atmospheric humidity. The analytical concentrations of **1** and Br_2 in these solutions are reported in Table II, which also includes the calculated equilibrium concentrations of all present species. The UV spectra were immediately measured at 25 ± 0.05 °C in 0.1-, 1-, or 4-cm cells, as required, in a Pye-Unicam SP8-400 UV-vis spectrophotometer in the 250-600-nm range. Occasional checks showed that identical spectra were obtained in several consecutive recordings. A complete list of the absorbances of the solutions used in the fittings is supplied as supplementary material.

Computations were carried out with a FORTRAN program for a fast minicomputer (GOULD 32/87) or a personal computer. Only data collected in the 250-420-nm wavelength range were used, since no additional useful information was contained above this range. The values of the standard deviations for the fitting parameters given in the text are those obtained directly from the fitting program. However, due to the strong nonlinearity of the fitting function,[23a] a reliable estimate of the confidence interval of the parameters requires multiplying the standard deviations by at least a factor of 3.

The conductivities of the solutions listed in Table II were measured at 25 ± 0.05 °C with a Philips PW 9509 digital conductivity meter. The conductivity values are supplied as supplementary material.

Attempts at kinetic measurements were carried out at 25 ± 0.05 °C with a Durrum stopped-flow kinetic spectrophotometer.[10] The lowest reactant concentrations (3×10^{-5} M **1** and 3×10^{-4} M Br_2) leading to **2** and **3** in concentrations suitable to try to monitor the transformation of the former into the latter were chosen. Absorbance values consistent with those measured with the Pye-Unicam spectrophotometer were instantaneously attained, showing that the formation of both species was too fast for the stopped-flow time scale.[20b]

Acknowledgment. This work was financed in part by a NATO grant and in part by grants from the Consiglio Nazionale delle Ricerche and Ministero della Pubblica Istruzione of Italy, the NSERC of Canada, and the University of Alberta.

Registry No. 2, 118761-15-2; **3**, 24315-87-5; **4**, 118725-12-5.

Supplementary Material Available: A table containing all the measured data (temperature, optical path, concentration, absorbance, and conductivity) used in the determination of the formation constants and spectral parameters relative to equilibria 1, 2, 3, and 7 (1 page). Ordering information is given on any current masthead page. Further details on the computational procedure are available directly from the authors (inquiries to R.A.) to any nonprofit organization.

Concerted Acetyl Group Transfer between Substituted Phenolate Ion Nucleophiles: Variation of Transition-State Structure as a Function of Substituent

Salem Ba-Saif, Ajay K. Luthra, and Andrew Williams*

Contribution from the University Chemical Laboratories, Canterbury, England CT2 7NH.
Received August 11, 1988

Abstract: Second-order rate constants (k_{ArO}) have been measured for the concerted displacement of aryl oxide from aryl acetates in aqueous solution by substituted phenoxide ions. Values of k_{ArO} obey linear Brønsted correlations when either the leaving group or the attacking phenolate ion structures are varied. The Brønsted coefficients obey the equations $\beta_{nuc} = 0.20\ pK_{lg} - 0.68$ and $\beta_{lg} = 0.15pK_{nuc} - 1.73$ to a good degree of precision, and the variation indicates that the structure of the transition-state changes within the range of phenolate ions studied; this also provides confirmation that a concerted mechanism operates. The equations for β_{nuc} and β_{lg} predict the equation ($\log k_{ii} = 0.17pK_a{}^2 - 2.41pK_a + C$) for k_{ii}, the rate constant for the reaction of aryl oxide ion with acetates bearing identical aryl oxide leaving groups. The identity rate constants may be interpolated from the observed rate constants (k_{ArO}) and exhibit excellent fit to the above equation with the single disposable parameter, C, set at 6.5. This is the first report of curvature in a Brønsted plot of identity rate constants. Effective charge development and loss on leaving and attacking oxyanions is fully balanced in the transition state when entering and leaving nucleophiles have a pK_a of 7.1. Tetrahedral or acylium ion-like transition-state structures are predicted for hypothetical phenols with pK_a's of 11.7 and 2.0, respectively.

Recent observations of linear Brønsted correlations for attack of phenolate ion nucleophiles on phenyl esters and pyridines on *N*-acylpyridinium ions[1,2] are consistent with single transition states for these reactions because the pK_a values of the nucleophiles lie significantly above and below that predicted for the breakpoint for the putative stepwise process. In order to investigate these novel concerted mechanisms for acyl group transfer it will be necessary to study the state of the forming *and* breaking bonds in the transition state; such a study will give information as to the state of coupling[3a] between the two major bond changes. Application of single uncalibrated β or ρ values is not appropriate to elucidate transition-state structures for reactions involving two or more major bond changes.[3a]

Since the concerted carbonyl-transfer reaction between similar nucleophiles is essentially symmetrical, the transition state will lie close to the tightness diagonal[3b,4,5a] illustrated in Figure 1 for the transfer of the acetyl group between phenolate ion nucleophiles. The transition state for the reaction where nucleophile and leaving group are identical will fall *on* the tightness diagonal. Kreevoy and his collaborators[4,5]a proposed a relationship (eq 1) between

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(1) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362.

(2) Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040.

(3) (a) Williams, A. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; p 127. (b) This diagonal is called the "disparity mode" by Grunwald (Grunwald, E., *J. Am.* Chem. *Soc.* **1985**, *107*, 125).

(4) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87.

(5) (a) Kreevoy, M. M.; Lee, I. S. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550. (b) Reactions in solution require that any effect on the transition-state and ground-state energies results from bonding *and* solvation changes. These cannot be easily separated in the observed parameter; since it is false from many points of view to consider *only* changes in bonding, measures of "bond order" should relate to the *total* of bond and solvation changes. Effective charge changes derived from Brønsted β or Hammett ρ values from proper calibration procedures[13d,19] are proportional to the change in charge resulting from both solvation and bonding changes. Paper mechanisms invariably omit solvent and treat all reactions as though they were occurring in the gas phase. We use the term "bond order" in this paper as a *combination* of binding and solvation changes which are proportional to changes in effective charge. (c) A transition state with a structure close to that of a tetrahedral intermediate is called a "tight" transition state and will have $\delta = +1$ because the phenolate attacking group *loses* one unit of negative charge (going from ground to transition state). A loose or "exploded"[6,7] transition-state structure resembles an acylium ion and has $\delta = -1$ because the leaving oxygen *gains* negative charge (one unit) from ground to transition state. The transition state for the concerted mechanism where changes in effective charge on entering and departing oxygens are balanced has $\delta = 0$.

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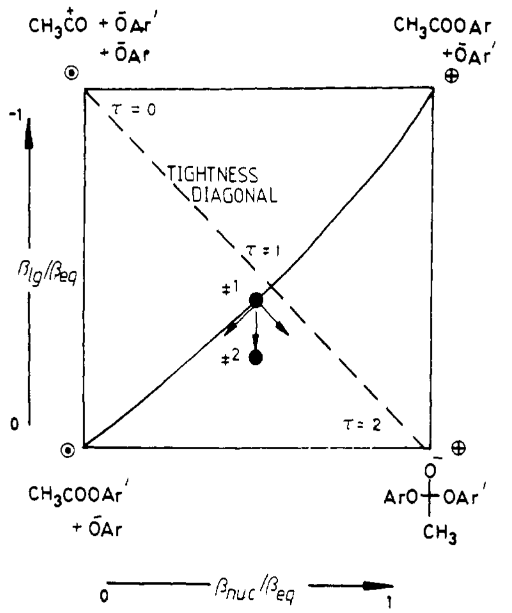

Figure 1. Reaction map for transfer of the acetyl group between phenolate ion nucleophiles. The edges are calibrated by the appropriate β value normalized by its corresponding β_{eq}. the sign ⊙ indicates that the direction of motion is upwards for the region of the surface as a result of increasing the pK_a of the nucleophile while keeping the leaving group constant; the arrows in the surface represent the direction of resultant change in structure of the transition-state no. 1 to transition-state no. 2.

the Brønsted dependence of k_{ii}, the identity rate constant, and the value of τ, the tightness parameter. The tightness parameter is the sum of the bond orders[5b] (η) of the forming and breaking bonds in the transition state (eq 2); K_{ij} is the equilibrium constant

$$\tau - 1 = \delta = d \ln k_{ii}/d \ln K_{ij} = \beta^{ii}/\beta^{eq} \qquad (1)$$

$$= \eta_{nuc} + \eta_{lg} \qquad (2)$$

for the reaction keeping the acceptor nucleophile (j) constant and varying the donor (i).[5c] Carbonyl transfer between pyridines or phenolate ions does not have transition states along the edges of the potential energy map (see for example Figure 1),[1,2] and the concerted mechanism has no structures on its reaction coordinate similar to those at the corners of the reaction surface (Figure 1). The mechanism is not "enforced concerted"[6-8] although almost certainly the energies of the putative intermediate structures (at the corners of Figure 1) will have very high energies thus forcing the reaction path to be more "central" in the figure.

The study of tightness parameters has been useful in determining bonding in hydride transfer,[5a] phosphoryl and sulfuryl group transfer,[9] and transfer of the alkyl group.[10] Transfer of the acetyl group between phenolate ion nucleophiles presents a good opportunity to apply this approach to carbonyl group transfer because the rate constants of the identity reactions can be readily estimated with some accuracy by interpolation or minor extrapolation from linear Brønsted plots. This report is of a study of the rate constants for reaction of aryl oxide anions with aryl acetates (eq 3) as a function of varying leaving group and varying nucleophile structures.

$$Ar\text{-}O^- + CH_3CO\text{-}O\text{-}Ar' \xrightarrow{k_{ArO}} CH_3CO\text{-}O\text{-}Ar + {}^-O\text{-}Ar' \qquad (3)$$

Experimental Section

Materials were as described earlier,[1] and the physical and analytical characteristics of the extra aryl acetates employed in this study are recorded in the Supplementary Material table. Kinetic and other methods including the instruments employed are described in previous papers.[1,2]

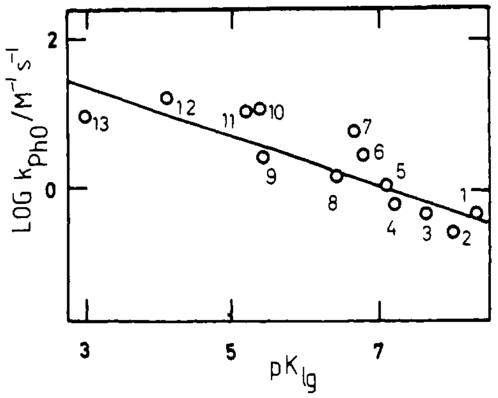

Figure 2. Dependence on pK_a of the leaving phenolate ion for log k_{PhO} for attack of phenolate ion on substituted phenyl acetates; parameters are from Table II, and the line is calculated from the eq in Table III.

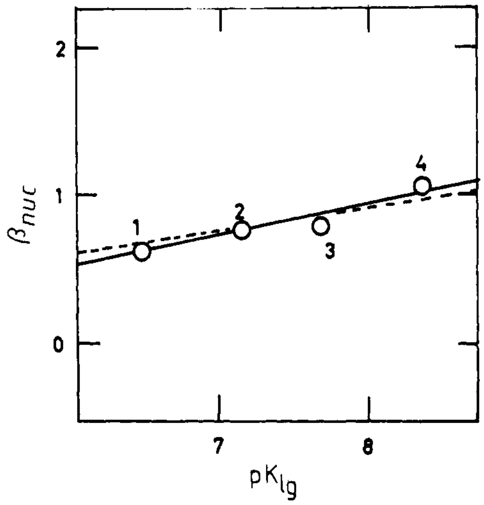

Figure 3. Dependence of β_{nuc} on pK_{lg} for attack of phenolate ions of varying structure on phenyl esters; parameters are from Table III, and the line is calculated from eq 4. The significance of the dashed line is described in the text.

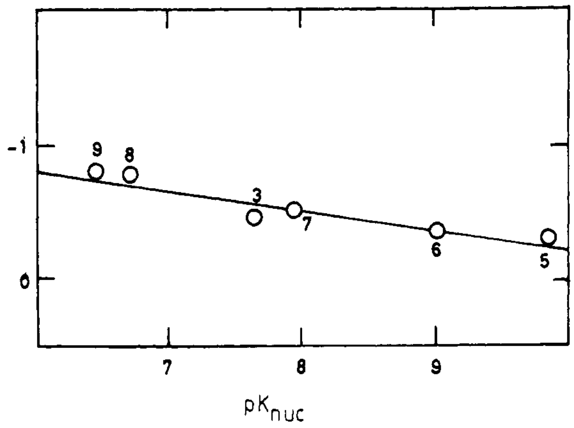

Figure 4. Dependence on pK_{nuc} of β_{lg} for attack of phenolate ions on aryl esters with leaving groups of varying structure; parameters are from Table III, and the line is calculated from eq 5.

Results

First-order kinetics for release of phenolate ion from substituted phenyl acetates were treated as previously described[1] to yield the second-order rate constants for the bimolecular process; the data and conditions of the measurements are given in Tables I and II. The rate constants obey good linear Brønsted equations against the pK_a of the attacking phenol (β_{nuc}) when the leaving phenoxide ion structure is constant; they also fit good linear equations against the pK_a of the leaving phenolate ion (β_{lg}) when the structure of the nucleophile is constant (see Figure 2 for example). The

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(6) Jencks, W. P. *Chem. Soc. Rev.* (*London*) **1981**, *10*, 345.

(7) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161.

(8) Luthra, A. K.; Ba-Saif, S.; Chrystiuk, E.; Williams, A. *Bull. Soc. Chim. Fr.* **1988**, 391.

(9) Williams, A. *J. Am. Chem. Soc.* **1985**, *107*, 6335.

Table I. Nucleophilic Reactivity of Sets of Phenolate Anions Against Phenyl Acetates with Constant Leaving Groups[a]

	substituent	pK_{nuc}[b]	k_{ArO^-}, $M^{-1}\ s^{-1}$[c]	FB[d]	pH[e]	N[f]	[phenol]/mM[g]	$\Delta k_{obsd} \times 10^5$, s^{-1}[h]
			4-Chloro-2-nitrophenyl Acetate (λ = 400 nm)					
1	H	9.86[i]	1.53	0.110	9.00	5	10.8–54	270–1000
2	3-Cl	9.02	0.69	0.488	9.00	4	6.6–33	270–1140
3	4-CN	7.95	0.077	0.415	7.80	4	5–20	14.7–55.8
4	4-CHO	7.66	0.030	0.580	7.80	5	5–20	12–37
5	2,4,5-Cl_3	6.72[j]	0.015	0.656	7.00	4	2–8	2.6–8.5
6	2,3,5-Cl_3	6.43[j]	0.0091	0.788	7.00	4	2–8	2.1–5.7
7	F_5	5.49[i]	0.0034	0.970	7.00	4	5.2–20.8	2.3–7.4
			4-Formylphenyl Acetate (λ = 333 nm)					
1	4-MeO	10.20	1.57	0.387	10.00	5	5–20	480–1300
2	H	9.86[i]	0.52	0.635	10.00	10	5.3–21.2	250–660
3	4-Cl	9.38	0.35	0.840	10.00	5	5.5–20.2	259–783
4	3-Cl	9.02	0.25	0.506	9.00	4	6.8–33	10–40
5	2-F	8.81	0.094	0.608	9.00	4	3.6–13	10–40
6	3,4-Cl_2	8.62[j]	0.085	0.023	7.00	4	1.6–2.6	0.3–6
7	2-Cl	8.48	0.029	0.768	9.00	4	5–15	40–98
8	4-CN	7.95	0.0085	0.420	7.80	5	5.1–20.4	2.5–7.1
9	2,3-Cl_2	7.71[j]	0.0072	0.557	7.80	4	6.2–31	0.5–12.8
10	3,4,5-Cl_3	7.68[i]	0.026	1.00	9.00	4	5.0–25	10–70
11	4-NO_2	7.14	0.0026	from ref 1				
12	2,4,5-Cl_3	6.72	0.0025	0.656	7.00	5	1.6–6.4	0.4–1.3
13	2,3,5-Cl_3	6.43	0.0015	0.788	7.00	5	1.6–6.4	0.3–0.8
14	F_5	5.49[i]	3.6×10^{-4}	0.973	7.00	5	10–100	0.3–1.4
			3-Nitrophenyl Acetate (λ = 400 nm)					
1	H	9.86[i]	0.5	0.560	10.00	5	5.0–30.6	250–970
2	3-Cl	9.02	0.15	0.488	9.00	4	6.6–33	60–270
3	2-F	8.81	0.080	0.608	9.00	4	5.0–15.0	35–84
4	2-Cl	8.48	0.040	0.172	7.80	4	2.5–15.2	5–14
5	4-CN	7.95	0.0061	0.415	7.80	5	7.2–28	2.4–6.6
6	4-CHO	7.66	0.0031	0.580	7.80	5	5.1–20.4	1.4–3.7

[a] 25 °C, ionic strength made up to 0.1 M with KCl. [b] Except where stated pK_a's are from Jencks, W. P.; Regenstein, J. In *The Handbook of Biochemistry*; 2nd. ed.; Sober, H. A., Ed.; Chemical Rubber Publishing Co.: Cleveland, OH, 1970; Section j-187. [c] Errors in the rate constants are less than ±5%. [d] Fraction of phenol ionized. [e] Average pH; individual pH values did not differ by more than 0.02 from the average. Buffer components for pH 8 (phosphate at 0.018 M) and at pH 10 (carbonate at 0.025 M). [f] Number of data points not including duplicates. [g] Range of phenol concentrations. [h] Range of k_{obsd}. [i] Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 45. [j] Drahanowsky, J.; Vacek, Z. *Coll. Czech. Chem. Commun.* **1971**, *36*, 3431.

Brønsted correlations are illustrated in the Supplementary Material figures, and the equations of the lines are recorded in Table III. We include chloro or nitro ortho substituents in the Brønsted correlations because these give no significant deviation from lines for either β_{nuc} or β_{lg}. Any steric effect of a single ortho substituent is thus not significant, and points 1, 8, and 9 in Figures 3 and 4 are therefore valid for inclusion in correlations of β_{lg} and β_{nuc} with pK_{nuc} and pK_{lg}. Previous work[1] indicates a significant deviation when both ortho positions are occupied in the nucleophile; when both these positions are filled in the leaving group omission of these points from the correlations $\neq$ 3, 5, and 7 (leaving group variation in Table III) only improves the correlations slightly (Table III: $\neq$ 5, −0.33 → −0.43; $\neq$ 7, −0.51 → −0.55; $\neq$ 3, −0.46 → −0.50). We choose to include 2,6-disubstituted phenyl in the correlations for leaving-group variation. The better fit of 2,6-disubstituted phenyl groups for leaving-group variation probably reflects a relatively small steric effect from hindered ester to hindered transition state; the poor fit when the *nucleophile* is 2,6-disubstituted is due to a large change in steric requirement from relatively unhindered free phenolate ion to the hindered transition state.

Values of β_{nuc} and β_{lg} depend on the pK_a of the leaving and attacking phenolate ion, respectively; the data fit good linear correlations and these are illustrated in Figures 3 and 4 and quantified in eq 4 and 5. The dashed line in figure 3 has the slope of the plot for β_{lg}, and this illustrates the close similarity between the slopes.

$$\beta_{nuc} = 0.20 \pm 0.04 pK_{lg} - 0.68 \pm 0.3 \quad (r = 0.965) \qquad (4)$$

$$\beta_{lg} = 0.15 \pm 0.03\ pK_{nuc} - 1.73 \pm 0.23 \pm 0.23 \quad (r = 0.932) \qquad (5)$$

Identity rate constants, k_{ii}, for the transfer of the acetyl group between phenolate ions have been interpolated or estimated by minor extrapolation from the Brønsted equations in Table III; values of k_{ii} are recorded in Table III, and the plot of log k_{ii} vs the pK_a of the attacking and leaving phenolate ion is illustrated in Figure 5. The accuracy of our estimates of log k_{ii} are given in the figure where the verticle lines on the points are the probable errors. Perusal of Table III indicates that log k_{ii} may be calculated for the 4-formylphenol from two different correlations and that the two values so obtained agree. Previous work on sulfuryl and phosphoryl group transfer[9] has indicated similar good agreement between k_{ii} values obtained by two methods, and this gives us confidence in the approach for obtaining identity rate constants. Although the identity rate constants can be force fit to a linear correlation (see Figure 5), there is considerable nonrandom scatter, and a nonlinear fit is better. Lewis and Hu[10] record that β_{ii} is given by eq 6, substitution from eq 4 and 5 yields eq 7, and integration of eq 7 gives eq 8.

$$\beta_{ii} = d \log k_{ii}/d\ pK_{lg} = \beta_{nuc} + \beta_{lg} \qquad (6)$$

$$\beta_{ii} = 0.35 \pm 0.07 pK_{lg} - 2.41 \pm 0.53 \qquad (7)$$

$$\log k_{ii} = 0.17 \pm 0.03 pK_{lg}^2 - 2.41 \pm 0.53\ pK_{lg} + C \qquad (8)$$

Fitting the data to eq 8 gives an excellent correlation if the single disposable parameter, C, has the value 6.5. The fit is shown in Figure 5 and is remarkably good in view of the fact that all except one of the parameters are calculated from the variation of Brønsted coefficients with the pK_a of a nucleophile or a leaving group. It

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

Table II. Leaving Group Reactivity of Sets of Phenyl Acetates Against Constant Phenolate Anions[a]

	substituent	pK_{lg}[b]	k_{ArO}, $M^{-1}\ s^{-1}$[c]	FB[d]	λ, nm[i]	pH[e]	N[f]	[phenol]/mM[g]	$k_{obsd} \times 10^3$, s^{-1}[h]
				Phenolate Anion					
1	3-NO_2	8.35	0.50	from Table I					
2	4-CH_3CO	8.05	0.28	0.560	335	10.00	5	5.7–34.2	1.5–5.5
3	4-CHO	7.66	0.52	from Table I					
4	2-NO_2	7.23	0.65	0.560	425	10.00	5	2.1–21.2	2.3–8.0
5	4-NO_2	7.14	1.24	from Table I					
6	3-Cl-4-NO_2	6.80	3.01	0.121	400	9.00	4	5.1–30.6	2.2–8.3
7	3,5-$(NO_2)_2$	6.68	6.38	0.121	410	9.00	4	5.3–21.2	8.9–18.8
8	4-Cl-2-NO_2	6.46	1.53	from Table I					
9	2-Cl-4-NO_2	5.45	2.78	0.121	410	9.00	5	5.4–54	1.9–12.7
10	3,4-$(NO_2)_2$	5.42	11.4	0.121	410	9.00	4	5–20	8–28.7
11	2,5-$(NO_2)_2$	5.22	11.3	0.121	440	9.00	4	6.5–26.0	10.2–34.8
12	2,4-$(NO_2)_2$	4.11	17.0	0.121	400	9.00	4	5.4–21.6	12–40
13	4-Cl-2,6-$(NO_2)_2$	3.00	8.93	0.121	460	9.00	4	1.0–3.0	0.65–3.1
				3-Chlorophenolate Ion					
1	3-NO_2	8.35	0.15	from Table I					
2	4-CH_3CO	8.05	0.095	0.488	335	9.00	4	6.6–33	0.4–1.6
3	4-CHO	7.66	0.25	from Table I					
4	4-NO_2	7.14	0.32	from Table I					
5	4-Cl-2-NO_2	6.46	0.69	from Table I					
6	2-Cl-4-NO_2	5.45	0.86	0.488	410	9.00	4	6.6–33	3.9–14.9
7	2,4-$(NO_2)_2$	4.11	5.08	0.488	400	9.00	4	6.6–33	20–86.9
				4-Cyanophenolate Ion					
1	3-NO_2	8.35	0.0061	0.415	400	7.80	5	7.2–28.8	2.4–6.6
2	4-CH_3CO	8.05	0.0046	0.415	335	7.80	4	10.2–20.4	2.5–4.1
3	4-CHO	7.66	0.0085	from Table I					
4	2-NO_2	7.23	0.017	0.415	425	7.80	4	5.1–15.3	4.6–14.5
5	4-NO_2	7.14	0.023	from Table I					
6	3-Cl-4-NO_2	6.80	0.074	0.415	400	7.80	4	5.4–21.6	21.2–61.4
7	3,5-$(NO_2)_2$	6.68	0.14	0.415	410	7.80	4	5–20	36.2–132
8	4-Cl-2-NO_2	6.46	0.077	from Table I					
9	2-Cl-4-NO_2	5.45	0.072	0.918	410	9.00	4	5.1–20.4	43–190
10	3,4-$(NO_2)_2$	5.42	0.40	0.918	410	9.00	4	5.0–20	332–853
11	2,5-$(NO_2)_2$	5.22	0.50	0.918	440	9.00	4	5.0–20	337–997
12	2,4-$(NO_2)_2$	4.11	0.64	0.918	400	9.00	4	5.1–20.4	440–1310
13	2,6-$(NO_2)_2$	3.71	0.72	0.918	460	9.00	5	5.1–20.4	376–1324
				4-Formyl Phenolate Ion					
1	3-NO_2	8.35	0.0031	0.580	400	7.80	5	5.1–20.4	1.4–3.7
2	2-NO_2	7.23	0.0081	0.580	425	7.80	5	5.0–20.0	3.0–9.6
3	4-NO_2	7.14	0.014	from Table I					
4	3-Cl-4-NO_2	6.80	0.032	0.580	400	7.80	5	5.1–20.4	13–41
5	3,5-$(NO_2)_2$	6.68	0.073	0.580	410	7.80	5	5.1–20.4	28–92
6	4-Cl-2-NO_2	6.46	0.030	from Table I					
7	2-Cl-4-NO_2	5.45	0.048	0.580	410	7.80	5	5.0–20.0	15.6–57.3
8	3,4-$(NO_2)_2$	5.42	0.18	0.580	410	7.80	5	5.1–20.4	63.0–218
9	2,5-$(NO_2)_2$	5.22	0.28	0.580	440	7.80	5	5.1–20.4	8.0–334
10	2,4-$(NO_2)_2$	4.11	0.32	0.956	400	9.00	5	5.0–20.0	298–722
11	2,6-$(NO_2)_2$	3.71	0.40	0.956	460	9.00	5	5.0–20.0	40–800
				2,3,5-Trichlorophenolate Anion					
1	4-Cl-2-NO_2	6.46	0.0091	from Table I					
2	4-NO_2	7.14	0.0038	from Table I					
3	4-CHO	7.66	0.0015	from Table I					
4	3-NO_2	8.35	0.00019[k]						
				2,4,5-Trichlorophenolate Anion					
1	4-Cl-2-NO_2	6.46	0.015	from Table I					
2	4-NO_2	7.14	0.0083	from Table I					
3	4-CHO	7.66	0.0025	from Table I					
4	3-NO_2	8.35	0.00039[k]						

[a–h] Footnotes as in Table I. [i] Wavelength for kinetic study. [k] These values are extrapolated from the Brønsted equation for the attack of phenolate ions on 3-nitrophenyl acetate (Table III).

should also be noted that the single disposable parameter, *C*, only affects the vertical disposition of the theoretical line.

There is only one correlation given in Table III which has an "*r*" value less than 0.9; experimental error is not the main cause of the deviations from the linear Brønsted correlation. Such deviations, which are intrinsic to the system, have been discussed previously for sulfuryl and phosphoryl group transfer[9] and they place a theoretical limit on the accuracy of estimations from the Brønsted equations in Table III. The probable errors, shown in Figure 5, indicate that the accuracy is sufficient to enable us to detect curvature in the Brønsted plot of the identity rate constants. It is not surprising, however, that the difference between β_{nuc} and β_{lg} should equal the known value (β_{eq} = 1.7)[11] only within the standard deviation limits.

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(11) Gerstein, J.; Jencks, W. P. *J. Am. Chem. Soc.* **1964**, *86*, 4655.

Table III. Brønsted Parameter and Identity Rate Constants for Reaction of Phenolate Anions with Phenyl Acetates[a]

	leaving group substituent	pK_{1g}	β_{nuc}	C	r	log k_{ii}, M^{-1} s^{-1} [b]
	Variation of the Phenolate Anion Nucleophile					
1	4-Cl-2-NO_2	6.46	0.64 ± 0.05	−6.11 ± 0.37	0.986	−1.98
2	4-NO_2	7.14	0.75 ± 0.04	−7.28 ± 0.28	0.986	−1.93
3	4-CHO	7.66	0.79 ± 0.04	−8.01 ± 0.32	0.984	−1.96
4	3-NO_2	8.35	1.04 ± 0.09	−10.37 ± 0.83	0.989	−1.69
	nucleophile substituent	pK_{nuc}	β_{1g}	C	r	log k_{ii}, M^{-1} s^{-1} [b]
	Variation of the Phenolate Ion Leaving Group					
5	H	9.86	−0.33 ± 0.06	2.43 ± 0.39	0.850	−0.82
6	3-Cl	9.02	−0.37 ± 0.04	2.12 ± 0.28	0.971	−1.22
7	4-CN	7.95	−0.51 ± 0.09	1.97 ± 0.58	0.932	−2.08
3	4-CHO	7.66	−0.46 ± 0.06	1.51 ± 0.37	0.931	−2.01
8	2,3,5-Cl_3	6.43	−0.82 ± 0.10	3.36 ± 0.75	0.985	−1.91
9	2,4,5-Cl_3	6.72	−0.79 ± 0.11	3.43 ± 0.85	0.980	−1.88

[a] Conditions as in Tables I and II. The Brønsted law is $\log k = \beta pK +$ constant. [b] The equation $\log k_{ii}$, $M^{-1}\ s^{-1} = 0.30pK_a - 4.07$ ($r = 0.826$) is the "least-squares" fit of this data to a linear equation.

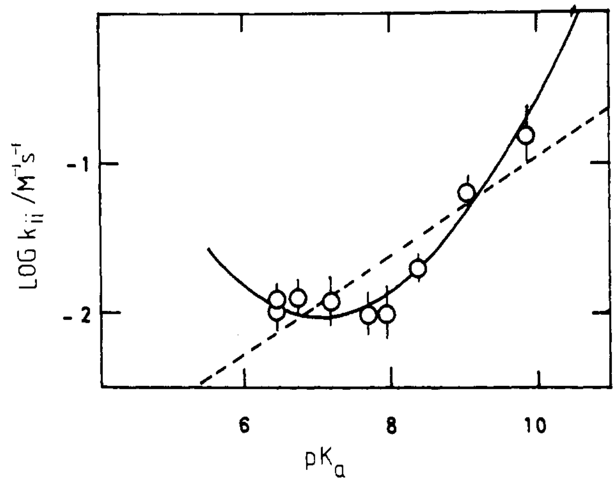

Figure 5. Dependence of the rate constant for the identity reaction on the pK_a of the entering and leaving phenolate ion; data are from Table III, and the line is calculated from eq 8. The linear correlation (dashed line) is the forced least-squares best fit to the data; the bars indicate the probable errors for the rate parameters. An average value for k_{ii} is determined from the two values for the 4-formylphenolate reaction given in Table III.

Discussion

Variation of β_{nuc} and β_{1g} with pK_{1g} and pK_{nuc}, respectively, is excellent evidence for a change in structure of the transition state consequent on change in that of nucleophile or leaving group. The existence of cross correlation indicates that there is coupling between entering the leaving bonds consistent with a concerted mechanism. Changes in pK_{1g} (pK_{nuc}) should not have an effect on β_{nuc} (β_{1g}) for a stepwise path because it would have a rate-controlling transition-state structure on one of the edges of the energy surface (Figure 1).

Significant curvature has not previously been reported for plots of log k_{ii} versus the appropriate pK_a values; curvature has been predicted on the basis that transition-state structures might move over curved areas of potential energy surface.[10] Previous observations of linear plots for the identity rate constants in other systems[5a,9,10] have been considered to be due to the small range of substituent structure where the corresponding area of potential energy surface will be small enough to be essentially planar.[10] Small changes in linearity are probably hidden in the error in the results for sulfuryl and phosphoryl group transfer[9] although Skoog and Jencks[12a] have evidence for slight nonplanarity in the phosphoryl group transfer case.

That the value of β_{ii} is not independent of pK_a also indicates change in transition-state structure in the range of phenolate ion structures studied; there is no evidence of significant curvature in the individual Brønsted correlations. There have been many observations of linear free energy relationships extending over wide ranges of reactivity and equilibrium constant.[12b] There is very little precedent for marked curvature in Brønsted plots for non-proton-transfer reactions as a result of possible change in transition-state structure other than that caused by changes in rate-limiting step or by gross mechanism change. In the present reaction an increase in pK_a of the nucleophilic phenoxide ion (^-OAr) should raise the left hand edge of the diagram (Figure 1). The transition-state structure would move along the reaction coordinate toward the bottom left corner and along the tightness diagonal toward the bottom right corner. The net result of this movement would be a change in β_{1g} to a more positive value, but there would be essentially no change in β_{nuc} giving rise to a linear Brønsted plot. Similar arguments indicate that increase in the pK_a of the leaving group ($^-OAr'$) will give more positive values of β_{nuc} with essentially no change in β_{1g}. These "compensation" arguments have been employed for other systems.[13a-c] Although the linear Brønsted dependence indicates that the bond under "observation" by the substituents does not change its structure in the transition state as nucleophile or leaving group changes, the bond not being "observed" certainly does change its structure. The present results indicate that, to a first approximation at least, substituents which "report" charge changes in the one bond (as a result of bonding and solvation changes) do not "see" charge changes in the other bond undergoing major change.

Transfer of acetyl from substituted phenyl acetates has a β_{eq} value independent of the pK_a of the acceptor phenolate ion[13d] so that the difference between β_{nuc} and β_{1g} ($=\beta_{eq}$) is independent of acceptor;[13d] eq 4 and 5 indicate that this is so within experimental error.

The dependence of log k_{ii} on the pK_a of the donor and acceptor nucleophiles is required to be nonlinear because the changes in β_{1g} and β_{nuc} which cancel and cause β_{eq} to be invariant will *augment* in the sum of these parameters unless the changes are zero (eq 7).

Nonlinear variation of log k_{ii} with pK_a indicates that the transition state for the perfectly symmetrical concerted reaction has a structure which moves along the tightness diagonal as the phenolate ion substituent changes. Increasing the pK_a of the entering and leaving group will increase the tightness from $\tau = 1$ (at $pK_a = 7.1$, see eq 8) where the bond changes are completely coupled to $\tau = 2$ at $pK_a = 11.7$.[14] This result is in agreement with the observations that nonactivated esters react via stepwise paths.[15-17] That very good leaving groups initiate reactions with acylium ion mechanisms[18] is consistent with the prediction from eq 8 that $\tau = 0$ for leaving and attacking phenolate ions with the low pK_a of 2.0. The estimations of the tightness parameter at its extremes must be considered as only qualitative because they depend on extrapolations of eq 4 and 5 beyond the observed range of pK_a for the equations (maybe beyond actual applicability) and moreover probably go over excessive ranges of the potential energy surface. Within the range of pK_a values studied the transition state of the concerted mechanism goes from one where the effective charge changes are almost completely balanced ($\tau = 0.92$ at $pK_a = 6.5$) to one where $\tau = 1.64$ (at $pK_a = 10$).

The application of tightness parameters to measure the extent of bond orders in transition-states of reactions with two or more major bond changes is directly related to the Leffler approach[13d] where the substituent effect on the rate constant is compared with that on the equilibrium constant of the overall reaction. Such

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[12] (a) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* **1984**, *106*, 7597. (b) See, for example: Kemp, D. S.; Casey, M. L. *J. Am. Chem. Soc.* **1973**, *95*, 6670 and the references therein.

[13] (a) Jencks, W. P. *Chem. Rev.* **1985**, *85*, 511. (b) Pross, A. *Adv. Phys. Org. Chem.* **1976**, *14*, 69. (c) Jencks, W. P. *Bull. Soc. Chim. Fr.* **1988**, 218. (d) Williams, A. *Acc. Chem. Res.* **1984**, *17*, 425. (e) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

[14] In these calculations β_{eq} is taken as 1.7.[11]

[15] Capon, B.; Ghosh, A. K.; Grieve, D. M. A. *Acc. Chem. Res.* **1981**, *14*, 306.

[16] McClelland, R. A.; Santry, L. J. *Ibid.* **1983**, *16*, 394.

[17] Shames, S. L.; Byers, L. A. *J. Am. Chem. Soc.* **1981**, *103*, 6170.

[18] Williams, A.; Douglas, K. T. *Chem. Rev.* **1975**, *75*, 627.

measures have been thoroughly examined, and, provided certain limitations are recognized, they yield good experimental figures for charge changes in the bond in question[13d,19] in solution reactions. As originally formulated the Leffler approach employed a model reaction with only one major bond change.[20] Since the majority of reactions involve *more* than one major bonding change, it is not surprising that conflicting results have often been obtained concerning advancement of the transition state by application of the simple theory. An explicit experimental test of the Leffler method moreover indicates its usefulness applied to an individual bonding change.[21] Studies on the nature of charge in only one bond in a reaction where more than one bond is changing are unlikely to give a proper description of the transition state.

If the tightness parameter is to be applied to the state of bonding in a transition state, it requires that the reaction be concerted otherwise the reaction is not symmetrical. The Leffler method is applied to *each* bond change in the reaction,[13d,19] and allowing for the negative sign of β_{lg} the Leffler parameter (α)[13d,19] for each changing bond indicates that the forming (η_{nuc}) and breaking (η_{lg}) bond orders are $\beta_{\text{nuc}}/\beta_{\text{eq}}$ and $(1 + \beta_{\text{lg}}/\beta_{\text{eq}})$, respectively; the total bond order is therefore the sum of these values and is the same as that obtained from the tightness parameter methodology by combining eq 1 and 6 to give eq 9.

$$\tau = \beta_{\text{nuc}}/\beta_{\text{eq}} + \beta_{\text{lg}}/\beta_{\text{eq}} + 1 \qquad (9)$$

This work confirms that the attack of phenolate anions on phenyl acetates has a concerted mechanism involving no structure on its reaction coordinate resembling that from complete bond formation as found at the corners of the reaction energy surface (Figure 1); it indicates that the transition state has a variable structure over this range. Concerted mechanisms with reaction coordinates passing through structures corresponding to complete bond formation are possible for unsymmetrical acyl group transfers such as those involving amine attack on activated esters;[13c] in these cases the transition state will lie near the edges of the reaction map meeting at the structure corresponding to the tetrahedral intermediate. Concerted mechanisms could also occur with a transition-state structure corresponding to that of the acylium ion.

We are not able to derive spatial information from the polar substituent effects except by inference. Presumably the transition-state geometry will vary as the transition-state structure travels along the tightness diagonal from square planar for the open transition state through some intermediate geometry to tetrahedral for the tight transition state.[22]

Acknowledgment. We thank the Government of Saudi Arabia for support (S.B.). This paper is dedicated to Myron Bender, a friend and teacher, who made inspired contributions to bioorganic chemistry particularly in the field of carbonyl group transfer in solution.

Registry No. 4-Chloro-2-nitrophenyl acetate, 60386-78-9; 4-formylphenyl acetate, 878-00-2; 3-nitrophenyl acetate, 1523-06-4; 4-acetylphenyl acetate, 13031-43-1; 2-nitrophenyl acetate, 610-69-5; 4-nitrophenyl acetate, 830-03-5; 3-chloro-4-nitrophenyl acetate, 89894-10-0; 3,5-dinitrophenyl acetate, 34253-18-4; 2-chloro-4-nitrophenyl acetate, 18855-84-0; 3,4-dinitrophenyl acetate, 10186-94-4; 2,5-dinitrophenyl acetate, 1523-08-6; 2,4-dinitrophenyl acetate, 4232-27-3; 4-chloro-2,6-dinitrophenyl acetate, 118869-96-8; 2,6-dinitrophenyl acetate, 1523-09-7; phenoxide ion, 3229-70-7; 3-chlorophenoxide ion, 18938-14-2; 4-cyanophenoxide ion, 14609-76-8; 4-formylphenoxide ion, 18938-17-5; 2,4,5-trichlorophenoxide ion, 45773-92-0; 2,3,5-trichlorophenoxide ion, 100414-67-3; pentafluorophenoxide ion, 26910-95-2; 4-methoxyphenoxide ion, 29368-59-0; 4-chlorophenoxide ion, 24573-38-4; 2-fluorophenoxide ion, 32376-32-2; 3,4-dichlorophenoxide ion, 45670-76-6; 2-chlorophenoxide ion, 29650-97-3; 2,3-dichlorophenoxide ion, 96541-70-7; 3,4,5-trichlorophenoxide ion, 60154-34-9; 4-nitrophenoxide ion, 14609-74-6.

Supplementary Material Available: Analytical table and figures for Brønsted correlations for attack of substituted phenolate ion on phenyl ester and of phenolate ion on substituted phenyl acetates (5 pages). Ordering information is given on any current masthead page.

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(19) Williams, A.; Thea, S. *Chem. Soc. Rev.* (*London*) **1986**, *15*, 125.
(20) Leffler, J. E. *Science* **1953**, *117*, 340.
(21) Hill, S. V.; Thea, S.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 437.
(22) The geometry along the tightness diagonal does not vary for other systems which have been studied by use of the identity rate method (phosphoryl,[9] sulfuryl,[9] hydride,[5a] and methyl[4] group transfer). In all these cases the method of study involved determination of charge development on the leaving or entering atom; such an approach is not indicative of geometry so that we believe that the method developed by Kreevoy and his colleagues is valid for the present case.

Molecules with Twist Bent Bonds. The Synthesis, Properties, and Reactions of *trans*-Bicyclo[4.1.0]hept-3-ene and Certain Methylated Derivatives

Paul G. Gassman,* Steven M. Bonser, and Kata Mlinarić-Majerski

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455. *Received August 19, 1988*

Abstract: *trans*-Bicyclo[4.1.0]hept-3-ene, 7-methyl-*trans*-bicyclo[4.1.0]hept-3-ene, and 7,7-dimethyl-*trans*-bicyclo[4.1.0]hept-3-ene have been synthesized. Comparison of their ease of oxidation with the ease of oxidation of the analogous *cis*-bicyclo[4.1.0]hept-3-enes has been made. Both the thermal and transition-metal complex promoted rearrangements of the *trans*-bicyclo[4.1.0]hept-3-enes have been studied. These systems thermally convert to the *cis*-bicyclo[4.1.0]hept-3-enes above 100 °C and are catalytically rearranged at ambient temperature. Trans to cis isomerization also occurs at ambient temperature under photoinduced single electron transfer conditions.

It has long been recognized that carbon–carbon σ bonds generally exist in one of two basic forms. The first is that which we associate with unstrained carbon–carbon σ bonds. These involve linear overlap of bonding atomic orbitals and result in the electron density of the bonding molecular orbital being symmetrically distributed around the C–C internuclear line. A second type of carbon–carbon σ bond is that traditionally associated with strained carbon–carbon σ bonds such as those found in cyclopropane and

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