

involved attack of the hydroxide ion on the neutral ester **1**, the reactivity for the anionic ester **2** would be expected to be only marginally less; the effect of changing the para substituent from -OH to -O<sup>-</sup> ( $\sigma = -0.37$  and  $-0.52$ ) would be to lower the reactivity by some 2-fold as calculated from the Hammett  $\rho$  value of 2.24.<sup>5</sup> The similarity in rate constants would lead to a narrow plateau region as illustrated in Figure 1 (Line B). Figure 1 indicates the presence of a hydroxide term which must represent bimolecular attack of hydroxide ion on the ionized ester; the rate constant comes close to the calculated value as does that for the alkaline hydrolysis of 2,4-dinitrophenyl benzenesulfonate.

A mechanism consisting of nucleophilic aromatic substitution is discarded by labeling studies which indicate that less than 0.2% of the reaction involves O-Ar bond cleavage; the 2,4-dinitrophenol from the reaction using <sup>18</sup>O-enriched water (5.796% enriched) had an  $M + 2$  peak at 1.230% enrichment (natural has 1.224%), and O-Ar cleavage should yield  $M + 2$  at 7.026% enrichment.

A low positive entropy of activation for  $k'$  for the 4-hydroxy ester is consistent with the proposed dissociative mechanism. The Arrhenius parameters at  $[\text{OH}^-] = 0.01$  M, ionic strength 0.2 M, and 20% dioxane/water are  $\Delta S^\ddagger = +0.71$  eu/mol and  $\Delta H^\ddagger = 21.1$  kcal/mol at 25 °C.

Trapping experiments with ammonia using HPLC product analysis indicate that at pH 10.19 and 1 M ammonium buffer (fraction of base = 0.8) 7% of the product is the sulfonamide. This yield is only 3-fold larger than that expected from the molar ratio of water and ammonia. The poor selectivity indicates that the intermediate is very reactive toward nucleophiles as would be expected from an analogue of sulfur trioxide. Methyl glycinate, imidazole, 2-picoline, carbonate, and ammonia showed no  $S_NAr$  reaction; piperidine, morpholine, aniline, pyridine, benzylamine, and phenol gave some aromatic substitution.

Although the hypothesis that sulfoquinones can be formed by the action of bases on substituted 4-hydroxybenzenesulfonyl chloride was advanced in the first decade of this century,<sup>8</sup> subsequent work was not able to confirm it.<sup>9</sup> As far as we are aware, this is the first definitive evidence for the existence of a sulfoquinone in a reaction pathway.

Registry No. **1**, 80540-65-4; **3**, 80540-66-5.

(8) T. Zincke and R. Brune, *Chem. Ber.*, **41**, 902 (1908).

(9) W. L. Hall, *J. Org. Chem.*, **31**, 2672 (1966).

## Why Do Rate-Equilibrium Relationships Break Down?

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One of the fundamental concepts of physical organic chemistry is the idea of the rate-equilibrium relationship.<sup>1,2</sup> This relationship, expressed by eq 1 suggests that perturbations on equilibria

$$\Delta(\Delta G^\ddagger) = \alpha \Delta(\Delta G^\circ) \quad (1)$$

will only be partially reflected in the reaction rates, i.e.,  $\alpha$  will take on values between 0 and 1. This idea has taken on added scope with the development of Marcus theory<sup>3a,b</sup> which attempts

(1) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1936**, *32*, 1340; **1938**, *34*, 11.

(2) (a) Leffler, J. E. *Science (Washington, D.C)* **1953**, *117*, 340. (b) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; p 156.

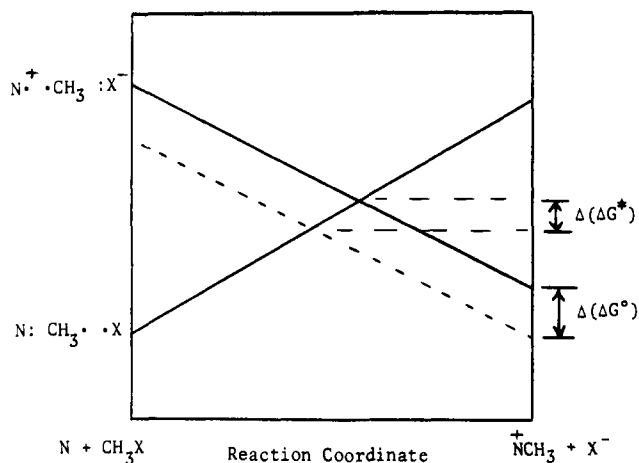


Figure 1. Energy plot of reactant ( $\text{N:CH}_3 \cdot \text{X}$ ) and product ( $\text{N}^+ \cdot \text{CH}_3 \cdot \text{X}^-$ ) configurations as a function of reaction coordinate. Effect of a perturbation [ $\Delta(\Delta G^\circ)$ ] on product stability is only partially reflected in the transition state [ $\Delta(\Delta G^\ddagger)$ ].

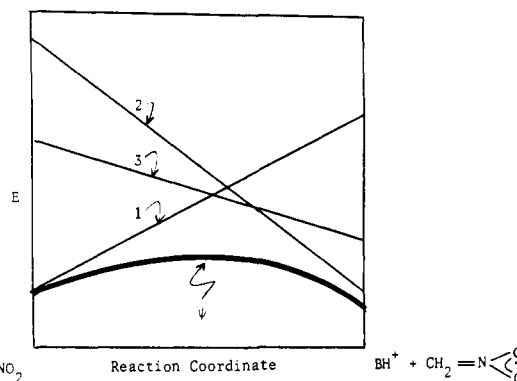


Figure 2. Energy plot of the reactant (1), product (2), and intermediate (3) configurations (see text) for the deprotonation reaction of  $\text{CH}_3\text{NO}_2$  by a base (B).

to relate the free energy of activation for a given reaction to the "intrinsic barrier,  $\Delta G_0^\ddagger$  ( $\Delta G^\ddagger$  when  $\Delta G^\circ = 0$ ), and the free energy change,  $\Delta G^\circ$ , of the reaction. On the basis of Marcus theory,  $\alpha$  is given by eq 2.<sup>3c</sup> Yet it is apparent, despite the

$$\alpha = 1/2 + \Delta G^\circ / 8\Delta G_0^\ddagger \quad (2)$$

conceptual advance associated with these ideas and their successful application to a wide range of reaction types, electron transfer,<sup>3</sup> proton transfer,<sup>4</sup> and methyl transfers<sup>5</sup> that breakdowns exist. A particularly controversial example is the deprotonation reaction of nitroalkanes which has been the subject of intense study, since for this system  $\alpha$  values outside the range 0-1 were observed.<sup>6,7</sup>

(3) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155. (b) Marcus, R. A. In "Special Topics in Electrochemistry"; Rock, P. A., Ed.; Elsevier: Amsterdam, 1977. (c) Strictly speaking, for bond-making and bond-breaking reactions, eq 2 is an approximation to Marcus' hyperbolic tangent equation. See eq 35 of: Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891.

(4) (a) Bell, R. P. "The Proton in Chemistry", 2nd ed.; Chapman and Hall: London, 1973. (b) Caldin, E., Gold, V., Eds. "Proton Transfer Reactions"; Chapman and Hall: London, 1975.

(5) (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) Kreevoy, M. M.; Oh, S. *J. Am. Chem. Soc.* **1973**, *95*, 4805.

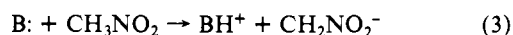
(6) (a) Bordwell, F. G.; Boyle, W. J., Jr.; Hautala, J. A.; Yee, K. C. *J. Am. Chem. Soc.* **1969**, *91*, 4002. (b) Bordwell, F. G.; Boyle, W. J., Jr.; Yee, K. C. *Ibid.* **1970**, *92*, 5926. (c) Bordwell, F. G.; Boyle, W. J., Jr. *Ibid.* **1972**, *94*, 3907. (d) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3107.

(7) For various explanations of the anomalous  $\alpha$  values, see: (a) Agmon, N. *J. Am. Chem. Soc.* **1980**, *102*, 2164. (b) More O'Ferrall, R. A. In "Proton Transfer Reactions"; Caldin, E., Gold, V., Eds.; Chapman and Hall: London, 1975. (c) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224. (d) Kresge, A. J. *Ibid.* **1970**, *92*, 3210; *Can. J. Chem.* **1974**, *52*, 1897. (e) Reference 6. (f) Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69.

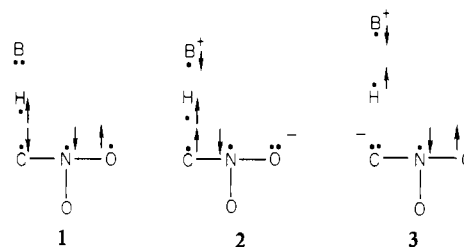
In recent years the use of configuration mixing and avoided crossings to generate reaction profiles has become more widespread.<sup>8-13</sup> We, in particular, have utilized the approach to understand  $S_N2$ <sup>11</sup> and elimination<sup>12</sup> reactions. In this communication we aim to show that the configuration mixing model quite clearly illustrates that normal rate-equilibrium relationships are only likely to be observed for a certain class of reactions and that deviations are to be expected for organic reactions which do not fall into this category. Specifically, *reaction series which may be adequately described by just two configurations—reactant and product—will tend to obey the normal rate-equilibrium formulation<sup>12</sup> while reaction series which require at least one additional configuration—generally one describing a hypothetical intermediate along the reaction coordinate—may exhibit deviations from the normal rate-equilibrium relationship.* Let us illustrate this simple idea with two reactions, the  $S_N2$  reaction of methyl derivatives which generally obey the rate-equilibrium relationship,<sup>5a,14</sup> and the deprotonation reaction of a series of  $\text{ArCH}_2\text{NO}_2$  which is the classical example of the anomalous rate-equilibrium relationship.<sup>6,7</sup> We, first, briefly state the essence of the configuration mixing approach: any reaction profile may be built up from a linear combination of valence-bond configurations while the character of the transition state will be reflected by the weight of each of the contributors to the linear combination at the transition state.<sup>12</sup>

The  $S_N2$  reaction profile of methyl derivatives has been shown by us<sup>13</sup> to be simply represented, primarily by the avoided crossing of two configurations, one being  $\text{N}:\text{H}_3\text{C}\cdot\text{X}$  and the other  $\text{N}^+\cdot\text{CH}_3:\text{X}^-$ . This is shown in Figure 1. Any change in the free energy of the reaction  $[\Delta(\Delta G^\circ)]$  will only be partially reflected in the transition-state  $\Delta(\Delta G^\ddagger)$  (Figure 1, eq 1). The factor  $\alpha$  will be a function of the curve form and slope and will lie in the range  $0 < \alpha < 1$ . In fact extensive work, both experimental<sup>5a,15</sup> and theoretical,<sup>14</sup> supports this idea for the  $S_N2$  reaction of methyl derivatives. Possible intermediate-type configurations,  $\text{N}:\text{CH}_3^+:\text{X}^-$  and  $\text{N}^+\cdot\text{CH}_3^-\cdot\text{X}$ , for most N and X, do not significantly mix into the transition state.<sup>16</sup>

Let us now examine the corresponding situation for the base-catalyzed deprotonation of nitromethane (reaction 3). This is illustrated in Figure 2.



In this case reactant and product configurations, which are primarily responsible for generating the reaction profile, are represented by **1** and **2**,<sup>19</sup> respectively (the arrows denote electron spins).



Along the reaction coordinate, the reaction configuration **1** increases in energy since a repulsive  $\text{B}\cdot\text{H}$  three-electron interaction is generated while an attractive two-electron  $\text{H}\cdot\downarrow\text{C}$  interaction is destroyed.<sup>20</sup> The product which is described primarily by configuration **2** is initially high in energy in relation to **1**. This is because **2** is generated from **1** by double electron excitation: first, electron transfer from B: to  $\text{O}\cdot$  and, second, the uncoupling of the C-H bond pair. The energy of **2** drops sharply along the reaction coordinate since a stable  $\text{B}\cdot\uparrow\downarrow\text{H}$  interaction is generated.<sup>20</sup> Configuration **3**,<sup>19</sup> in which the negative charge is localized on the carbon, also contributes to the product but to a lesser extent than **2**, since the electron prefers to reside on the more electronegative O atom. The key point, however, is that at the starting point **3** is lower than **2** in energy since **3** is a monoexcited configuration, while **2** is a diexcited configuration. Thus in the vicinity of the transition state, **3** makes a *larger contribution to the makeup of the transition state than it does to the final product*. This means that there will be a *larger* negative charge on carbon in the transition state than in the product, as suggested by Bordwell<sup>6b</sup> and More O'Ferrall,<sup>7b</sup> and as a consequence a *larger carbon substituent effect on rates than on equilibria*. Model calculations of deuterium isotope effects in the deprotonation reaction of nitroalkanes by McLennan and Burton<sup>21</sup> also lend support to this view.

Finally, we would add that the above argument does not rule out other factors which may influence the magnitude of  $\alpha$  values.<sup>7a,22</sup> Rather, our purpose has been to emphasize the idea that for a one-step process *the character of the transition state is not necessarily intermediate between that of reactants and products*. The transition state may take on characteristics which are only weakly present or even totally absent in both reactants and products, and this will occur for those reactions in which "intermediate" configurations (such as **3**) mix strongly and preferentially into the transition state. Examples of systems which appear to fall into this category include (in addition to the deprotonation of nitroalkanes) nucleophilic substitution of benzyl derivatives (where N:  $\text{R}^+:\text{X}^-$  and  $\text{N}^+\cdot\text{R}^-\cdot\text{X}$  ( $\text{R} = \text{PhCH}_2$ ) may now play an important role), concerted elimination reactions, and Diels-Alder reactions (which may possess substantial charge-transfer character in the transition state).

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Registry No.  $\text{CH}_3\text{NO}_2$ , 75-52-5.

(8) For a theoretical analysis, see: Shaik, S. *J. Am. Chem. Soc.* **1981**, *103*, 3692.

(9) For recent reviews, see: (a) Epiotis, N. D.; Shaik, S.; Zander, W. In "Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; Academic Press: New York, 1980. (b) Epiotis, N. D.; Shaik, S. In "Progress in Theoretical Organic Chemistry"; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1977; Vol. 2. (c) Epiotis, N. D. "Theory of Organic Reactions"; Springer-Verlag: Heidelberg, 1978.

(10) For a recent application to electron transfer and nucleophilic attack on peroxides, see: Walling, C. *J. Am. Chem. Soc.* **1980**, *102*, 6854.

(11) Pross, A.; Shaik, S. *J. Am. Chem. Soc.* **1981**, *103*, 3702.

(12) Pross, A.; Shaik, S. *J. Am. Chem. Soc.*, in press.

(13) Pross, A.; Shaik, S. *J. Am. Chem. Soc.* **1982**, *103*, 187. Shaik, S. *Now. J. Chim.*, in press.

(14) Wolfe, S.; Mitchell, D. J. *J. Am. Chem. Soc.*, in press.

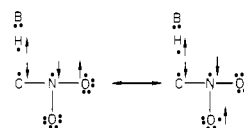
(15) (a) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892. (b) Arnett, E. M.; Petro, C. *Ibid.* **1976**, *98*, 1468.

(16) Significant mixing of  $\text{N}:\text{CH}_3^+:\text{X}^-$  would lead to a loose transition state while mixing of  $\text{N}^+\cdot\text{CH}_3^-\cdot\text{X}$  would lead to a tight transition state. Recent calculations by Wolfe and Mitchell<sup>17</sup> indicate that a total bond order of 1 is maintained in the methyl transition state. Also Kevill<sup>18</sup> has argued that the absence of a significant  $\alpha$ -substituent effect in methyl-transfer reactions also argues against the development of significant charge of  $\text{C}_\alpha$ .

(17) Wolfe, S.; Mitchell, D. J.; Schlegel, H. B. *J. Am. Chem. Soc.*, in press.

(18) Kevill, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, 421.

(19) Each of these configurations (1-3) actually involves an additional VB structure which makes the two oxygen atoms equivalent; e.g., **1** is



(20) For rules governing the interaction between groups within a configuration, see ref 12.

(21) McLennan, D. J.; Burton, G. W., private communication.

(22) Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 4410.