrophenolate ion leaving group indicate that even if there were a two-step mechanism any change in the rate-limiting step would not significantly alter the slopes. Thus, we can estimate a value of β_{eq} which is not dependent on any assumptions of mechanism. The value of β_{eq} reflects the sensitivity to the polar substituent of the equilibrium for transfer of the triazinyl group between a constant ligand and substituted phenolate ions; the equilibrium is more sensitive than the standard ionization, and this reflects a greater change in effective charge on the aryl oxygen compared with the transfer of the hydrogen group in the standard equilibrium. The effective charge on the oxygen of the aryl ether is +0.48, indicating that the triazinyl function is less electropositive than acetyl ($CH_3C(O)OAr$ has an effective charge of +0.7).[15]



(11)

The variation of β_{nuc} and β_{lg} as a function of pK_{lg} and pK_{nuc}, respectively, is good evidence for a change in structure of the transition state as a result of a change in the entering or departing ligand. It is necessary to rationalize why such a change in electronic structure is not reflected by the observation of a nonlinear Brønsted equation. Brønsted relationships, nonlinear due to changing transition state structure, are rare, and linearity may be explained in general and in our case by a compensation effect whereby the structural change of the transition state in

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(14) (a) Renfrew, A. H. M.; Taylor, J. A.; Whitmore, J. M. J.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 2383. (b) Dietze, P. E.; Jencks, W. P. *J. Am. Chem. Soc.* **1986**, *108*, 4549. (c) Skoog, M.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 5797. (d) Bourne, N.; Chrystiuk, E. C.; Davis, A. M.; Williams, A. *J. Am. Chem. Soc.* **1988**, *110*, 1890.

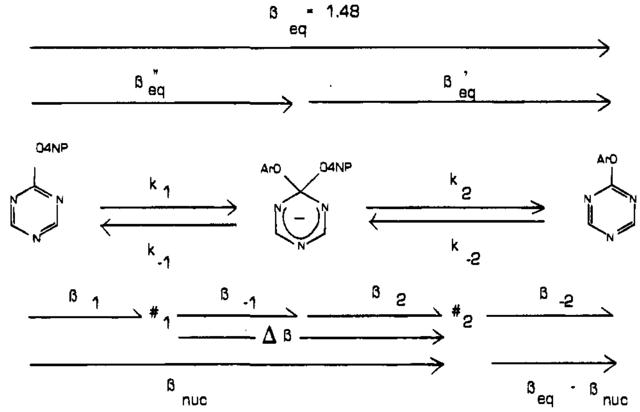
(15) Williams, A. *Adv. Phys. Org. Chem.* **1992**, *17*, 1.

Table 5. Reaction of Hydroxide Ion[h] with 2-(Substituted phenoxy)-4,6-dimethoxy-1,3,5-triazines[a]

substituent	λ_{max}[b]/nm	k_{OH}[c]/(10^{-2} M^{-1} s^{-1})	k_{OH}^{OMe}[d]/(10^{-2} M^{-1} s^{-1})	k_{obs}[e]/(10^{-3} s^{-1})	A_∞(obs)[g]	A_∞(calc)[f,g]
4-CHO	330	1.80 ± 0.14	1.52 ± 0.21	0.2−1.4	0.32	0.617
4-NO_2	400	2.6 ± 0.1	3.5 ± 0.1	0.3−2.5	0.425	1.04
4-Cl-3-NO_2	400	2.8 ± 0.03	2.6 ± 0.2	0.4−1.9	0.065	0.123
4-NO_2-3-Cl	400	5.7 ± 0.03	3.9 ± 0.2	0.6−3.8	0.71	1.29
3,5-$(NO_2)_2$	400	7.6 ± 0.7	7.6 ± 0.6	0.7−6.0	0.103	0.239
3,4-$(NO_2)_2$	400	10.5 ± 0.4	6.6 ± 0.3	0.9−6.6	0.285	0.449

[a] Conditions as in Table 2, footnote *h*. [b] Wavelength for kinetic study. [c] Term for attack of hydroxide ion at the 2 position. [d] Term for attack of hydroxide ion at the methyl group of the methoxy function. [e] Range of observed overall rate constants. [f] The value of the change in absorbance calculated from extinction coefficents and the concentration of triazinyl species. [g] Value of k_2 obtained by multiplying the overall second-order rate constant by A_∞(obs)/A_∞(calc). [h] The hydroxide ion concentration range throughout this section was from 0.006 to 0.04 M.

Scheme 3. Effective Charge Map for the Putative Stepwise Process for Phenoxide Ion Attack on 4-Nitrophenoxytriazines[a]



[a] Substituents on the triazine ring are omitted.

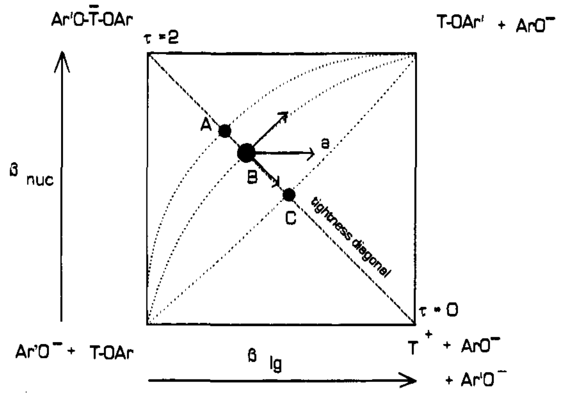
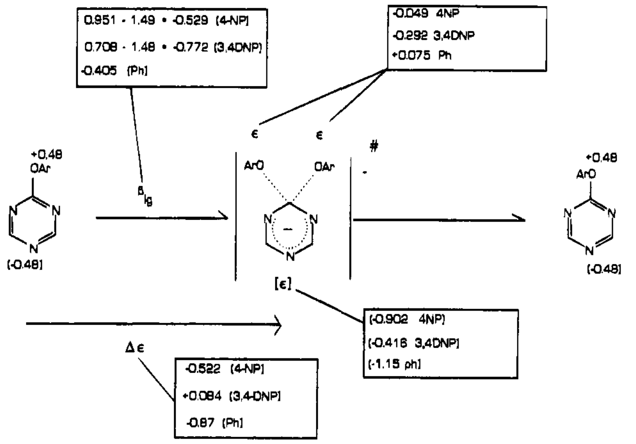


Figure 5. More O'Ferrall–Jencks diagram for the displacement of phenolate ions from 2-(aryloxy)triazines (T-OAr). Points A, B, and C are the transition state structures for the identity ligands phenoxy, 4-nitrophenoxy, and 3,4-dinitrophenoxy, respectively. Line a is the locus of movement of the transition state structure as the phenolate nucleophile becomes a weaker base (see text).

Scheme 4. Effective Charge Maps for the Identity Displacement of Aryl Oxide Ions[a]



[a] (4NP = 4-nitrophenoxy; 3,4DNP = 3,4-dinitrophenoxy; Ph = phenoxy. Substituents on the triazine ring are omitted. Values in boxes refer to the effective charges computed for the various phenoxy ligands.

the More O'Ferrall–Jencks diagram (Figure 5)[16] is along a line of either constant β_{nuc} (for a change in pK_{lg}) or constant β_{lg} (for a change in pK_{nuc}). As the pK_a of the phenolate ion is decreased, both southeast and southwest corners of the diagram become more stable. This change moves the structure of the transition state toward the southeast corner (perpendicular to the reaction coordinate) and toward the northeast corner (along the reaction coordinate) by Thornton and Hammond effects, respectively. The constant slope of the Brønsted plot would result from the movement of the transition state structure along an east–west axis due to a cancellation of the north and south motions (see Figure 5).

The effective charge map for displacement of the 4-nitrophenolate ion is described in Scheme 4. The transition state structure will lie on the tightness diagonal[17] of Figure 5 for a concerted identity reaction (in this case when the entering and departing ligand is 4-nitrophenoxy). Moreover, the effective charge on entering and leaving ligands will be identical in the transition state (Scheme 4). Since it is reasonable to assume conservation of effective charge, the value of +0.48 on the ether oxygen will be balanced by an effective charge of −0.48 spread over the triazine nucleus in the reactant or product.

The effective charge maps for the identity displacements of 3,4-dinitrophenolate and phenolate ions may be obtained from the β_{nuc} and β_{lg} from Table 4 (+0.708 and −0.405, respectively) and are shown in Scheme 4.

Bonding of Ligands in the Transition State. The data of Table 4 for the various Brønsted slopes yield identity rate constants (k_{ii}) which may be plotted against the pK_a of the identity ligand (Figure 4). Scatter in this plot is due to the combination of uncertainties in estimating k_{ii}, but the data may be reasonably fitted to a theoretical equation (7b) because there they have only one disposable parameter (*C*). The value of the slope of the line, β_{ii}, is predicted to vary with a change in pK_{ii} from negative through zero to positive and is a measure of the

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(16) Jencks, W. P. *Accs. Chem. Res.* **1980**, *13*, 161.

(17) (a) The parameter τ is the sum of the bond orders η of the forming and breaking bonds in the transition state.[17b] The parameters are defined as follows: $r_a = a/a_{product}$, $\eta_a = (r_{a(RC)} - r_a)/(r_{a(RC)} - 1)$, and $\tau = \eta_a + \eta_b$, where *a* is the bond length of the forming bond at any point on the reaction coordinate, $a_{product}$ is the bond length in the product, and $r_{a(RC)}$ is the value of r_a in the reaction complex. Corresponding definitions apply to the breaking bond (b). The Leffler α parameters are defined as $\alpha_{lg} = -\beta_{lg}/\beta_{eq}$ and $\alpha_{nuc} = \beta_{nuc}/\beta_{eq}$. The parameter τ may be defined alternatively as $\tau = 2\alpha_{nuc}$ or $\tau = 2(1 - \alpha_{lg})$[17c,d] and measures points along the "tightness" diagonal[17d] or "disparity mode".[17e] (b) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (c) Ba-Saif, S. A.; Colthurst, M.; Waring, M. A.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1901. (d) Kreevoy, M. M.; Lee, I. S. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550. (e) Grunwald, E. *J. Am. Chem. Soc.* **1985**, *107*, 125.

"tightness" (τ)[17] of the transition state. The limiting values of β_{ii} would be $+\beta_{eq}$ and $-\beta_{eq}$ corresponding to τ values of 2 and 0, respectively (eqs 12 and 13[18]).

$$\tau = \beta_{ii}/\beta_{eq} + 1 \qquad (12)$$

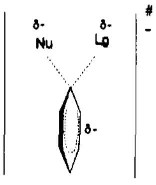
$$\beta_{ii} = \mathrm{d} \log k_{ii}/\mathrm{dp}K_{ii} = (\beta_{nuc} + \beta_{lg}) \qquad (13)$$

The value τ is defined to increase linearly from 0 to 2 along the tightness diagonal (Figure 5).[17d] We may calculate from eq 7b that a reaction with $\tau = 1$ (or $\beta_{ii} = 0$) occurs for an identity ligand with a pK_{ii} at the minimum of the line in Figure 4 (pK_{ii} = 4.79). Likewise, mechanisms involving anionic and cationic intermediates should ensue when τ = 2 and 0, respectively (pK_{ii} = 18.00 and −8.42).

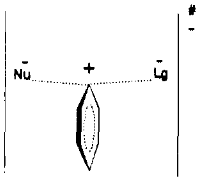
The identity ligand, 3,4-dinitrophenolate ion, has an α_{lg}[17a] of 0.478, indicating a τ value of 1.04. Since the bond orders[17a] of entering and leaving ligands must be identical, in a concerted identity reaction $\eta_a = \eta_b \approx 0.5$ and there is no imbalance of effective charge.[19] Imbalance occurs for all the other identity reactions; for example, the phenolate ion ligand has a τ value of 1.53; thus, $\eta_a = \eta_b = 0.726$ and the "excess" negative effective charge is fed to the hetero ring to maintain neutrality. The changes in effective charge are illustrated in Scheme 4 for the identity reactions with the phenoxy, 4-nitrophenoxy, and 3,4-dinitrophenoxy ligands.

Reaction of Hydroxide Ion with 2-(Aryloxy)-4,6-dimethoxy-1,3,5-triazines. Attack of hydroxide ion on the (aryloxy)-triazines involves displacement of the aryloxy group as well as attack at the methyl function. The similarity of the Hammett ϱ values for both reactions is consistent with similar changes in effective charge (about −0.3 unit) at the aryl oxygen atom from reactants to each transition state. In the case of aryloxy group displacement it is likely that the ArO−triazine bond is not substantially broken in the transition state of the rate-limiting step because the high basicity of the hydroxide ion would skew the More O'Ferrall−Jencks diagram, forcing the mechanism to go through a Meisenheimer adduct (northwest corner of Figure 5). The very small charge change is similar to that experienced by the aryl oxygen in the transition state for substitution at the methyl function.

Speculation Concerning the Transition State Structure of the Concerted Mechanism. Various bonding pathways have been discussed by Bunnett and Zahler[4] for nucleophilic aromatic substitution, and any in-line geometry for a concerted displacement was excluded. Similar considerations were applied recently by Bunnett to putative concerted mechanisms of an analogous reaction, namely, nucleophilic displacement at an aromatic radical anion.[20] It is likely that the geometry of the transition state resembles that of a Meisenheimer complex except that the forming and breaking bonds will be longer than in an adduct. Geometry **1** will only be permitted if the benzenoid resonance is not maintained. Such a geometry would vary for transition state structures along the tightness diagonal of Figure 5; it would be Meisenheimer adduct-like when τ is 2 ($\beta_{ii} = +\beta_{eq}$) (see eqs 12 and 13). When τ tends toward zero ($\beta_{ii} = -\beta_{eq}$) the geometry would become more like **2** (almost "in-line") because the ligand bonding to the essentially aromatic carbocation would have overriding electrostatic character; at the very southeast corner of the diagram (Figure 5) the structure involves free ligands and free aromatic carbocation (within the reaction complex).



(1)



(2)

The observation of a concerted process in the phenolysis reactions is because the northwest and southeast extremes of the More O'Ferrall−Jencks diagram are of sufficiently high energy to favor the concerted path. The stabilities of the ligands are relatively important as highly basic species could raise the energies of the south corners and the northeast corner of the diagram, pushing the structure of the transition state toward the northwest, thus encouraging Meisenheimer adduct formation.

The structural conditions likely to give rise to a concerted pathway include weakly basic ligands because these will skew the diagram away from a relatively stable northeast corner. Similar considerations have been applied to other nucleophilic displacement reactions including those at the almost directly analogous carbonyl centers. We note here that changing the ligands to pyridinyl functions in the triazine case causes the system to take a stepwise path.[14a]

It is pertinent to mention concerted mechanisms for nucleophilic displacement reactions at vinyl centers. Such reactions are of current interest,[3,21] and the present studies might provide information for designing a vinyl system where a concerted process could be demonstrated using the Brønsted "methodology" of this paper.

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(18) Lewis, E. S.; Hu, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 3292.

(19) Bernasconi, C. F. *Accs. Chem. Res.* **1987**, *20*, 301; **1992**, *25*, 9.

(20) Bunnett, J. F. *Tetrahedron* **1993**, *49*, 4477.

(21) (a) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7; **1992**, *25*, 474. (b) Galli, C.; Gentili, P.; Rappoport, Z. *J. Org. Chem.* **1994**, *59*, 6786. (c) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1993**, *115*, 4527. (d) Bernasconi, C. F.; Fassberg, J.; Killion, R. B.; Schuck, D. F.; Rappoport, Z. *J. Am. Chem. Soc.* **1991**, *113*, 4937. (e) Bernasconi, C. F.; Fassberg, J.; Killion, R. B.; Rappoport, Z. *J. Org. Chem.* **1990**, *55*, 4568. *J. Am. Chem. Soc.* **1989**, *111*, 6862; *J. Org. Chem.* **1993**, *49*, 44.