Bonding in Phosphoryl ($-PO_3^{2-}$)† and Sulfuryl ($-SO_3^-$)† Group Transfer between Nitrogen Nucleophiles as Determined from Rate Constants for Identity Reactions

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Abstract: Rate constants have been measured for the bimolecular reactions of pyridines with pyridinium-*N*-phosphonates (k_y^{xp}) and pyridinium-*N*-sulfonates (k_y^{xs}) for aqueous solution at 25 °C and 0.1 M ionic strength. The Brønsted correlations with the p*K* of the entering or leaving pyridine can be used to calculate the rate constants for reactions where entering and leaving pyridines are identical. The *Brønsted* selectivities of the "identity" rate constants ($\beta_i = -0.53$ for k_x^{xp} and $\beta_i = -0.55$ for k_x^{xs}) predict tightness parameters (τ) of 0.35 and 0.56 and bond orders (η) of 0.17 and 0.28 for the N-P and N-S bonds in the transition states for the transfer processes. The data are consistent with first-order "Marcus" theory governing the energy surfaces of the reactions and in particular obey the relationship $\beta_i = \beta_{nuc} + \beta_{lg}$ predicted by Lewis and Hu.[16]

Group-transfer reactions in solution are important in organic chemistry and biochemistry. The mechanisms of these processes have been studied for transfer of the more important groups such as hydrogen (H-), alkyl (R-), carboxyl (RCO-), phosphoryl (O_3P^{2-}-), sulfuryl (O_3S^--), and sulfenyl (RS-). The group can retain its bonding electrons during passage from donor to acceptor atom (for example in hydride ion transfer), it can transfer without its bonding pair (as in proton transfer or the S_N1 alkyl substitution process), or it can take a charge structure intermediate between these extremes (as in the regular S_N2 mechanism of alkyl substitution).

The intermolecular transfers of phosphoryl and sulfuryl groups between electronegative nucleophiles pass through a single transition state on the way from reactants to products.[3-6] The transfer reaction between identical pyridine nucleophiles for both groups is thus adequately represented by a symmetrical potential energy diagram (Figure 1) where the single transition state must lie on the diagonal B-D. Albery and Kreevoy[7] have defined a value τ which is the sum of the bond orders η of the forming and breaking bonds in the transition state. The values are defined according to eq 1-3, where a is the bond length of the forming bond at any point on the reaction coordinate, $a_{(product)}$ is the bond length in

$$r_a = a/a_{(product)} \quad (1)$$

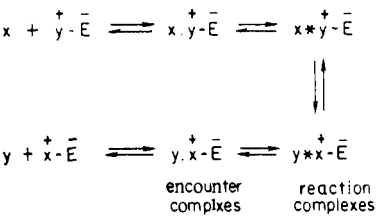
$$\eta_a = ((r_a)_{RC} - r_a)/((r_a)_{RC} - 1) \quad (2)$$

$$\tau = \eta_a + \eta_b \quad (3)$$

the product, and $(r_a)_{RC}$ is the value of r_a in the reaction complex. The cleaving bond (b) gives rise to values r_b and η_b. It is uncertain how bond orders are related to bond length because it depends to a large extent on how bond orders are defined. Equation 2 is a linear definition. There are some authorities who prefer a nonlinear relationship, but it seems to us that a more complicated relationship than eq 2 is not yet warrented.

For the purposes of this paper we separate the reaction into discrete steps (eq 4) although this may only be a formal representation of a more complicated process. The potential energy surface (Figure 1) commences at the reaction complex stage which is formed from the encounter complex via interpenetration and reorganization of the solvent shells and realignment of the partners.

The value τ may be related to observed quantities, in particular to substituent effects on the step from the reaction complex. The substituent effect is a gross quantity referring to the change in charge on a given atom (connected to the substituent) going from the separated solvated ground state to the transition state. It



(4)

is not likely that structural effects will alter the diffusion rate constants to form the encounter complex, but it is possible that the reorganization steps could be structure dependent. This contribution is unknown and for the present we shall neglect this.

Kreevoy and Lee[8] proposed a relationship between δ and τ which is represented in eq 5 for the transfer of phosphoryl or sulfuryl between pyridines. The value K_{xy} is the equilibrium constant for

$$\delta = \tau - 1 = d \ln k_x^{x-E}/d \ln K_{xy} = \beta_i/\beta_{eq} \quad (5)$$

the reaction (eq 5 and 6) where x is varied. The value β_i is defined as the slope of the Brønsted variation for a series of reactions with identical nucleophile and leaving group ($\beta_i = d \log k_x^{x-F}/dpK_x$). We can estimate η_a ($\eta_a = \eta_b$ for a symmetrical reaction) according to eq 5 provided we can determine the rate constant for the identity reaction (k_x^{x-E}) where a pyridine nucleophile expels an identical pyridine leaving group, the Brønsted slope (β_i), and the value of β_{eq} for variation of K_{xy} as a function of pyridine p*K*. The resultant value of δ will indicate whether the transferred species (-E) retains or gives up its bonding electrons or if it takes up an intermediate charge.

The transfer reactions (eq 6 and 7) are ideal for studying and determining "identity" rate constants. The reaction can be monitored easily over a significant variation in p*K* of attacking or leaving pyridine. Brønsted relationships can be determined and values of identity rate constants calculated for various pyridines. The reactions are readily followed for aqueous solvent because the background water hydrolysis term and the hydroxide

† Although the strict IUPAC nomenclature for the ($-SO_3^-$) and ($-PO_3^{2-}$) groups is "sulfonato" and "phosphonato", respectively,[15] we prefer to use the terms "sulfuryl" and "phosphoryl". We denote the pyridine nucleus with an x ring substituent as x and that with a y substituent as y; the sulfuryl or phosphoryl groups attached to the pyridine nitrogen are designated s and p, respectively.

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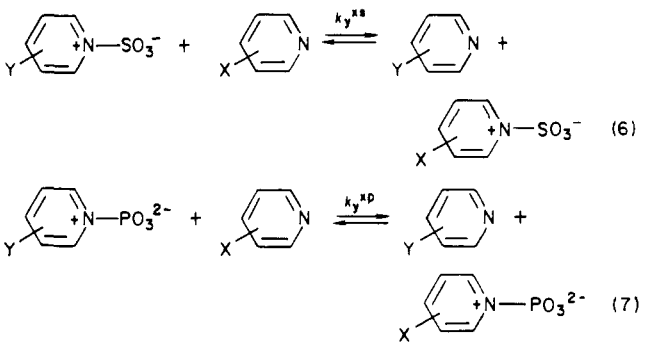
Table I. Reaction of Substituted Pyridines with Pyridinium-*N*-phosphonates[a]

y[j]	xp[j]	Z[h]	k_y^{xp}[f]	pK_x	N[d]	Δk[e]	k_{int}[i]	[y]/M[c]	pH	λ/nm[g]
3-picoline	pyridine	1	4.3	5.31	6	5.5	0.96	15	8.01	277
3-picoline	4-picoline	2	1.36	6.14	8	2	0.35	12.5	8.03	277
3-picoline	3,4-lutidine	3	0.55	6.45	6	0.9	0.1	20	7.89	276
3-picoline	isoquinoline	4	2.22	5.46	7	3.5	0.75	12.5	7.85	330
pyridine	3-picoline	5[b]	0.81	5.82						
pyridine	3,5-lutidine	6[b]	0.34	6.14						
pyridine	3-aminopyridine	7[b]	0.78	6.03						
pyridine	3,4-lutidine	8[b]	0.26	6.45						
pyridine	4-aminopyridine	9[b]	6.25×10^{-4}	9.14						
pyridine	isoquinoline	10[b]	1.43	5.46						
4-picoline	pyridine	11	4.83	5.31	7	10	1.05	20	7.95	270
4-picoline	3,4-lutidine	12	0.53	6.45	8	1.0	0.1	20	8.02	275.5
4-picoline	3-picoline	13	1.50	5.82	7	4.5	0.1	20	7.99	275.5
4-picoline	isoquinoline	14	2.95	5.46	8	4.5	0.55	15	8.04	325
3,4-lutidine	pyridine	15	3.5	5.31	8	7	0.95	20	8.02	273
3,4-lutidine	isoquinoline	16	2.31	5.46	7	3.5	0.6	25	8.01	330
3,4-lutidine	4-picoline	17	0.99	6.14	7	3.0	0.35	20	7.94	273
3,4-lutidine	3-picoline	18	1.60	5.82	8	4.5	0.1	15	7.85	275
3,4-lutidine	3,5-lutidine	19	1.03	6.14	6	1.5	0.1	15	7.98	278
3,5-lutidine	3,4-lutidine	20	0.69	6.45	9	3.5	0.1	15	7.91	284
3,5-lutidine	isoquinoline	21	2.28	5.46	8	3.5	0.75	12.5	7.93	330
3,5-lutidine	4-picoline	22	1.16	6.14	7	2.0	0.5	15	7.89	282.5
3,5-lutidine	pyridine	23	2.70	5.31	7	3.5	1.1	15	7.88	282.5

[a] Ionic strength maintained at 0.1 M with KCl, Tris buffer at 0.01 M adjusted to the appropriate pH with HCl, 25 °C. [b] Taken from previous work (0.2 M ionic strength, 25 °C).[4] [c] Maximal concentration of added pyridine starting from 0.005 M; molarity × 1000. [d] Number of data points including values for zero pyridine concentrations. [e] Range of rate constants from lowest to highest pyridine concentration; units 10^2 s^{-1}. [f] Error in the second-order rate constant is no greater than ±5%; units L mol^{-1} s^{-1}. [g] Wavelength for kinetic study. [h] Reaction code. [i] Rate constant at the intercept [x] = 0; units 10^2 s^{-1}. [j] xp and y are respectively the pyridinium-*N*-phosphonate substrate and pyridine nucleophile.

and oxonium ion catalytic terms are not large enough to interfere with the pyridine reaction at pH's between 5 and 10.



Experimental Section

Details of the experimental methods including sources of materials and kinetic procedures are given in previous papers.[4,9,10]

Results

The decomposition of pyridinium-*N*-sulfonates and pyridinium-*N*-phosphonates in pyridine buffers obeys pseudo-first-order rate constants linear in total pyridine concentration. The rate constant intercepts (k_{int}, eq 8) at zero pyridine concentration are due to background water or hydroxide ion catalyzed hydrolysis

$$k_{obsd} = k_{int} + k_x[x] \quad (8)$$

and to a small buffer catalysis component. Typically, tris(hydroxymethylamino)methane (Tris) was used as buffer as the pH's employed were usually outside the buffering range of the pyridines in question. Examples of the plots of pseudo-first-order rate constants against total pyridine concentration are illustrated in supplementary Figures 1 and 2 for the reactions respectively of 4-picoline with 3,4-lutidinium-*N*-phosphonate and 3,4-lutidine with 3-picolinium-*N*-sulfonate. Other examples of the data are recorded in previous work for similar systems.[4,9,10] The second-order rate constants for reaction of the pyridine (y) with pyridinium-*N*-phosphonate or sulfonate (k_y^{xp} or k_y^{xs}, respectively) were determined by dividing the slope of the linear pyridine buffer plots by the fraction of base form of the pyridine at the pH under examination. Previous work[4,9,10] has indicated that the rate laws involve the base form of the pyridine (eq 8).

The data for the second-order rate constants are recorded in Tables I and II for the phosphonate and sulfonate work, respectively. We include in these tables data from previous studies.

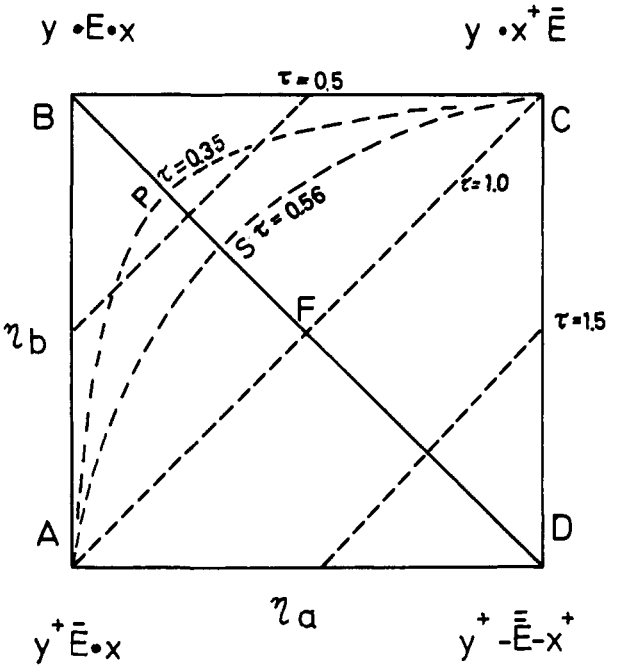


Figure 1. Idealized contour diagram of the potential energy surface for the transfer of a phosphoryl or sulfuryl group ($-E^- = -PO_3^{2-}$ or $-SO_3^-$) between pyridine donor and acceptor. The transition state must fall on the line BFD when the reaction is symmetrical. The dashed diagonal straight lines track the coordinates for transition states with the given τ values. The curved dashed lines represent the reaction coordinates for phosphoryl or sulfuryl group transfer.

(9) Bourne, N.; Hopkins, A.; Williams, A. *J. Am. Chem. Soc.* **1985**, *107*, 4327.
(10) Hopkins, A.; Day, R. A.; Williams, A. *J. Am. Chem. Soc.* **1983**, *105*, 6062.

Table II. Reaction of Substituted Pyridines with Pyridinium-*N*-sulfonates[a,d]

y[k]	xs[k]	Z[e]	k_y^{xs}[j]	pK_x	N[i]	Δk[g]	k_{int}[h]	[y][d]/M	pH	λ/nm[f]
pyridine	3,4-lutidine	1	2.55[b]	6.45						
pyridine	3,5-lutidine	2	5.35[b]	6.14						
pyridine	4-picoline	3	5.26[b]	6.14						
pyridine	3-picoline	4	9.4[b]	5.82						
pyridine	isoquinoline	5	21.0[c]	5.46	6	0.5	0.02	20	7.85	339
4-picoline	pyridine	6	74.7	5.31	10	2.2	0.1	25	7.94	270
4-picoline	isoquinoline	7	31.3[b]	5.46						
4-picoline	3,4-lutidine	8	3.68	6.45	12	0.12	0.01	20	7.85	274
4-picoline	3,5-lutidine	9	13.7	6.14	12	0.35	0.015	25	8.04	274
4-picoline	3-picoline	10	30.1	5.82	10	0.68	0.015	25	7.98	272
3,4-lutidine	4-picoline	11	15.6	6.14	10	0.4	0	25	7.85	274
3,4-lutidine	pyridine	12	110	5.31	13	3	0.1	20	7.96	274
3,4-lutidine	3,5-lutidine	13	15.4	6.14	12	0.4	0	25	8.05	277
3,4-lutidine	3-picoline	14	36.5	5.82	12	0.9	0.025	25	8.01	277
3,4-lutidine	isoquinoline	15	39.5[b]	5.46						
3,5-lutidine	4-picoline	16	15.5	6.14	10	0.35	0.015	20	7.97	286
3,5-lutidine	3,4-lutidine	17	8.35	6.45	12	0.23	0.02	25	8.02	283
3,5-lutidine	isoquinoline	18	37.0[b]	5.46						
3-picoline	3,4-lutidine	19	4.43	6.45	12	0.1	0	25	7.85	278
3-picoline	4-picoline	20	8.48	6.14	6	0.5	0	20	7.89	278
3-picoline	pyridine	21	81.5	5.31	8	2.2	0.12	25	7.94	278
3-picoline	isoquinoline	22	31.0[b]	5.46						

[a] Ionic strength maintained at 0.1 M with KCl, 25 °C, Tris buffer at 0.01 M adjusted to pH with HCl. [b] From the previous study.[9] [c] This value is the average of that of the previous work (0.207 L mol^{-1} s^{-1})[9] and of the present (0.212 L mol^{-1} s^{-1}). [d] Maximal concentration of pyridine starting from 0.005 M; molarity × 1000. [e] Reaction code. [f] Wavelength for the kinetic study. [g] Range of rate constants from lowest to highest pyridine concentrations; units 10^2 s^{-1}. [h] Rate constant at the intercept [x] = 0; units 10^2 s^{-1}. [i] Number of data points. [j] Error in the second-order rate constants is no greater than ±5%; units L mol^{-1} s^{-1}. [k] xs and y are respectively the x-substituted pyridinium-*N*-sulfonate and the y-substituted pyridine nucleophile.

Table III. Brønsted Equations for the Reactions of Substituted Pyridines with Pyridinium-*N*-phosphates[a]

Variation of the Nucleophile (y)

data points[b]	log k_x^{xp}[e]	pK_x	β_{nuc}[c]	C[c]	r[c]	x
1,11,15,23	0.69 ± 0.23	5.31	−0.14 ± 0.28	1.44 ± 1.72	0.338	pyridine
4,10,14,16,21[d]	0.256 ± 0.062	5.46	0.255 ± 0.119	−1.14 ± 0.71	0.567	isoquinoline
5,13,18	0.054 ± 0.010	5.82	0.271 ± 0.056	−1.52 ± 0.34	0.979	3-picoline
2,17,22	0.062 ± 0.002	6.14	−0.210 ± 0.01	1.35 ± 0.037	0.999	4-picoline
3,8,12,20	−0.074 ± 0.07	6.45	0.40 ± 0.12 (av 0.12)	−2.66 ± 0.72	0.918	3,4-lutidine

Variation of the Leaving Group (x)

data points	log k_x^{xp}[e]	pK_y	$\beta_{l.g.}$[c]	C[c]	r[c]	y
1,2,3,4	0.234 ± 0.007	5.82	−0.657 ± 0.139	4.05 ± 0.81	0.958	3-picoline
5,6,7,8,9,10	0.355 ± 0.05	5.31	−0.92 ± 0.02	5.24 ± 0.16	0.998	pyridine
11,12,13,14	−0.049 ± 0.023	6.14	−0.815 ± 0.06	4.96 ± 0.36	0.994	4-picoline
15,16,17,18,19	−0.186 ± 0.03	6.45	−0.602 ± 0.049	3.70 ± 0.29	0.990	3,4-lutidine
20,21,22,23	0.024 ± 0.011	6.14	−0.499 ± 0.038 (av −0.7)	3.09 ± 0.22	0.994	3,5-lutidine

[a] Conditions are given in Table I. [b] See Table I for reaction coding. [c] These parameters are for log $k = \beta(pK) + C$ and r is the correlation coefficient. [d] Data from this work yield a Brønsted equation similar to that for the investigation with a much more extensive range of nucleophilic pyridines under different conditions.[4] [e] "Identity" rate constant.

The conditions such as pH, background buffer, range of pyridine concentrations, intercept, and overall rate constant change are recorded in Tables I and II.

Brønsted-type plots of the logarithm of the second-order rate constant vs. either varying nucleophile pK or leaving group pK are illustrated for the attack of pyridines on a constant pyridinium-*N*-sulfonate (supplementary Figure 3), constant pyridine on pyridinium-*N*-sulfonates with varying leaving group (supplementary Figure 4), pyridines on a constant pyridinium-*N*-hosphonate (supplementary Figure 5), and constant pyridine on substituted pyridinium-*N*-phosphonates (supplementary Figure 6). The Brønsted parameters for these plots are shown in Tables III and IV for the phosphonates and sulfonates, respectively. Perusal of the figures indicates that there is better fit for the variation in leaving group. This is illusory because there is a larger selectivity to pK in these cases and deviations will not show up so well as in the variation of the nucleophile which has a lower Brønsted selectivity. We have included correlations in Tables III and IV which are relatively poor because these happen to be available as a result of work on the more precisely defined Brønsted relationships.

Four correlations have r values below 0.9 but are useful because they can interpolate an "identity" rate constant and any extrapolation is relatively small. The identity rate constants obtained from the four correlations have standard deviations from 70% to 13% of the value. The deviations quoted for the correlations could be misleading; where there are only a few points the good correlation could arise from fortuitous reasons. It is certain, from this and previous work,[3-5,9,10] that there are *natural deviations* which do *not* arise from the experimental method but from more underlying causes which we would term "microscopic medium effects". The Brønsted plots with the "wrong" sign (Tables III and IV, supplementary Figure 5) can be improved by including more points; there is little experimental inaccuracy in the individual rate parameters. Plots of pseudo-first-order rate constants against pyridine concentration have been observed to possess slight curvature for the transfer of the phosphoryl or sulfuryl groups.[3,11] This could be interpreted by a weak self-association of the pyridine catalyst[3] or by weak complexation between pyridine and substrate.

(11) Hopkins, A.; Bourne, N.; Williams, A., unpublished observations.

Table IV. Brønsted Correlations for the Reactions of Substituted Pyridines with Pyridinium-*N*-sulfonates[a]

Variation of the Nucleophile (y)						
data points[b]	log k_x^{xs}[d]	pK_x	β_{nuc}[c]	C[c]	r[c]	x
1,17,19,8	−1.12 ± 0.15	6.45	0.40 ± 0.26	−3.70 ± 1.52	0.737	3,4-lutidine
3,11,20,16	−0.90 ± 0.02	6.14	0.45 ± 0.09	−3.66 ± 0.52	0.964	4-picoline
2,9,13	−0.91 ± 0.01	6.14	0.42 ± 0.07	−3.50 ± 0.43	0.986	3,5-lutidine
6,12,21	−0.22 ± 0.16	5.31	0.20 ± 0.19	−1.27 ± 1.19	0.715	pyridine
4,10,14	−0.75 ± 0.01	5.82	0.54 ± 0.08	−3.87 ± 0.46	0.990	3-picoline
previous work[5,9]	−0.65 ± 0.02	5.46	0.23 ± 0.01 (av 0.37)	−1.91 ± 0.04	0.995	isoquinoline
Variation of the Leaving Group (x)						
data points[b]	log k_x^{xs}[d]	pK_y	β_{lg}[c]	C[c]	r[c]	y
1,2,3,4,5	−0.56 ± 0.02	5.31	−0.90 ± 0.03	4.22 ± 0.19	0.998	pyridine
6,7,8,9,10	−0.99 ± 0.05	6.14	−0.98 ± 0.19	5.02 ± 1.11	0.948	4-picoline
11,12,13,14,15	−1.07 ± 0.11	6.45	−0.87 ± 0.18	4.54 ± 1.04	0.942	3,4-lutidine
16,17,18	−0.85 ± 0.01	6.14	−0.64 ± 0.07	3.08 ± 0.45	0.993	3,5-lutidine
19,20,21,22	−0.75 ± 0.05	5.82	−1.02 ± 0.14 (av −0.88)	5.19 ± 0.84	0.981	3-picoline

[a] Conditions as given in Table II. [b] See Table II for reaction coding. [c] Parameters are for log $k = \beta(pK) + C$ and r is the correlation coefficient. [d] "Identity" rate constant.

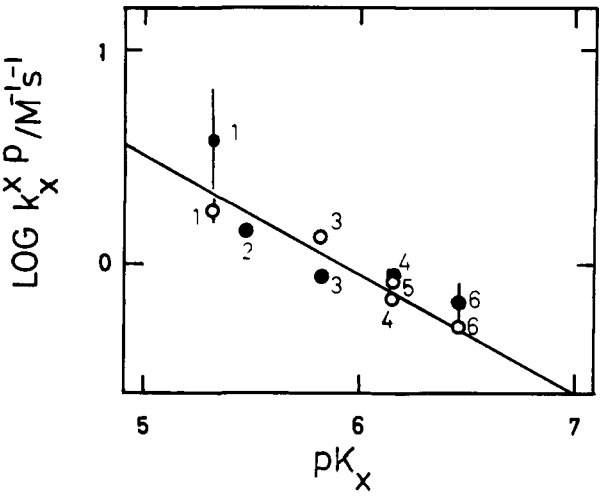


Figure 2. Dependence on the pK of the pyridine of the "identity" rate constant (k_x^{xp}) for transfer of the phosphoryl group between substituted pyridines. Bars represent standard deviations on each point, and the line is calculated from eq 9. The data are from Table III and the values are estimated from leaving group variation (○) and nucleophile variation (●). Points are identified as the following: pyridine, 1; isoquinoline, 2; 3-picoline, 3; 3,5-lutidine, 4; 4-picoline, 5; 3,4-lutidine, 6.

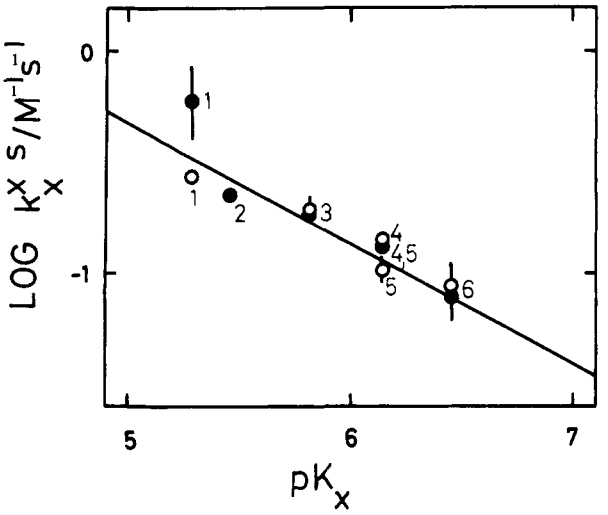


Figure 3. Dependence on pK of the pyridines of the "identity" rate constant (k_x^{xs}) for transfer of the sulfuryl group between substituted pyridines. Bars represent standard deviations on each point and the line is calculated from eq 10. The data are from Table IV and the values are estimated from leaving pyridine variation (○) and nucleophilic pyridine variation (●). Points are identified as the following: pyridine, 1; isoquinoline, 2; 3-picoline, 3; 3,5-lutidine, 4; 4-picoline, 5; 3,4-lutidine, 6.

Such association, which has precedent,[12] could give rise to random deviation of points due to weak interactions in the complex remote from the reaction center causing slight variations in association constant. Complexation by secondary valence forces has been discussed previously.[13] An extreme form of such complexation leading to very large scatter has been reported by Bender[14] for the reactions of phenyl esters with a cycloamylose.

It is encouraging that identity rate constants calculated from correlations for varying the nucleophile and varying the leaving group are in good agreement; this is because most of the calculations are *interpolations*. Thus we might expect a good value even if the Brønsted slope has the wrong *sign*—for example, pyridines with 4-picolinium-*N*-phosphonate and with pyridinium-*N*-phosphonate. Even when the calculation of identity rate constants requires *extrapolation*, the agreement with the interpolated values is quite good on a logarithm scale.

The values of the identity rate constants are illustrated in Figures 2 and 3 for the phosphonate and sulfonate, respectively; they obey the Brønsted eq 9 and 10. No reason is advanced for

$$\log k_x^{xp} = (-0.53 \pm 0.08)pK_x + 3.24 \pm 0.47 \qquad (r = 0.937) \tag{9}$$

$$\log k_x^{xs} = (-0.55 \pm 0.11)pK_x + 2.44 \pm 0.65 \qquad (r = 0.859) \tag{10}$$

the deviation of the pyridine point (determined in both cases from variation in the nucleophile) except that a long extrapolation is unavoidable in these cases.

Discussion

If the transition-state structures for the reactions of eq 6 and 7 involve complete ionization of the N–S or N–P bonds the selectivity (δ) of the identity rate constants would be +1 if measured against the transfer equilibrium of eq 11 as the calibrating equilibrium. The selectivity would be negative if the transition

$$x^+—E^- + x \rightleftharpoons |x \cdot x \cdot E|^{\ddagger} \rightleftharpoons x^+—E^- + x \tag{11}$$

state has two full N–S (or N–P) bonds as in eq 12. We shall assume in this work that the selectivity (against the calibrating

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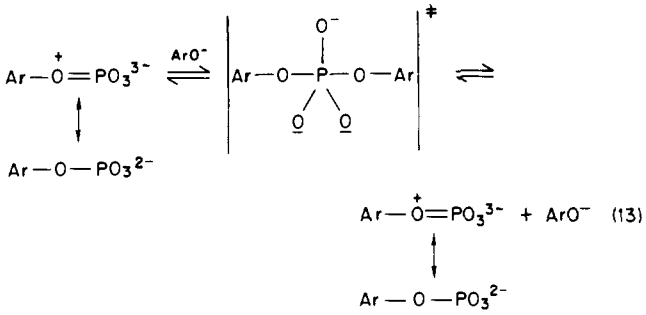
$$x^+—E^- + x \rightleftharpoons |x^+—E^{2-}—x^+|^{\ddagger} \rightleftharpoons x^+—E^- + x \qquad (12)$$

equilibrium of equation 11) would be −1 for a transition state like that in eq 12 representing a position D in Figure 1. This assumption is not strictly correct because the calibrating equilibrium for this transition state is that for the formation of the (hypothetical) pentacoordinate intermediate. Kreevoy and Lee[8] make essentially the same assumption in their treatment of hydrogen transfer, namely that positions D, F, and B on the potential energy diagram have respectively $\delta = -1$, 0, and +1. This assumption may be true for hydrogen and methyl transfer because it is unlikely that the bonding of these ligands to the central group in the ground and product states is different from a single bond order. Sulfuryl and phosphoryl group transfer provide the opportunity for multiple bonding in the ground and product states between the ligand and the central atom (eq 13). A zero value of δ could be obtained in the example shown because the negative charge gained on the



(13)

ether oxygen in going from the ground state to the transition state could be balanced by the positive charge gained on the attacking nucleophile. A similar problem would arise with sulfuryl group transfer between oxygen ligands. This is an important problem as it is known that there must be double bond character in ArO–P and ArO–S bonds from the considerable positive effective charge on the oxygen[2,10,15] in these esters. Ambiguity in δ could also arise in carboxyl group transfer studies as carboxylate esters have multiple bonding between ligand oxygen and the acyl group carbon. The effective charges on the nitrogen of pyridinium-*N*-sulfonate and pyridinium-*N*-phosphonate are close to unity,[3-5,9,10] indicating that the N–P and N–S bonding is first order. There would also seem to be no reason to expect multiple bonding from the nitrogen in the pyridinium species. For these reasons we believe the assumption for δ for the position D is justified in the present case.

The slope of the Brønsted correlation of the "identity" rate constants against the p*K* of the pyridine β_i divided by β_{eq} yields δ (−0.65 and −0.44 for phosphoryl and sulfuryl, respectively). For the purposes of this work we use the average value of β_{eq} (0.82 and 1.25 respectively for phosphoryl and sulfuryl) derived from the difference between the average β_{nuc} and the average β_{lg}. The values of the average β_{eq} agree reasonably will with those obtained previously from a smaller number of β values (1.07[4,15] and 1.05[3] for phosphoryl and 1.13[5,9,10] for sulfuryl). In our opinion the differences for the β_{eq} values for the two group transfers reflect randomness due to microscopic medium effects on the rate constants for individual substituents in the Brønsted correlations. This effect is accentuated in this study where, of necessity, only a small number of substituents has been utilized.

The application of eq 5 leads to a value of τ of 0.35 for phosphoryl group transfer and 0.56 for sulfuryl group transfer. These values give rise to bond orders (η) of 0.17 and 0.28 for N–P and N–S, respectively, in the transition states. This agrees with our previous conclusions for these reactions with use of a different approach. Kreevoy and Lee[8] indicated that δ is directly related to the charge change on the transferred group. In the present case there is a *reduction* in negative charge of 0.44 and 0.65 for the SO_3 and PO_3 groups of atoms, respectively. If we employ β_{eq} values obtained previously from a larger range of substituents to determine δ from β_i, the bond order for sulfuryl transfer does not alter significantly. The bond order for the phosphoryl group transfer comes out at $\eta = 0.25$ which is not very different from 0.17 derived above.

There have been relatively few experimental tests of Marcus or related theories as applied to solution group transfer reactions. Recently, Kreevoy[8] and Lewis[16] discussed two approaches which can be used here to indicate that the Marcus theory is applicable to the energy surfaces for sulfuryl and phosphoryl group transfer between pyridine nucleophiles. The value of β_{nuc} is dependent on τ according to eq 14 derived from Marcus theory by Kreevoy and Lee.[8] The term λ, the "intrinsic barrier" energy, is that defined previously.[8] When nucleophile and leaving pyridine have the same p*K* (in our case we choose p*K* = 6 as it lies at the center of the

$$\beta_{nuc}/\beta_{eq} = 0.5\tau - RT \ln K_{xy}/\lambda - (RT \ln K_{xy}/\lambda)^2(\tau - 1) \qquad (14)$$

range of p*K*'s studied) the value of K_{xy} becomes unity and $\beta_{nuc} = 0.5$. Sulfuryl and phosphoryl group transfers between pyridines are predicted to have β_{nuc} values of 0.35 and 0.14, taking β_{eq} to be 1.25 and 0.82, respectively. These values agree with the average values for β_{nuc} (Tables III and IV) for attack of pyridines on *N*-sulfonate (0.37) and *N*-phosphonate (0.12).

Lewis and Hu[16] derived the expression in eq 15 using Marcus theory. If we take the average of the β_{nuc} values for phosphoryl

$$\beta_i = \delta\beta_{eq} = \beta_{nuc} + \beta_{lg} \qquad (15)$$

group transfer (Table III) and the average of the β_{lg} values (Table III) the calculated value for $\delta\beta_{eq}$ is −0.58. This value is quite close to the experimental one for phosphoryl group transfer (−0.53, eq 9). Analogous calculations using the data of Table IV lead to a calculated value of $\delta\beta_{eq}$ of −0.51 for sulfuryl group transfer compared with the experimental value (−0.55, eq 10).

This work can say very little about second-order effects of the leaving group on β_{nuc} and of the nucleophile on β_{lg}. Jencks and Skoog[3] observed that the pyridinolysis of pyridinium-*N*-phosphonates has a more positive β_{nuc} as the basicity of the leaving pyridine increases. These cross-correlation effects (p_{xy})[17] were used to calculate the shape of the potential energy surface in the neighborhood of the transition state.

Larger variations in β_{nuc} and β_{lg} are found in the present investigation for both phosphoryl and sulfuryl group transfer. There is considerable scatter in the present correlations of β_{nuc} and β_{lg} with the appropriate p*K*, and this is probably due to the limited number of second-order rate constants measured over the p*K* range employed rather than to experimental error. Using the available data we can detect qualitative variations in β for both group-transfer reactions which are consistent with a transition state close to position B in the potential energy diagram (Figure 1). Probably the surface has a shallow curvature in this region for both group-transfer reactions as suggested for phosphoryl transfer by Skoog and Jencks.[3]

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Supplementary Material Available: Eight supplementary figures showing reactivities and Brønsted dependence (9 pages). Ordering information is given on any current masthead page.

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