Unusual Slopes of Free Energy Plots in Kinetics

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Abstract: Theoretical equations[1] are used to comment on the relation between the slope of activation free energy–standard free energy of reaction plots and the concept of the position of the transition state along the reaction coordinate. The equations are then used to consider some recent experimental findings of unusual Brønsted coefficients.

In the present article we use some theoretical equations[1] to consider the relation between the slope of free energy plots in kinetics and the concept of "position of the transition state along the reaction coordinate." The results are then used to comment on recent experimental observations of unusual slopes.[2]

In a recent communication, Bordwell and coworkers[2] have reported unusual values for the Brønsted coefficient β of the deprotonation of several series of substituted nitroalkanes, *i.e.*, values of β outside the usual

$$RCH_2NO_2 + B \longrightarrow RCH{=}NO_2^- + BH^+ \qquad (I)$$

range 0 to +1. The base B was OH^- in their case, and they determined β by varying R. In contrast, previous workers[3] determined β by varying B and found a β in the neighborhood of +0.5.

Bordwell, *et al.*, attribute the unusual β to structural reorganization of the compound containing the varying group R. They questioned, at least for carbon acids, in virtue of their β, a common concept in the literature that β is a measure of the position of the transition state along the reaction coordinate.

We apply our equation of ref 1 and 4 to consider the meaning of β, the validity of the above concept, and an interpretation of the data of ref 2.

Theory

Elsewhere we have expressed the free energy barrier of a reaction ΔF^* in terms of thermodynamic ($\Delta F^{\circ\prime}$) and intrinsic (Λ) factors[1,4,5]

$$\Delta F^* = \Lambda[1 + (\Delta F^{\circ\prime}/4\Lambda)]^2 \qquad (1)$$

where $\Delta F^{\circ\prime}$ is the "standard" free energy of the reaction in the prevailing medium. Λ is the intrinsic barrier for the reaction, *i.e.*, the barrier at $\Delta F^{\circ\prime} = 0$.[6] The only applications of this equation thus far, other than to electron transfers,[6] are cited in ref 4.

When a group Y in a reactant is varied, both $\Delta F^{\circ\prime}$ and Λ may vary. The slope of the free energy plot, $d\Delta F^*/d\Delta F^{\circ\prime}$, therefore equals

$$\beta = 0.5(1 + x) + (1 - x^2)\beta_1 \qquad (2)$$

where

$$x = \Delta F^{\circ\prime}/4\Lambda \text{ and } \beta_1 = (d\Lambda/dY)/(d\Delta F^{\circ\prime}/dY) \qquad (3)$$

When Λ is constant in a reaction series, *i.e.*, when β_1 vanishes, eq 2 reduces to

$$\beta = 0.5(1 + x) \qquad (4)$$

β then lies in the conventional range of 0 to +1 for, in all cases explored thus far,[4] x lies within (indeed usually well within) the interval −1 to +1 (see also footnote 12 later).

For the several models considered in ref 1 and leading to the derivation of eq 4, it was shown[1] that the "position along the reaction coordinate"[7] is given by the expression $0.5(1 + x)$. Thus, for such systems β reflects the position of the transition state along the reaction coordinate only when eq 4 applies, that is, only when Λ is constant for a reaction series. Information about this constancy of Λ is obtained[8] by noting that Λ for a reaction

$$AX + B \longrightarrow A + XB \qquad (II)$$

($X = H^+$ in I) is approximately the mean of those for the exchange reactions[1,4]

$$AX + A \longrightarrow A + XA \qquad (III)$$

$$BX + B \longrightarrow B + XB \qquad (IV)$$

under certain conditions. For the present purposes we shall suppose that this relation is at least roughly valid.[9]

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(1) R. A. Marcus, *J. Phys. Chem.*, 72, 891 (1968).

(2) F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *J. Am. Chem. Soc.*, 91, 4002 (1969). Other examples reflecting negative Brønsted coefficients are cited by these authors. I am indebted to Dr. Bordwell for showing me his results in advance of publication.

(3) (a) Cited in ref 3 of ref 2; (b) see particularly M. J. Gregory and T. C. Bruice, *J. Am. Chem. Soc.*, 89, 2327 (1967).

(4) A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 72, 4249 (1968).

(5) (a) The $\lambda/4$ in ref 1 and 4 is denoted in eq 1 by Λ. Further, work terms and steric and statistical factors are omitted from eq 1 for notational brevity and clarity. Their inclusion does not alter the present discussion. The more complete equations are given in ref 1 and 4. (b) Equation 1 applies to the case of $|\Delta F^{\circ\prime}| \leq 4\Lambda$. When $-\Delta F^{\circ\prime} > 4\Lambda$, $\Delta F^* \cong 0$; when $\Delta F^{\circ\prime} > 4\Lambda$, $\Delta F^* \cong \Delta F^{\circ\prime}$, as in ref 1 and 4.

(6) Equation 1 was derived originally for electron-transfer reactions [R. A. Marcus, *J. Chem. Phys.*, 24, 966 (1956), and subsequent papers in that series, cited in ref 1]. More recently an approximate derivation of eq 1 was given for atom transfers,[1] with the aid of a bond energy–bond order model for breaking and forming bonds. Proton transfers have features in common with electron transfers (solvent reorganization) and with atom transfers (bond rupture and formation). Equation 1 has been applied to electron transfers and, based on the above argument,[4] to atom and proton transfers (*cf.* references cited in ref 1). A different derivation of eq 1 for proton transfers (mainly at electrodes) was given by V. G. Levich, R. R. Dogonadze, and A. M. Kuznetsov, *Electrochim. Acta*, 13, 1025 (1968); *Electrokhymiya*, 3, 739 (1967). Their derivation assumes, in effect, very small "resonance energy" for the structural pair [AH^+, B and A, HB^+] in the activated complex of the proton transfer, $AH^+ + B \rightarrow A + HB^+$. It thus disagrees with the potential energy profile of the present Figure 1.

(7) For example, in the BEBO model this term represented the bond order of the newly forming bond in the activated complex. In an outer-sphere electron-transfer reaction the term represented the extent to which the orientation polarization of the medium surrounding the activated complex resembled that surrounding the equilibrated products for the given separation distance.

(8) Compare discussion of reaction XXII in ref 4 and of effects of substituents on conjugation and, thereby, on Λ.

(9) However, it probably is not accurately so when one of the Λ's is small.[1,4]

Therefore, when the varied group in reaction I is B, the variation in Λ is related to the variation in Λ of eq IV. It is a rather striking situation in almost all proton-transfer literature, including that of eq I, that since the B's have been oxygen bases or nitrogen bases, reaction IV is very rapid, frequently diffusion controlled, and its Λ is therefore small.[10] Since such a Λ can make only a small contribution to the Λ of reaction I, the corresponding β_1 is small or negligible and eq 2 reduces to eq 4.

In contrast, when the varied group in reaction I is R, as in ref 2, the corresponding exchange reaction III is

$$RCH_2NO_2 + {}^-O_2N{=}CHR \longrightarrow RCH{=}NO_2^- + O_2NCH_2R \quad (V)$$

and the free energy barrier of this reaction (and hence its Λ) is not small. If, as suggested by Bordwell, *et al.*, the structural reorganization is influenced by R, the Λ of reaction V will vary with R and the β_1 in eq 2 will no longer be negligible. This structural reorganization can be both intramolecular and solvational.

Some of the features described above are illustrated in Figure 1. A particular reaction with a $\Delta F^{\circ\prime} = 0$ (for simplicity) is given by curve P. The result of introducing a substituent which decreases Λ but leaves $\Delta F^{\circ\prime}$ unchanged is indicated by curve Q. The result of introducing a substituent which decreases $\Delta F^{\circ\prime}$ but leaves Λ unchanged is indicated by curve R. Evidently, the latter substitution induces a correlation between position of the transition state along the reaction coordinate and change of ΔF^*, while the former substitution does not.

In summary, under the conditions of reaction I studied by previous workers[3] (B varied), it is reasonable to suppose that β_1 is small and that their β does indeed reflect the position of the transition state along the reaction coordinate. Under the conditions studied by Bordwell, *et al.* (R varied), β_1 is not small, eq 2 is to be considered rather than eq 4, and the resulting β no longer reflects the position of the transition state.[11] The results of Bordwell, *et al.*, in conjunction with those of previous workers, provide information about the structural reorganization effect, about β_1, for example. From these results one finds[12] β_1 to be 1.1 for the series RNO_2, where R = CH_3, C_2H_5, *i*-C_3H_7.

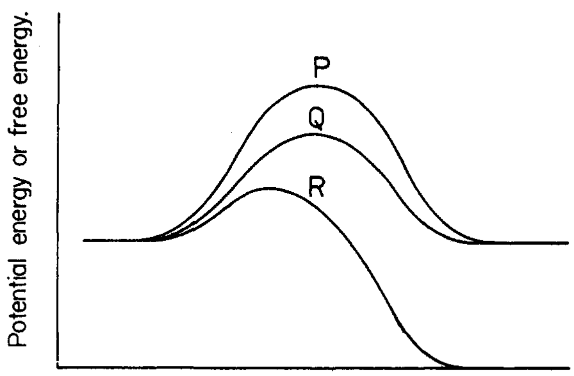

Figure 1. Plot of potential energy of system (*e.g.*, as in gas reactions) or free energy of system (*e.g.*, as in solution reactions in which solvation contributes significantly to ΔF^*) *vs.* reaction coordinate for a reaction $AX + B \rightarrow A + BX$. In curve Q the intrinsic barrier Λ has been reduced from that in curve P. In curve R the $\Delta F^{\circ\prime}$ has been made more negative than that in curve P.

In some reactions, *e.g.*, electron-transfer reactions and Walden inversion reactions, it is possible to measure the rates of both eq III and IV directly. When the arithmetic mean rule holds for Λ, such measurements provide an independent determination of β_1.

Equation 4 can be tested (when β_1 is negligible) by measuring Λ and $\Delta F^{\circ\prime}$ and hence predicting β. Equation 4 (in the form of eq 1) was shown to be consistent with the available data,[4,13] but more data are needed. In the case of the nitroalkane deprotonation reaction I, predictions of β can be made for any average $\Delta F^{\circ\prime}$, using the Λ estimated in footnote 12.

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[10] In an exchange reaction III or IV, $\Delta F^{\circ\prime}$ vanishes so that[5] its ΔF^* equals its Λ (eq 1).

[11] Parenthetically, as one sees from eq 2, it may be noted that even when a series of reactants does not contribute to Λ, the reactants contribute to β since they alter $\Delta F^{\circ\prime}$.

[12] The data of ref 3b are used. Use of the plot in Figure 3 for secondary amines avoids statistical factor corrections, since the reaction is then $RCH_2NO_2 + R'NH^- \rightarrow RCH{=}NO_2^- + R'NH_2$. When $pK_a' = pK_{aNE}'$ in that plot [K_{aNE}' is 6.2×10^{-9}, when referred to the same statistical basis as the secondary amines], the resulting reaction has $\Delta F^{\circ\prime} = 0$ and the resulting rate constant (*ca.* 2 M^{-1} min^{-1}) provides the value of Λ. Λ thus equals $-2.3RT \log (2/10^{11} \times 60)$, *i.e.*, about 17 kcal mole^{-1}. Since the typical $\Delta F^{\circ\prime}$ in the plot was about 2 kcal mole^{-1} a common x was about 0.1, which makes only a minor contribution to β. Thus from eq 4, β_1 when R is varied equals the difference of β's found in ref 2 and 3b, namely about 1.1.

[13] The plots in ref 4 can actually be drawn to cover twice the range of $\Delta F^{\circ\prime}$ indicated, by including the ΔF^*'s for both forward and reverse reactions. Fulfillment of eq 1 for the forward reaction automatically ensures its fulfillment for the reverse reaction.