

can be worked out, if the pathway is known or assumed. This is possible mainly for small molecules where there are few available pathways and reactions tend to be fast enough to fall in the measurable range. For larger molecules with many reaction pathways, the secondary reactions tend to be slow, giving slopes close to simple mass ratios.

In methyl iodide, for instance, the peak slopes for the reactions leading to $\text{CH}_2^+ + \text{I}^+$, $\text{CH}^+ + \text{I}^+$, $\text{C}^+ + \text{I}^+$, and $\text{H}^+ + \text{I}^+$ are all slightly smaller than the mass ratios for production of the lighter fragments by decay of methyl ions. All four deviations are explained if CH_3^+ first separates from I^+ to a distance of about 1 nm and then breaks down into the various final products. The reaction time is approximately 300 fs. Similar deductions can be made on the secondary decay of H_3^+ from charge separations in the methyl compound dications, where lifetimes of the order of 20 fs are found.²⁵ Alternative interpretations involving directed secondary energy releases would be possible, but the fast reaction interpretation is more natural and is supported by the agreement between times for different reactions and for different isotopic species.

V. Concluding Remarks

Charge-separation mass spectrometry is an absolutely new technique, being used at present by just three groups worldwide. The experiments are not yet routine in any laboratory, and it generally takes several hours to gather a spectrum; this situation may soon improve as no fundamental difficulties are involved. The emphasis hitherto has been on the formation and stability of doubly charged ions, and extensions to triple and

higher multiple ionization are already being investigated, but the characteristics of the technique, described in this Account, should make it more widely useful than just a tool for the study of highly charged ions. For instance, the pair-sum spectra, and presumably the equivalent spectra from higher multiple ionization, emphasize high masses, including parent ions even though high-energy radiation is used. Reference to the full CSMS spectra then gives a fragmentation pattern for each high-mass species. This suggests applications similar to those of "soft" ionization methods in characterization of large or delicate molecules, such as biopolymers or van der Waals clusters in molecular beams. The mechanistic information available from peak shapes in the spectra is unparalleled, including the identity of neutral species, kinetic energy releases, and sometimes reaction rates. Peak shapes in CSMS should be an important complement to metastable peaks in conventional mass spectra as a probe of singly charged ion fragmentations, because they refer to fast, majority reaction processes rather than to a possibly unrepresentative minority of slow reactions. Applications to analysis are speculative at present and must await the technical developments, now in progress, toward higher mass resolution, greater sensitivity, and the study of nonvolatile samples.

I am most grateful to my co-workers in Oxford and Paris who have made major contributions to this work and to Prof. K. Kimura at the Institute for Molecular Science, Okazaki, Japan, for hospitality during the writing process. Prof. R. J. Fleming kindly read parts of the manuscript and suggested valuable changes. Thanks are also due to the SERC who have supported the research in Oxford.

Concerted Mechanisms of Acyl Group Transfer Reactions in Solution

ANDREW WILLIAMS

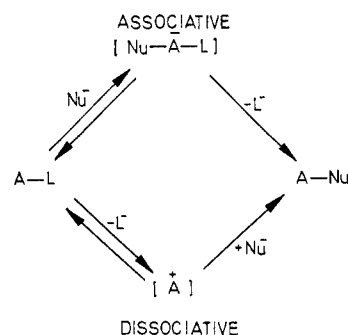
University Chemical Laboratories, Canterbury, England CT2 7NH

Received January 23, 1989 (Revised Manuscript Received June 22, 1989)

This Account describes recent studies of acyl group transfer reactions in aqueous solution using polar substituent effects in systems where it is possible to discriminate between concerted and nonconcerted mechanisms. Distinction between concerted and stepwise mechanisms is a major problem in chemistry because there are few reactions involving a single bond change; this importance is amply recognized by the attention devoted to the subject. The most celebrated discussions of concertedness refer to pericyclic reactions,¹ base-catalyzed elimination,^{2a} and nucleophilic aliphatic substitution reactions.^{2b} It is conceptually impossible to demonstrate a concerted mechanism which may be defined as a process with a single transition state;³

Andrew Williams has been the subject of a previous biographical note in this journal (*Acc. Chem. Res.* 1984, 17, 425). Since that time he has become Chairman of the Chemistry Department at the University of Kent.

Scheme I Stepwise Mechanisms for the Transfer of the Acyl Group (A) between Nucleophiles (L^- and Nu^-)



nonconcerted mechanisms can be demonstrated by the observation or inference of the existence of an inter-

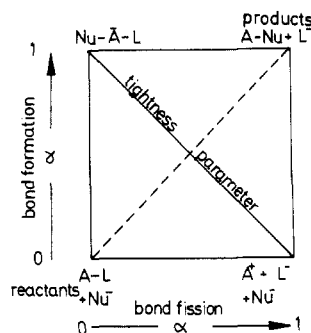
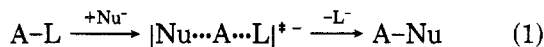


Figure 1. Reaction map for displacement of the leaving group (L^-) by a nucleophile (Nu^-) of similar structure. The "bonding" change (bond and solvation) for a bond in the transition state is measured as a function of the overall change in the bond fission or formation by $\alpha = \beta/\beta_{eq}$. A symmetrical concerted reaction has its transition state somewhere on the "tightness" diagonal. The dashed line represents the concerted pathway where bond formation is balanced by bond fission in the transition state. The representation is of a reaction surface where the energy of the system is a vertical coordinate.

mediate. Investigations of concertedness as described above are therefore of necessity subject to considerable scrutiny and critique.⁴

Concerted mechanisms of acyl group transfer between nucleophilic donors (L^-) and acceptors (Nu^-) have hitherto been thought to play a minor role compared with those of the well-established stepwise processes generalized in Scheme I. We shall use the term "acyl" to mean the electrophilic component (A) of any acid ($A-OH$) such as carbonyl (RCO), phosphoryl (O_3P^{2-}), sulfuryl (O_3S^-), sulfonyl (RSO_2), sulfenyl (RS), or phosphinyl (R_2PO). Carbonyl group transfer reactions between strong nucleophiles were elegantly shown to involve an associative mechanism by Bender;⁵ contemporary thought on acyl group transfer reactions is still dominated by the idea of associative intermediates although there is now a substantial body of definitive evidence for the dissociative path (Scheme I).⁶

The existence of mechanisms of acyl group transfer reactions with two extremes of timing of bond formation and fission begs the existence of a concerted process under certain conditions (eq 1) which has "in between" timing. The three types of mechanism can be repre-



sented on a single reaction map (Figure 1) describing the energy surface of the reaction. The concerted pathway can traverse any portion of the reaction map and is not confined to the diagonal between reactants and products.⁷

(1) Isaacs, N. S. *Physical Organic Chemistry*; Longman Scientific and Technical: London, 1987; Chapter 4.

(2) (a) Reference 1, Chapter 11. (b) Reference 1, Chapter 10.

(3) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 209.

(4) (a) Bordwell, F. G. *Acc. Chem. Res.* **1972**, *5*, 374; **1970**, *3*, 281. (b) Abraham, M. H.; McLennan, D. J. *J. Chem. Soc., Perkin Trans. 2* **1977**, 873. (c) Snee, R. A. *Acc. Chem. Res.* **1973**, *6*, 46. (d) McLennan, D. J. *Ibid.* **1976**, *9*, 281. (e) Ollis, W. D.; Rey, M.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1009. (f) Chantropromma, K.; Ollis, W. D.; Sutherland, I. O. *Ibid.* **1983**, 1049.

(5) (a) Bender, M. L. *J. Am. Chem. Soc.* **1951**, *73*, 1626. (b) Bender, M. L. *Chem. Rev.* **1969**, *60*, 53.

(6) (a) Williams, A.; Douglas, K. T. *Ibid.* **1975**, *75*, 627. (b) Thea, S.; Cevasco, G.; Guanti, G.; Hopkins, A.; Kashefi-Naini, N.; Williams, A. *J. Org. Chem.* **1985**, *50*, 2158. (c) Cevasco, G.; Guanti, G.; Hopkins, A.; Thea, S.; Williams, A. *Ibid.* **1985**, *50*, 479.

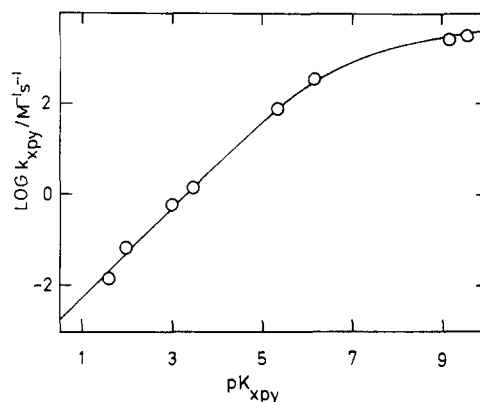
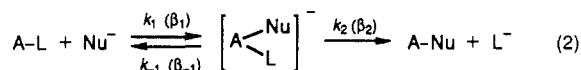


Figure 2. Nonlinear Brønsted plot for reaction of substituted pyridines (xpy) with acetic anhydride to yield *N*-acetylpyridinium ion product. Data are redrawn from ref 9b; the break point cannot be predicted from simple considerations, but its observation is definitive of an intermediate.

Polar Substituent Effects

We utilize as a diagnostic tool the effect of polar substituents on reaction rates and equilibria. This effect, in the form of a Hammett or Brønsted slope, measures the charge difference on an atom between states. Effective charge is defined as the magnitude of charge required to give the observed polar effect compared with that obtained for a defined unit change of charge in a standard ionization equilibrium.⁸ Thus the Brønsted β is the change in effective charge for a reaction relative to the charge change in the ionization against which the Brønsted plot is measured.

The observation of a nonlinear Brønsted, Hammett, or other type of free energy plot relating to polar substituents is classic evidence for a change in the structure of a transition state. A "convex upward" break in the free energy plot is evidence of a mechanism with consecutive transition states which change their dominance in the range of the correlation. An excellent example of such a nonlinear plot is shown in Figure 2.⁹ A change in rate-limiting step which refers to the general equation 2^{10a} occurs when the partitioning ratio (k_2/k_{-1})



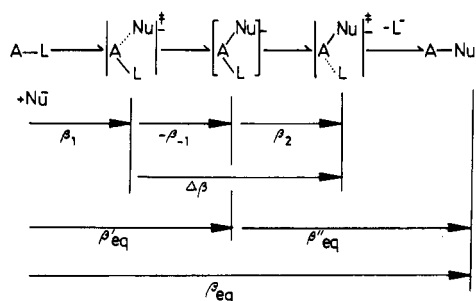
(7) (a) The transition state of the concerted path can be like one of the intermediates; the bonds can be strong or weak in the transition state, which can then be referred to respectively as "tight" or "open" (associative or dissociative respectively). The reaction coordinate can even pass through a structure corresponding to that of an intermediate and still be concerted provided that the structure has a lifetime less than that of a bond vibration; such a process is called an "enforced" concerted mechanism.^{7b,c} (b) Jencks, W. P. *Acc. Chem. Res.* **1980**, *13*, 161. (c) An "enforced" mechanism should not be confused with a mechanism forced to take a concerted path because the transition-state energy is more favorable than that of a relatively stable intermediate on a stepwise path.

(8) (a) Williams, A. *Acc. Chem. Res.* **1984**, *17*, 425. (b) Thea, S.; Williams, A. *Chem. Soc. Rev.* **1986**, *15*, 125.

(9) (a) Batty, P. J.; Ihsan, E. M.; Moodie, R. B. *J. Chem. Soc., Perkin Trans. 2* **1980**, 741. (b) Castro, C.; Castro, E. A. *J. Org. Chem.* **1981**, *46*, 2939. (c) Castro, E. A.; Moodie, R. B. *J. Chem. Soc., Chem. Commun.* **1973**, 828. (d) Bond, P. M.; Castro, E. A.; Moodie, R. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 68. (e) Castro, E. A.; Freudenberger, M. *J. Org. Chem.* **1980**, *45*, 906. (f) Castro, E. A.; Santander, C. L. *Ibid.* **1985**, *50*, 3595. (g) Castro, E. A.; Gil, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 7611.

(10) (a) Each rate constant in eq 2 has its own linear Brønsted equation, and k_{nuc} is the overall, composite, second-order rate constant. (b) The sign of $\Delta\beta$ is negative for a stepwise acyl group transfer reaction where the variation is on Nu^- ; the value k_0 is a disposable parameter. (c) Equation 2 reduces to $\log k_{nuc}/k_0 = \beta_1\Delta(pK)$ when $\Delta(pK) > 0$; it reduces to $\log k_{nuc}/k_0 = (\beta_1 - \beta_{-1} + \beta_2)\Delta(pK)$ when $\Delta(pK) < 0$. (d) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362.

Scheme II
Effective Charge Diagram for the Reaction of Eq 2^a



^a β refers to the change in effective charge on the variant nucleophile (Nu^-).

changes from less than 1 to greater than 1. Figure 2 is definitive evidence for a change in rate-limiting step and hence for a stepwise mechanism.

Linearity of a free energy plot is not, of its own, evidence of a mechanism with a single transition state; it indicates that the transition state has constant structure over the range of substituents employed. If it can be predicted that a change in rate-limiting step for a putative stepwise process will occur in the substituent range utilized, the observation of a linear plot is evidence of a concerted mechanism.

Prediction of the position of a break in a free energy correlation is not normally possible but can be made for reactions involving displacement of leaving groups by nucleophiles of similar structure. If the nucleophilic substituent in eq 2 is varied and the leaving group is invariant, the Brønsted plot of rate constant and $\text{p}K$ of nucleophile is governed by eq 3¹⁰ and consists of two

$$k_{\text{nuc}}/k_0 = 10^{\beta_1 \Delta(\text{p}K)} / (1 + 10^{\Delta\beta \Delta(\text{p}K)}) \quad (3)$$

straight lines intersecting smoothly at $\Delta(\text{p}K) = 0$ ($\Delta(\text{p}K) = \text{p}K_{\text{nuc}} - \text{p}K_{\text{lg}}$).^{10b-d} The intersection is only predictable if the rate constants k_2 and k_{-1} refer to the loss of structurally similar groups (L^- and Nu^- , respectively) obeying the same "microscopic" linear Brønsted law. The parameter $\Delta\beta$ is the effective charge difference for the nucleophile (Nu^-) between the two transition states (Scheme II). When the value of $\Delta\beta$ ($\beta_{-1} - \beta_2$) is 0, the effective charge on the two transition states (Scheme II) is the same, and this can only be the case if they are of the same structure; in other words, there is a single transition state in the reaction mechanism, which is therefore concerted. Under these circumstances, eq 3 reduces to a linear Brønsted plot.

Diagnosis of a single transition state requires data over a range of $\Delta(\text{p}K)$ values above and below 0. A value of $\Delta\beta = 0$ for best fit of the data indicates conservatively that the difference in effective charge on the two transition states in the putative stepwise mechanism is less than the error in $\Delta\beta$. A typical uncertainty of 0.1 in $\Delta\beta$ means that the effective charge on the putative intermediate differs from that on one of its transition states by less than 0.05 units. In carbonyl transfer this difference is compared with an overall change of 1.7 units, making it difficult to account for the stability of such an intermediate.^{11,12}

Curvature in a Brønsted correlation can be caused by alterations in transition-state structure in a concerted

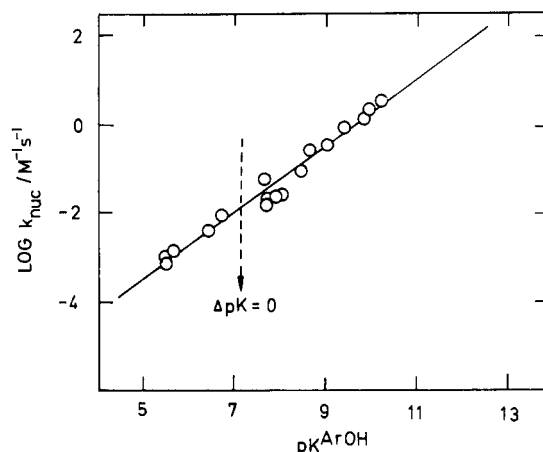


Figure 3. Brønsted type dependence of k_{nuc} for attack of phenolate ions on 4-nitrophenyl acetate. Graph is redrawn from ref 10d, and the position of the predicted $\text{p}K_{\text{ArOH}}$ for the change in rate-limiting step of the putative stepwise mechanism is indicated by the dotted arrow.

reaction.¹³ This phenomenon is usually very small^{11,12} and would not be associated with a particular $\Delta(\text{p}K)$ value.

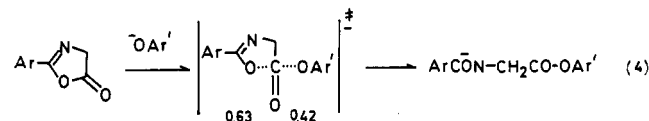
Transition-State Structure

The change in effective charge obtained from β , ρ , or some other parameter may be used to position the transition state in the reaction map (Figure 1) relative to those of the four discrete states. This can be done by comparing the effective charge change to the transition state with that to the product state for each of the two bonding changes; this ratio, α , is called the Leffler index ($\alpha = \beta/\beta_{\text{eq}}$).^{8a} The index α for a particular bond change refers to the effective charge change caused by both solvation and bonding effects. For convenience, we omit solvent in the descriptions of transition states in the text. The index α effectively compares *states*, not *bonds*.

Carbonyl Group Transfer

Carbonyl group transfer between strong nucleophiles has been amply justified to involve an addition intermediate.¹⁴ It is interesting to note that Bender's demonstration of associative intermediates in carbonyl group transfer between strong nucleophiles^{5a} was contemporary with Dewar's discussion of a concerted process.¹⁵

Leffler's index was measured for both bond formation and fission for the attack of aryl oxide ions on the carbonyl in oxazolinones (eq 4).^{16,17} It was determined



(13) Jencks, W. P. *Chem. Rev.* 1985, 85, 512.

(14) (a) Ingold, C. K., *Structure and Mechanism in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1951. (b) Capon, B.; Ghosh, A. K.; Grieve, D. M. A. *Acc. Chem. Res.* 1981, 14, 306. (c) Capon, B.; Dosunnu, M. I.; Matos-Sanchez, M. de N. *Adv. Phys. Org. Chem.* 1985, 21, 37. (d) McClelland, R. A.; Santry, L. J. *Acc. Chem. Res.* 1983, 16, 394.

(15) Dewar, M. J. S. *The electronic theory of organic chemistry*; Oxford University Press: Oxford, 1948.

(16) Curran, T. C.; Farrar, C. R.; Niazy, O.; Williams, A. J. *Am. Chem. Soc.* 1980, 102, 6828.

(11) Skoog, M. T.; Jencks, W. P. *J. Am. Chem. Soc.* 1984, 106, 7597.
(12) Dietze, P. E.; Jencks, W. P. *Ibid.* 1986, 108, 4549.

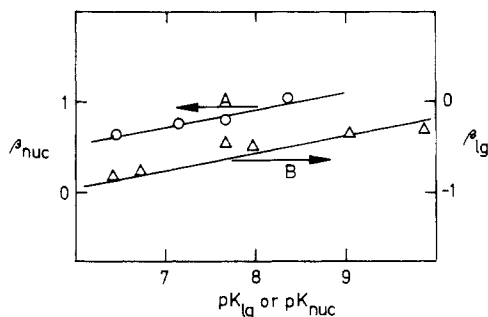


Figure 4. Dependence of β_{ig} (B) and β_{nuc} (A) on pK_{nuc} and pK_{ig} , respectively, for the reaction of aryl oxide ions with aryl acetates. The slopes of the lines are the cross correlation coefficients (ρ_{xy} ; Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* 1977, 88, 7948) which are equal to each other. The data is redrawn from ref 19.

that the same transition state was being measured for both indices so that the observation of substantial bond changes in both forming and breaking bonds is strongly suggestive of a concerted pathway;¹⁸ bond formation is slightly in advance of bond fission.

Displacement of 4-nitrophenolate ion from 4-nitrophenyl acetate by reaction with aryl oxide ions obeys a linear Brønsted dependence (Figure 3) over values of $\Delta(pK)$ significantly greater than and less than 0.^{10d} This may be explained on the basis of a concerted mechanism. If only those values of k_{nuc} are used that lie in the region of $\Delta(pK) < 0$ for the putative stepwise mechanism, the β_{nuc} is approximately 0.8 and will refer to the charge difference between reactants and the transition state of the second step (k_2). The value of β'_{eq} for formation of the addition intermediate is less than β_{nuc} (see Scheme II) because $\beta_{nuc} = \beta_1 + \beta_2 - \beta_{-1}$ and $\beta'_{eq} = \beta_1 - \beta_{-1}$. The value of β''_{eq} for formation of ester product from the addition intermediate should exceed 0.9 because $\beta''_{eq} = \beta_{eq} - \beta'_{eq}$ and $\beta_{eq} = 1.7$ (see Scheme II). The observed change in charge for k_1 (measured by β'_{eq}) is smaller than that for k_2 (measured by β''_{eq}), which is absurd because k_1 involves full bond formation and k_2 involves no bond change to the nucleophile bearing the polar substituent variation. The absurdity disappears if the mechanism involves a single transition state.

Values of β_{nuc} and β_{ig} , obtained from the Brønsted slopes for varying nucleophile and leaving group, respectively, vary significantly as a function of pK_{ig} and pK_{nuc} .¹⁹ Such an observation (Figure 4) is excellent evidence for a concerted process and indicates that the transition-state structure varies within the range of structurally related nucleophiles studied. The position of the transition state on the reaction map for acetyl group transfer between identical phenolate ion nucleophiles can be located from the Brønsted plot with either nucleophile or leaving-group variation. For example, the Brønsted dependence for attack of aryl oxide ions on 4-nitrophenyl acetate is linear, and thus the slope at the point for attack of 4-nitrophenolate ion may be calculated; division of this slope by 1.7 (the β_{eq} for

(17) Chrystiuk, E.; Jusoh, A.; Santafianos, D.; Williams, A. *J. Chem. Soc., Perkin Trans. 2* 1986, 163.

(18) The numbers attached to the bonds in the structures represent the Leffler α values for the formation of the bonds from either product or reactant regardless of whether the bond is being formed or broken in the actual reaction.

(19) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* 1989, 111, 2647.

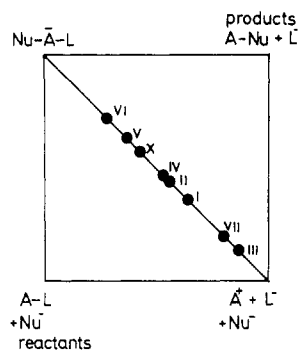
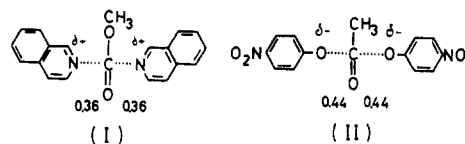


Figure 5. Reaction map for the concerted transfer of a general acyl group (A) between identical leaving group and nucleophile. The transition states lie on the "tightness" diagonal, and the points are identified by roman numerals in the text.

reaction) gives the position for a transition state containing both 4-nitrophenolate leaving and attacking groups. Figure 5 illustrates the positions of the transition state for a number of virtual reactions. The transition state is tighter for the more basic nucleophiles.

The Brønsted dependence of the rate constants for displacement of isoquinoline from *N*-(methoxycarbonyl)isoquinolinium ion by pyridine nucleophiles is linear over $\Delta(pK)$ values less than and greater than 0.²⁰ This observation is consistent with a concerted process, and the Leffler index (0.36)^{17b} indicates a transition state (I) that has bond fission slightly in advance of bond formation similar to that for the 4-nitrophenolate reaction (II).



Moodie and Castro showed that the reactions of pyridines with aryl esters involve addition intermediates⁹ as do the reactions of thiolate ions with thioesters;²¹ the latter result could be explained on the basis of divalent sulfur stabilization of adjacent negative charge.²² Although the reaction mechanism of hydroxide ion attack on aryl esters is concerted, the transition state is like the associative intermediate.²³

Both Kevill²⁴ and Bentley²⁵ demonstrate that acyl chloride solvolysis is concerted, and there is good evidence from ion cyclotron resonance spectroscopy for concerted carbonyl group transfer in the gas phase.²⁶ Theoretical studies support concerted and stepwise gas-phase transfer of the formyl group, depending on the structure of the nucleophile.²⁷

(20) Chrystiuk, E.; Williams, A. *Ibid.* 1987, 109, 3040.

(21) Hupe, D. J.; Jencks, W. P. *Ibid.* 1977, 99, 451.

(22) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965.

(23) Shames, S. L.; Byers, L. D. *J. Am. Chem. Soc.* 1981, 103, 6170.

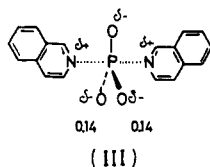
(24) Kevill, D. N.; Kim, C. B. *Bull. Soc. Chim. Fr.* 1988, 383; *J. Chem. Soc., Perkin Trans. 2* 1988, 1353.

(25) (a) Bentley, T. W.; Carter, G. E.; Harris, H. C. *J. Chem. Soc., Chem. Commun.* 1984, 387; *J. Chem. Soc., Perkin Trans. 2* 1985, 983. (b) Bentley, T. W.; Harris, H. C. *Ibid.* 1986, 619.

(26) (a) Kim, J. K.; Caserio, M. C. *J. Am. Chem. Soc.* 1981, 103, 2124. (b) Pau, K. K.; Kim, J. K.; Caserio, M. C. *Ibid.* 1978, 100, 3831. (c) Takashima, C.; Jose, S. M.; do Amaral, A. T.; Rivero, J. M. *J. Chem. Soc., Chem. Commun.* 1983, 1255. (d) Han, C. C.; Brauman, J. I. *J. Am. Chem. Soc.* 1987, 109, 589.

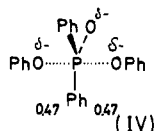
Concerted Acyl Group Transfer in the Phosphorus Acid Series

A concerted mechanism can be inferred from the linear Brønsted plot over a wide range of positive and negative $\Delta(\text{p}K)$ values for the transfer of the phosphoryl group (O_3P^{2-}) from *N*-phosphorylisoquinolinium ion to substituted pyridines.²⁸ A similar observation was also made for other pyridine donors.¹¹ The Leffler index (0.14) for the attack of the isoquinoline nucleophile on the *N*-phosphorylisoquinolinium ion indicates a very open transition state (III) where bond fission is considerably advanced over formation. Possibly the me-



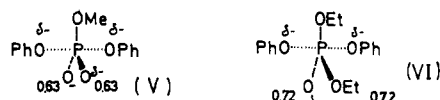
taphosphate ion like structure has some residual stability, which is not, however, sufficient to promote a discrete intermediate. In the present case, the stereochemistry of the transition state is probably trigonal bipyramidal, but there seems to be no reason why constrained molecules should not participate in a mechanism where nucleophiles enter and leave on the same side of the central atom.²⁹

Linearity of the Brønsted plot for attack of aryl oxide ions on 4-nitrophenyl diphenylphosphinate over a wide range of $\Delta(\text{p}K)$ values indicates a single transition state in this transfer reaction.³⁰ The position of the transition state in the reaction map is dependent on the basicity of the aryl oxide ions. For phenolate ion leaving and attacking groups, the Leffler index indicates that extent of bond formation and fission is balanced (IV).



Since the dianionic phosphoryl group transfer and the transfer of the neutral diphenylphosphinyl group are concerted, it is reasonable to assume that the transfer of a monoanionic phosphoryl function is also concerted under suitable conditions, in particular, where the leaving group and nucleophile are weakly basic. The attack of phenolate anion on aryl esters of diethyl phosphate and methyl phosphate monoanion ($\text{ArOPO}(\text{OEt})_2$ and ArOPO_2OMe respectively) have almost identical values of β_{1g} , indicating that the oxyanion in the latter ester does not participate significantly in the expulsion of the leaving group.³¹ Bond formation is relatively advanced over bond fission in the transfer of both the diethoxyphosphoryl group and the methoxyphosphoryl monoanion between unsubstituted pheno-

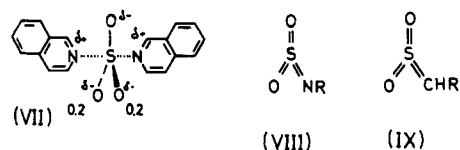
late ion nucleophiles (V and VI respectively) where the transition states are relatively "tight".



Stereochemical probes have also demonstrated the existence of both concerted and nonconcerted pathways in the transfer of the phosphorus acyl group.^{32,33}

Concerted Acyl Group Transfer in the Sulfur Acid Series

Transfer of the sulfonyl group (O_2S^-) has been shown to be concerted in the reaction of substituted pyridines with *N*-(sulfonyl)isoquinolinium ion. The linear Brønsted correlation³⁴ over a wide range of $\Delta(\text{p}K)$ values has a slope of 0.23, which when combined with the β_{eq} value (1.25) gives a Leffler index of 0.18, indicating a very open transition state for the symmetrical transfer of sulfonyl between isoquinoline nucleophiles (VII). Even though the sulfur trioxide monomer is



known in the gas phase,³⁵ its stability is not sufficient to give rise to a discrete intermediate. So far as we are aware, the sulfur trioxide monomer has never been demonstrated in a condensed phase. Replacing one of the oxygens of the sulfur acid by NR^- or CHR^- yields acyl functions which transfer through the stepwise dissociative pathway involving sulfene imine (VIII) and sulfene (IX) intermediates.^{36,37}

Both stepwise and concerted mechanisms have been actively proposed for transfer of the neutral sulfonyl group.³⁸ The reaction of oxyanions with 4-nitrophenyl 4-nitrobenzenesulfonate possesses a Brønsted dependence consistent with a concerted displacement mechanism.³⁹ The slope of the Brønsted plot indicates that the Leffler index for the symmetrical reaction for transfer of the sulfonyl group between 4-nitrophenolate ion has bond formation slightly in advance of bond fission ($\alpha = 0.57$), as illustrated in X. A study of the ring fission of a sultone by displacement at the sulfonyl group with aryl oxide ions indicates that bond forming and bond fission are equally advanced in the transition state of the concerted mechanism (XI).⁴⁰

The results of a study of the variation of substituent on the reaction of aryl thiolate anions with sulfenate

(27) (a) Bayly, C. I.; Grein, F. *Can. J. Chem.* **1988**, *66*, 149. (b) Blake, J. F.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1987**, *109*, 3856. (c) Burgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563. (d) Williams, I. H.; Spangler, D.; Maggiora, G. M.; Schowen, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 7717. (e) Williams, I. H.; Maggiora, G. M.; Schowen, R. L. *Ibid.* **1980**, *102*, 7831. (f) Sheldon, J. C. *Aust. J. Chem.* **1981**, *34*, 1189.

(28) Bourne, N.; Williams, A. *J. Am. Chem. Soc.* **1984**, *106*, 7591.

(29) Usher, D. A.; Erenrich, F. S.; Eckstein, F. *Proc. Natl. Acad. Sci. U.S.A.* **1972**, *69*, 115.

(30) Bourne, N.; Chrystiuk, E.; Davis, A. M.; Williams, A. *J. Am. Chem. Soc.* **1988**, *110*, 1890.

(31) Unpublished observations by Davis, A. M., and Ba-Saif, S., University of Kent, 1989.

(32) Hall, C. R.; Inch, T. D. *Tetrahedron* **1980**, *36*, 2059.

(33) (a) Harnett, S. P.; Lowe, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1416. (b) Lowe, G. *Acc. Chem. Res.* **1983**, *16*, 244. (c) Buchwald, S. L.; Friedman, J. M.; Knowles, J. R. *J. Am. Chem. Soc.* **1984**, *106*, 4911. (d) Cullis, P. M.; Iagrossi, A.; Rous, A. *J. Ibid.* **1986**, *108*, 7869. (e) Cullis, P. M.; Iagrossi, A. *Ibid.* **1986**, *108*, 7870.

(34) Bourne, N.; Hopkins, A.; Williams, A. *Ibid.* **1985**, *107*, 4327.

(35) Rys, P. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 807.

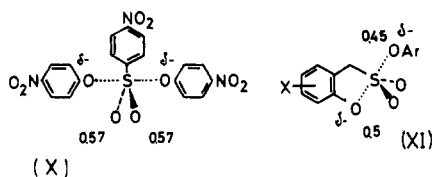
(36) Williams, A.; Douglas, K. T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1727.

(37) (a) Davy, M. B.; Douglas, K. T.; Loran, J. S.; Steltner, A.; Williams, A. *J. Am. Chem. Soc.* **1977**, *99*, 1196. (b) King, J. F.; Beatson, R. P. *Tetrahedron Lett.* **1975**, 973.

(38) (a) Ciuffarin, E.; Fava, A. *Prog. Phys. Org. Chem.* **1968**, *6*, 81. (b) Kice, J. L. *Adv. Phys. Org. Chem.* **1980**, *17*, 65.

(39) D'Rozario, P.; Smyth, R. L.; Williams, A. *J. Am. Chem. Soc.* **1984**, *106*, 5027.

(40) Deacon, T.; Farrar, C. R.; Sikkel, B. J.; Williams, A. *Ibid.* **1978**, *100*, 2525.



esters⁴¹ indicate that this acyl function is transferred via a concerted pathway. Stereochemical probes indicate that derivatives of sulfur acids at the tetravalent and hexavalent levels of oxidation transfer the acyl function via concerted mechanisms.⁴² There is, however, ample preparative evidence for the stability of

(41) (a) Hupe, D. J.; Pohl, E. R. *Isr. J. Chem.* 1985, 26, 395. (b) Freter, R.; Pohl, E. R.; Wilson, J. M.; Hupe, D. J. *J. Org. Chem.* 1979, 44, 1771. (c) Wilson, J. M.; Bayer, R. J.; Hupe, D. J. *J. Am. Chem. Soc.* 1977, 99, 7922.

(42) (a) Sabol, M. A.; Andersen, K. K. *Ibid.* 1969, 91, 3603. (b) Andersen, K. K.; Caret, R. L.; Karup-Nielsen, I. *Ibid.* 1974, 96, 8026. (c) Tillett, J. G. *Chem. Rev.* 1976, 76, 747.

possible associative intermediates in sulfur acid acyl group transfer.⁴³

Conclusions

Acyl group transfer reactions in solution should not be assumed to involve only addition or associative intermediates in their mechanisms. Discussion of mechanism for transfer of acyl groups between nucleophiles should seriously consider the concerted pathway as well as the stepwise mechanisms following dissociative and associative routes. Strongly basic donor and acceptor nucleophiles favor "tight" transition states whereas weakly basic nucleophiles encourage "open" or dissociative transition states. Concerted mechanisms of acyl group transfer are more common among derivatives of all acids than was previously supposed.

(43) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* 1974, 96, 6735.

Toward Molecular Magnets: The Metal-Radical Approach

ANDREA CANESCHI, DANTE GATTESCHI,* and ROBERTA SESSOLI

Department of Chemistry, University of Florence, Florence, Italy

PAUL REY

Departement de Recherche Fondamentale, Centre d'Etudes Nucleaires, Grenoble, France

Received June 2, 1988 (Revised Manuscript Received July 25, 1989)

Molecular materials are characterized by being made up by discrete molecules. This structural property gives in principle many possibilities to modulate the bulk electrical, magnetic, and optical properties of the material by choosing appropriately the constituent molecules. At the same time, however, it is a challenge to develop synthetic strategies that allow the control of the spatial distribution of the molecules in the lattice. In fact, the bulk properties are always determined by cooperative interactions between the constituent molecules, which consequently must be assembled in the lattice in such a way as to maximize the bulk response.

Beyond the basic problem of establishing structure-property correlations, molecular materials appear as promising in order to develop new properties or novel associations of properties. As examples, we can mention

the active research on organic materials with nonlinear optical properties¹ and the studies on organic conductors and superconductors.² In this framework, an area of growing interest is that of high-spin molecules³⁻⁷ and molecular magnetic materials,^{8,9} which aims at the synthesis of compounds that have spontaneous magnetization below a critical temperature. Molecular magnets are desirable because they may have magnetic properties associated with light weight (plastic magnets), solubility in organic solvents, or optical transparency, which could make them useful in the development of new electronic devices. Further, they provide the fun of the intellectual challenge to synthesize new classes of compounds that do not yet exist.

In this Account we provide a concise resume of magnetic phenomena, report briefly on the different strategies that have been developed up to the moment for designing molecular magnetic materials, and then summarize our own approach and the main results that

Andrea Caneschi was born in 1958. He got a Laurea in Chemistry at the University of Florence in 1983 and has now completed his doctorate work under the instruction of Prof. D. Gatteschi.

Dante Gatteschi was born in 1945. He got a Laurea in Chemistry at the University of Florence in 1969 and was appointed as Assistente in the same university in the same year. In 1980 he became Professor of General and Inorganic Chemistry in the University of Florence, where he served as Chairman of the Department of Chemistry in 1985-1988. His main research interests are in the areas of physical inorganic chemistry, EPR spectroscopy, and magnetism of transition-metal compounds.

Roberta Sessoli was born in 1963. She got a Laurea in Chemistry at the University of Florence in 1987. At present she is a graduate student under the instruction of Prof. D. Gatteschi.

Paul Rey was born in 1940. He got his Ph.D. in Chemistry at the University of Grenoble in 1971 with a thesis on the chemistry of nitroxides. He is Directeur de Recherche at the Centre d'Etude Nucleaire de Grenoble. His main research interests are in the coordination chemistry of free radicals and in magnetic materials.

(1) *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: Orlando, 1987; Vols. 1 and 2; Williams, J. M. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 690.

(2) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* 1985, 18, 309. Wudl, F. *Acc. Chem. Res.* 1984, 17, 227. Torrance, J. B. *Acc. Chem. Res.* 1979, 12, 79. Williams, J. M. *Prog. Inorg. Chem.* 1985, 33, 183.

(3) McConnell, H. M. *J. Chem. Phys.* 1963, 39, 1910.

(4) Mataga, N. *Theor. Chim. Acta* 1968, 10, 372.

(5) Ovchinnikov, A. A. *Dokl. Akad. Nauk. SSSR* 1977, 236, 957; *Theor. Chim. Acta* 1978, 47, 297.

(6) Breslow, R. *Pure Appl. Chem.* 1982, 54, 927.

(7) Iwamura, H. *Pure Appl. Chem.* 1986, 58, 187.

(8) Miller, J. S.; Epstein, A. J.; Reiff, W. R. *Acc. Chem. Res.* 1988, 21, 114.

(9) Kahn, O. *Angew. Chem., Int. Ed. Engl.* 1985, 24, 834.