JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 29–31 (1988)

MARCUS–GRUNWALD THEORY AND THE NITROALKANE ANOMALY

W. JOHN ALBERY
Department of Chemistry, Imperial College of Science and Technology, South Kensington, London SW7 2AY, England
CLAUDE F. BERNASCONI
Thimann Laboratories, University of California, Santa Cruz, California 95064, U.S.A.
AND
A. JERRY KRESGE
Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 1A1 Canada

ABSTRACT

The disparity reaction proposed in a recent application of Marcus–Grunwald theory to nitroalkane ionization is shown to put the reaction's transition state in an energy-diagram region where electronic rearrangement leads proton transfer, contrary to experimental evidence; it is suggested that addition of solvent reorganization to electronic rearrangement as the second reaction progress variable would remedy this situation.

Marcus theory[1] provides a useful framework upon which analysis of rate–equilibrium relationships in chemical reactions may be based. The theory is limited, however, to cases that can be described by a single reaction progress variable. In systems with two (or more) reaction events, such as, for example, the proton transfer and electronic rearrangement in reaction of

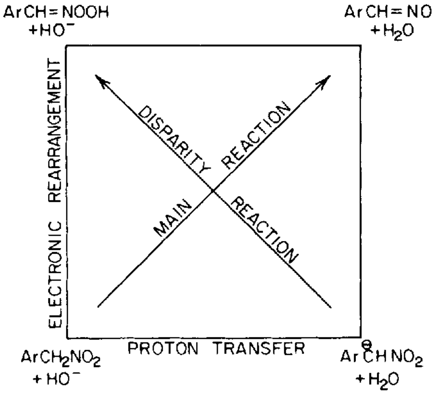

Figure 1. Energy diagram for the reaction of ring-substituted phenylnitromethanes with the hydroxide ion using proton transfer and electronic rearrangement as the reaction progress variables

0894–3230/88/010029–03$05.00

Received 6 November 1987

arylnitromethanes with hydroxide ion, shown as the horizontal and vertical coordinates of Figure 1, the theory requires these events to develop in a completely synchronous manner. This confines the system to motion along the reactant–to-product diagonal of an energy diagram such as Figure 1; it permits only parallel or Hammond displacements of the transition state and does not allow perpendicular or Thornton effects.[2]

Grunwald has recently shown how this restriction may be lifted by adding an additional term to the Marcus equation.[2] His treatment introduces a second model process or 'disparity reaction' which connects the two remaining corners of the energy diagram and provides a second diagonal perpendicular to the 'main reaction' path.

In applying his treatment to the reaction of ring-substituted arylnitromethanes with hydroxide ion, Grunwald took the disparity reaction to be the conversion of a hypothetical nitronate anion, with its negative charge localized on carbon, to the corresponding nitronic acid, equation (1).

$$\mathrm{Ar^{-}CHNO_2 + H_2O \rightarrow ArCH{=}NOOH + HO^{-}} \qquad (1)$$

It is instructive to estimate the free energy change for this process. This may be done by taking the sum of the free energy changes for transformation of the charge-localized nitronate ion to the real, charge-delocalized ion, equation (2), protonation of

$$\mathrm{Ar^{-}CHNO_2 \rightarrow ArCH{=}NO_2{}^{-}} \qquad (2)$$

$$\mathrm{ArCH{=}NO_2{}^{-} + H^{+} \rightarrow ArCH{=}NO_2H} \qquad (3)$$

$$\mathrm{H_2O \rightarrow H^{+} + HO^{-}} \qquad (4)$$

the real ion to give the nitronic acid, equation (3), and ionization of water, equation (4). The acid dissociation constant of the nitronic acid derived from phenylnitromethane has been measured, $pK_a = 3{\cdot}89$,[3] and that gives $\Delta G° = -5{\cdot}3\,\mathrm{kcal\,mol^{-1}}$ for equation (3), while the autoprotolysis constant of water provides $\Delta G° = 19{\cdot}1\,\mathrm{kcal\,mol^{-1}}$ for equation (4). It is more difficult to obtain a value of $\Delta G°$ for equation (2), because its reactant is a hypothetical species, but an upper limit can be set in the following way. The process of equation (2) is also the event that takes place along the right vertical edge of the diagram in Figure 1. The lower right corner of this diagram, which contains this hypothetical species, is an energy maximum, below, or at, which the transition state of the reaction must lie. The energy of the transition state is therefore a lower limit for the energy of the hypothetical charge-localized ion, and the energy decrease in going from the transition state to reaction products must be an upper limit for the energy change of equation (2). The rate and equilibrium constants for the reaction of phenylnitromethane with hydroxide ion[4] then give $\Delta G° \leqslant -24{\cdot}2\,\mathrm{kcal\,mol^{-1}}$ for equation (2). This leads to $\Delta G° \leqslant -10{\cdot}4\,\mathrm{kcal\,mol^{-1}}$ for the disparity reaction of equation (1).

This estimate makes the disparity reaction an exoergic or downhill process. Since disparity reactions provide perpendicular or Thornton perturbations on the position of transition states, the effect of this exoergic process will be to move the transition state off the main reaction diagonal in a direction toward the upper left corner of Figure 1. This is the region where electronic rearrangement *leads* proton transfer. All existing experimental evidence on this and other nitroalkane ionization reactions, however, require electronic rearrangement to *lag behind* proton transfer.[1b,4,5] The process of equation (1) therefore cannot be the disparity reaction for nitroalkane ionization.

This situation might be remedied by keeping proton transfer to and from carbon as the horizontal coordinate of the energy diagram, but adding solvent reorganization to the electronic rearrangement which has been taken as the vertical coordinate (Figure 2). As one of

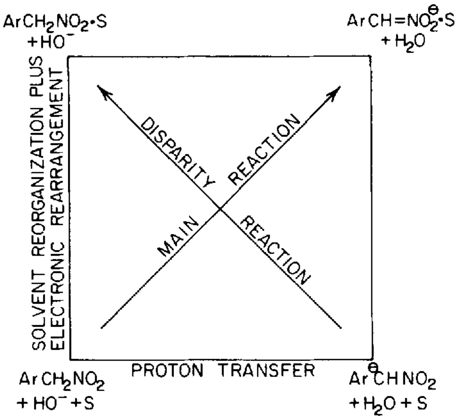

Figure 2. Energy diagram for the reaction of ring-substituted phenylnitromethanes with the hydroxide ion using proton transfer and solvent reorganization plus electronic rearrangement as the reaction progress variables

us has already pointed out,[6] this would place an improperly solvated nitroalkane molecule in the upper left corner of the diagram. Such a substance, with solvent shell appropriate to a nitronate ion rather than a neutral nitro compound, would surely be an unstable species. It is quite likely that the instability would be sufficient to make the new disparity reaction an endoergic or uphill process, and that would put the transition state below the main reaction diagonal in a region where electronic rearrangement quite properly lags proton transfer.

This proposition is supported by the effect on nitroalkane ionization of changing the solvent for this reaction from water to dimethyl sulphoxide. One manifestation of the nonsynchronous evolution of reaction events in nitroalkane ionization is the occurrence of anomalous Brønsted exponents, *i.e.* exponents outside the limits zero to one; hence the term 'nitroalkane anomaly'.[5a] For the ionization of ring-substituted phenylnitromethanes, the Brønsted exponent is $\alpha = 1{\cdot}5$ in aqueous solution,[4] but in dimethyl sulphoxide, which is a much poorer anion-solvating medium, the exponent drops to the less anomalous value $\alpha = 0{\cdot}9$.[7]

ACKNOWLEDGEMENT

We are grateful to Professors E. Grunwald, J. W. Bunting, and J. R. Keeffe and Mr. D. Stefanidis for valuable discussion.

REFERENCES

1. (a) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968).
   (b) A. J. Kresge, *Chem. Soc. Rev.* **2**, 475 (1973).
2. E. Grunwald, *J. Am. Chem. Soc.*, **107**, 125 (1985).
3. V. M. Belikov, *et al.*, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1675, 1960; S. G. Mairanovskii, *et al.*, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1787, 1960; V. M. Belikov, T. B. Korchemnaya, and N. G. Faleev, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1383, 1969.
4. F. G. Bordwell, W. J. Boyle Jr., *J. Am. Chem. Soc.*, **94**, 3907 (1972).
5. (a) A. J. Kresge, *Can. J. Chem.*, **52**, 1897 (1974).
   (b) F. G. Bordwell, *Faraday Society Symposium*, **10**, 100 (1975).
6. C. F. Bernasconi, *Pure Appl. Chem.*, **54**, 2335 (1982).
7. J. R. Keeffe, J. Morey, C. A. Palmer, J. C. Lee, *J. Am. Chem. Soc.*, **101**, 1295 (1979).