On the Slope of Free Energy Plots in Chemical Kinetics

by Audrey O. Cohen and R. A. Marcus

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61801 *(Received June 5, 1968)*

In current electron-transfer theory, an activation free energy term, ΔF^*, depends in a simple way on the "standard" free energy of reaction, $\Delta F^{\circ\prime}$, in the prevailing medium. Namely, $\Delta F^* = {}^1/_4\lambda[1 + (\Delta F^{\circ\prime}/\lambda)]^2$, apart from small work terms; $\lambda/4$ is ΔF_0^*, the value of ΔF^* at $\Delta F^{\circ\prime} = 0$; and λ obeys a simple additivity property. As an exploratory step an equation of the same functional form is applied in the present paper to data on Brønsted slopes of 16 proton- and atom-transfer reaction series. Thereby, the instantaneous slope of a ΔF^* *vs.* $\Delta F^{\circ\prime}$ plot is calculated to be ${}^1/_2[1 + (\Delta F^{\circ\prime}/4\Delta F_0^*)]$. Thus far the experimental results are consistent with this equation, but more data are needed. Other applications of the ΔF^* equation, including one to the kinetic isotope effect, are also discussed. A rather approximate derivation of the above equation for atom and other transfers was given in an earlier paper of this series.

Introduction

There have been many successful two-parameter empirical correlations of reaction rates and equilibrium properties for series of related reactions.[1-4] In the present paper, the possibility of the calculating of the slopes of such plots *a priori* is explored.

In the case of electron-transfer reactions a simple functional dependence of ΔF^* on ΔF° has been derived (eq 1 and 11 below)[5] and has been in encouraging agreement with the experimental data.[6] More recently approximate theoretical arguments have been given leading to an equation of substantially this functional form for atom and other transfers.[7] Needless to say, the derivation was less elaborate and rigorous than that for electron transfers. (Even the $H + H_2 \rightarrow H_2 + H$ system is only now yielding to fairly accurate quantum mechanical calculation.[8]) Therefore, the present work, an application of the foregoing, is an exploratory one.

Equations

An approximate equation relating free energy barriers of reactions in solution to standard free energies of reaction is[7,9]

$$\Delta F^* = \frac{\lambda}{4}\left(1 + \frac{\Delta}{\lambda}\right)^2 \quad (|\Delta| \leq \lambda) \tag{1a}$$

$$\Delta F^* = 0 \quad (\Delta \leq -\lambda)$$
$$\Delta F^* = \Delta \quad (\Delta \geq \lambda) \tag{1b}$$

where

$$\Delta = \Delta F^{\circ\prime} + RT \ln (s^r/s^p) \tag{2}$$

ΔF^* is an activation free energy related to the rate constant of an elementary step of a reaction by the equation

$$\Delta F^* = -RT \ln (k_{rate}/Zs^r) \tag{3}$$

λ is a reorganization property, $\Delta F^{\circ\prime}$ is the "standard" free energy of reaction at the prevailing temperature and electrolyte condition, Z is a collision number ($\sim 10^{11}$ l. mol^{-1} sec^{-1}), and s^r and s^p are statistical factors.[9] λ has an additivity property given by eq 11 below.

For gas-phase reactions we explore the comparison of bond and activation energies with an equation of similar functional form[10]

$$E_a = \frac{\lambda^E}{4}[1 + (\Delta E^\circ/\lambda^E)]^2 \quad (|\Delta E^\circ| \leq \lambda^E) \tag{4a}$$

(1) (a) J. N. Brønsted and K. Pederson, *Z. Phys. Chem.* (Leipsig), 108, 185 (1924); (b) R. P. Bell, "Acid-Base Catalysis," Oxford University Press, New York, N. Y., 1941.

(2) (a) L. P. Hammett, *Chem. Rev.*, 17, 125 (1935); (b) H. H. Jaffé, *ibid.*, 53, 191 (1953).

(3) (a) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 32, 1333 (1936); 34, 11 (1938); (b) N. N. Semenov, "Some Problems of Chemical Kinetics and Reactivity," Vol. 1, Pergamon Press Inc., New York, N. Y., 1958, p 8.

(4) (a) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, pp 279, 396; (b) P. R. Wells, *Chem. Rev.*, 63, 171 (1963); (c) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964.

(5) *Cf.* R. A. Marcus, *Ann. Rev. Phys. Chem.*, 15, 155 (1964), and references cited therein.

(6) N. Sutin and B. M. Gordon, *J. Amer. Chem. Soc.*, 83, 70 (1961); M. H. Ford-Smith and N. Sutin, *ibid.*, 83, 1830 (1961); M. Gordon, L. L. Williams, and N. Sutin, *ibid.*, 83, 2061 (1961); N. Sutin, *Nature*, 190, 438 (1961); R. J. Campion, N. Purdie, and N. Sutin, *Inorg. Chem.*, 3, 1091 (1964).

(7) R. A. Marcus, *J. Phys. Chem.*, 72, 891 (1968). In the case of those proton transfers in which the major barrier arises from desolvation of one species and solvation of another, the argument was only sketchily given. A more detailed discussion of the latter is planned.

(8) H. Conroy and B. L. Bruner, *J. Chem. Phys.*, 47, 921 (1967); I. Shavitt, R. M. Stevens, F. L. Minn, and M. Karplus, *ibid.*, 48, 2700 (1968).

(9) Equations 1–3 differ from eq 1, 2, and 6 in ref 7 only in that we have excluded work and steric terms and included statistical factors s^r and s^p, for purposes of exploratory discussion. The work terms are the usual coulombic terms and are normally fairly small. Statistical factors are easily calculated and would not noticeably affect the results of this paper if they were omitted. For references describing calculation of s^r and s^p see ref 7.

(10) Equations 4a and b are similar to eq 8a and b in ref 7, except that the latter deal with potential energies. The notation differs in that ΔE° refers to a change in bond energy in this paper.

$$E_a = 0 \quad (\Delta E^\circ \leq -\lambda^E)$$
$$E_a = \Delta E^\circ \quad (\Delta E^\circ \geq \lambda^E) \tag{4b}$$

where λ^E is a reorganization property having an additivity described in eq 8c of ref 7.

If the Brønsted slope α is defined as the slope of ΔF^* *vs.* Δ or of the corresponding plot based on eq 4, we have

$$\alpha = {}^1/_2[1 + (\Delta/\lambda)] \quad (|\Delta| \leq \lambda) \tag{5a}$$

$$\alpha = 0 \quad (\Delta \leq -\lambda)$$
$$\alpha = 1 \quad (\Delta \geq \lambda) \tag{5b}$$

where in the case of eq 4 λ is replaced by λ^E and Δ by ΔE°.

From eq 1–3 and 5 one can also derive an approximate relationship between α and the kinetic isotope effect[7]

$$\ln (k_H/k_D) \cong \frac{\lambda_H - \lambda_D}{4RT} [1 - (2\alpha - 1)^2] \quad (|\Delta| \leq \lambda) \tag{6}$$

Comparison with Experimental Data

Data for 16 series of reactions are considered, 11 of them being proton transfers

$$HA_1 + A_2^- \longrightarrow A_1^- + HA_2 \tag{I}$$

where A_1^- and A_2^- are not necessarily singly charged. For the above reaction $\Delta F^{\circ\prime}$ can be obtained from the ionization constant of

$$HA_i + H_2O \underset{}{\overset{K_i}{\rightleftharpoons}} A_i^- + H_3O^+ \tag{II}$$

since $\Delta F^{\circ\prime}$ equals $-RT \ln (K_1/K_2)$.

The following reaction series are examined.

(*a*) *Proton Transfers of Known* ΔF^* *and* $\Delta F^{\circ\prime}$. Reactions III–X are examples of reaction I given in Table I and Figures 1–7.[11–19]

$$HA_1 + A_2^- \longrightarrow A_1^- + HA_2 \tag{III}$$

(HA_1 and HA_2 are conventional moderately weak acids)

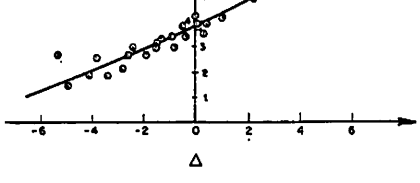


Figure 1. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for a series of weak acids and bases (reaction III).

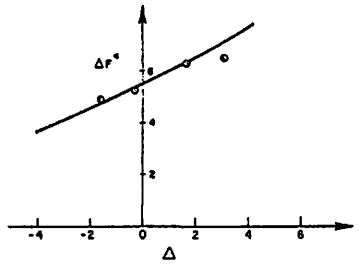


Figure 2. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for (reaction of thioglycols with amines and other bases (reaction IV).

$$HSCH_2CH_2OH + A_2^- \longrightarrow HOCH_2CH_2S^- + HA_2 \tag{IV}$$

$$CH_3COCHRR' + A_2^- \longrightarrow CH_3COCRR'^- + HA_2 \tag{V}$$

$$(CH_2)_4COCHCO_2Et + A_2^- \longrightarrow (CH_2)_4COCCO_2Et^- + HA_2 \tag{VI}$$

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1949, p 172; R. P. Bell and O. M. Lidwell, *Proc. Roy. Soc.*, A176, 88 (1940); R. P. Bell, E. Gelles, and E. Moller, *ibid.*, A198, 310 (1949).

(12) R. P. Bell, R. D. Smith, and L. A. Woodward, *ibid.*, A192, 479 (1948).

(13) R. P. Bell and H. L. Goldsmith, *ibid.*, A210, 322 (1952).

(14) For benzoylacetone, acetylacetone, and bromoacetylacetone, K_1 was obtained by correcting the gross acid dissociation constant, K_g, for enol content, $K_1 = K_g(1 + K_T)$, where $K_T = c_{enol}/c_{keto}$. This correction was negligible for the other ketones involved. Values of K_T were taken from G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, 27, 1701 (1944); M. L. Edinoff, *J. Amer. Chem. Soc.*, 67, 2073 (1945).

(15) R. P. Bell and T. Spencer, *Proc. Roy. Soc.*, A251, 41 (1959).

(16) (a) A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 83, 2877 (1961); (b) A. J. Kresge and Y. Chiang, *Proc. Chem. Soc.*, 81 (1961).

(17) M. Eigen, *Angew. Chem. Int. Ed.*, 3, 1 (1964).

(18) In reactions III–XIII the compounds or substituents used are the following: (III) HA_1: acetic acid, phenol, formic acid, chloroacetic acid, phosphoric acid, glucose, HCO_3^-, boric acid, fumaric acid; A_2^-: hydrazine, imidazole, aniline, *m*-chloroaniline, PO_4^{3-}, piperidine, propylamine, carbonate, ammonia, α-picoline, pyridine (the rate constants for these reactions were read from graphs, since no other data was available; points for maleic acid were not included in the tabulation); (IV) A_2^-: dimethylamine, trimethylamine, hydrazine, imidazole; (V) CHRR′: $CHBrCOCH_3$, $CH_3CO_2C_2H_5$, $CH_3COC_6H_5$, (see ref 5); A_2^-: $Cl_3C_6H_2O^-$, p-$NO_2C_6H_4CO_2^-$, $C_6H_5CO_2^-$, $C_6H_5CH_2CO_2^-$, $(CH_3)_3CHCO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, H_2O, $CH_3(CH_2)_8CO_2^-$, mannose anion, glucose anion, $(CH_3)_2C_6H_3O^-$, dimedone, $ClC_6H_4O^-$, p-$NO_2C_6H_4O^-$, pyridine, $HP_2O_7^{3-}$ (see ref 4; 15 points were taken from graphs in ref 16); (VI): A_2^-: $H_2PO_4^-$, H_2O (see ref 4); (VII) A_2^-: $(CH_3)_3CCO_2^-$, $CH_3CO_2^-$, $HOCH_2CO_2^-$, $ClCH_2CO_2^-$; (VIII) CHRR′: CH_3, CH_2Cl, CH_2Br, $CHCl_2$, CH_3COCH_3, $(CH_3)_2COCH_2$ (B = O, S); (IX) A_2^-: $CHCl_2CO_2^-$, $C_6H_5CH_2CO_2^-$, H_2O, pyridine, α-picoline (see ref 4); (X) HA_1: H_3O^+, H_2O, NH_4^+, $H_2PO_4^-$, HCO_2H, CH_3CO_2H, CH_2FCO_2H; (XI) A_2^-: OH^-, H_2O, HPO_4^{2-}, various phenolate anions, amines, alkyl carboxylate anions, aryl carboxalate anions (data available only at 15° were extrapolated to 25°; secondary and tertiary amines as well as divalent metal complexes are not included; the divalent metal complexes fall below the plots for reactions XI and XIII); (XII) HA_1: H_2O, various phenols, alkyl carboxylic acids, aryl carboxylic acids (first 47 compounds in ref 19 and H_2O are included; compounds excluded from graph are oximes, nitroethanes, etc., which one might expect to have different λ); (XIII) A_2^-: OH^-, glucosate anion, SO_4^{2-}, H_2O, carboxylate anion, amino acid anions, betaines (only points from ref 1b not included are those for divalent metal complexes).

(19) R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.*, A197, 141 (1949).

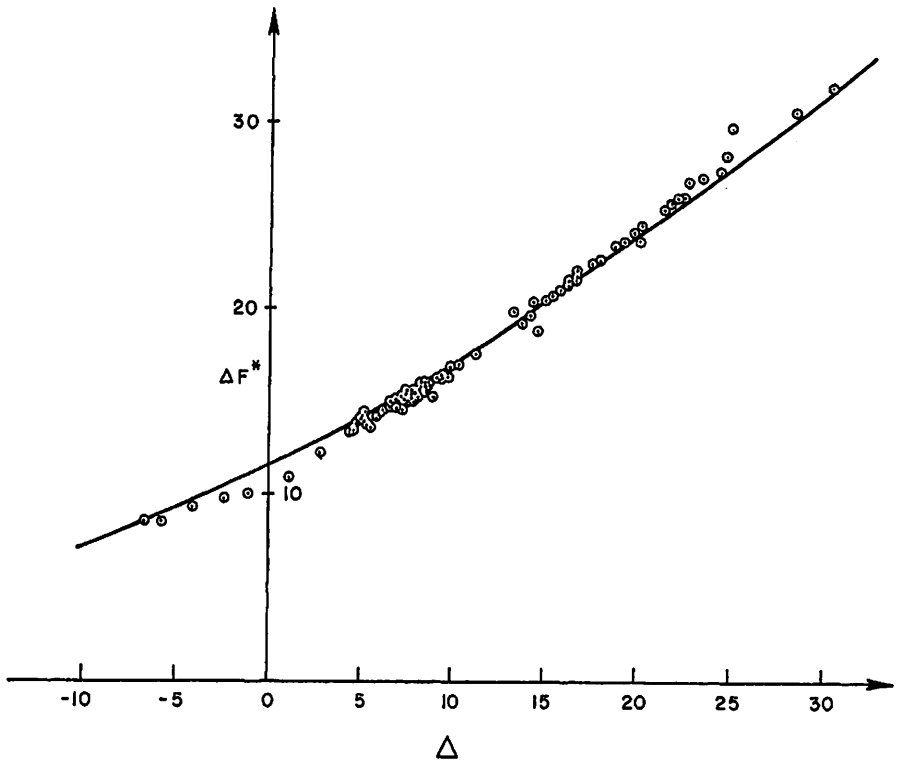


Figure 3. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for reaction of ketones with carboxylate anions and other bases (reaction V).

$$(CH_2)_6COCHCO_2Et + A_2^- \longrightarrow (CH_2)_6COCCO_2Et^- + HA_2 \quad (VII)$$

$$CH_3COCHRR' + BH^- \longrightarrow CH_3COCRR'^- + H_2B \quad (VIII)$$

$$NO_2CH_2CO_2Et + A_2^- \longrightarrow NO_2CHCO_2Et^- + HA_2 \quad (IX)$$

$$(CH_3O)_3C_6H_3 + HA_1 \longrightarrow (CH_3O)_3C_6H_4^+ + A^- \quad (X)$$

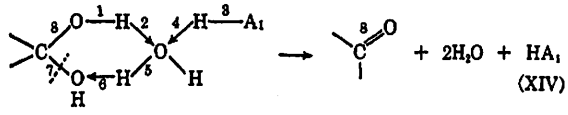
(*b*) *Reactions Involving Consecutive or Concerted Steps.* Reactions XI–XIII are the base-catalyzed decomposition of nitramide,[1a,18-24] the acid-catalyzed dehydration of acetaldehyde,[19] and the base-catalyzed mutarotation of glucose.[1b]

$$NH_2NO_2 + A_2^- \longrightarrow NHNO_2^- + HA_2 \xrightarrow{\text{fast}} N_2O + H_2O + A_2^- \quad (XI)$$

$$CH_3CH(OH_2)_2 + H_2O + HA_1 \longrightarrow CH_3CHO + 2H_2O + HA_1 \quad (XII)$$

$$D\text{-}C_6H_{16}O_6 + H_2O + A_2^- \longrightarrow L\text{-}C_6H_{16}O_6 + H_2O + A_2^- \quad (XIII)$$

Equation 1 refers to an elementary step. Since the standard chemical potential of $NHNO_2^-$ in reaction XI is unknown, the $\Delta F^{\circ\prime}$ for the first step is known only to an additive constant for the reaction series. Again, in a concerted mechanism[25] for reaction XII such as



bonds 2, 4, and 6 tend to be formed at the expense of bonds 1, 3, and 5 (and bond 8 doubled at the expense of bond 7). However, in a later stage along the reaction

(20) R. P. Bell and G. L. Wilson, *Trans. Faraday Soc.*, 46, 407 (1950).

(21) R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1288 (1949).

(22) L. K. J. Tong and A. R. Olson, *J. Amer. Chem. Soc.*, 63, 3406 (1941).

(23) R. P. Bell and E. C. Baughan, *Proc. Roy. Soc.*, A158, 464 (1937).

(24) The mechanism assumed for the base-catalyzed decomposition of nitramide was first proposed by Pedersen. See K. J. Pedersen, *J. Chem. Phys.*, 38, 581 (1934). For further discussion of this mechanism see A. Voipio, *Ann. Acad. Sci. Fennicae, Ser. A*, No. 92 (1958); E. F. Caldin and J. Peacock, *Trans. Faraday Soc.*, 51, 1217 (1955); R. P. Bell, *Advan. Catal.*, 4, 151 (1952). The concentration of HNN(OH)=O in solution was estimated from the deviation of the rate constant for decomposition of nitramide catalyzed by nitramide anion from the other rate constants as plotted by Tong, *et al.*[21] (See also ref 17.)

(25) Compare M. Eigen, *Discussions Faraday Soc.*, 39, 7 (1965).

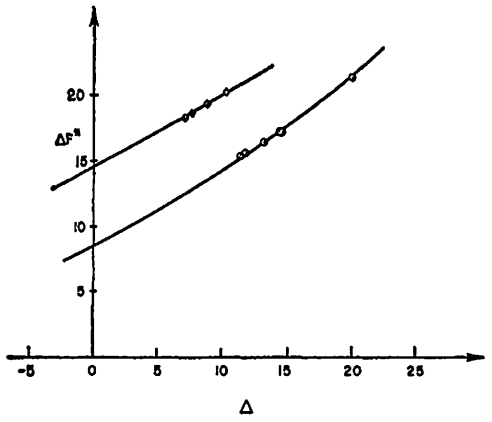


Figure 4. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for reaction of cyclic ketones with carboxylate anions and other bases: ⊙, reaction VI; ◇, reaction VII.

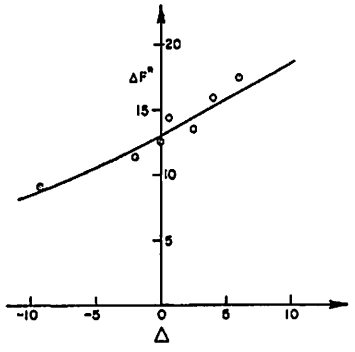


Figure 5. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for reaction of ketones with OH^- and SH^- (reaction VIII).

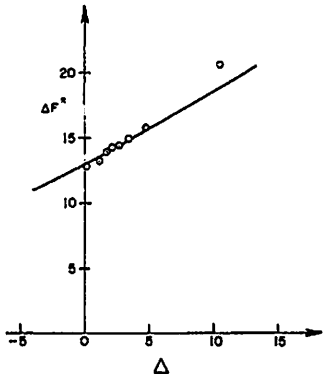


Figure 6. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for reaction of ethyl nitroacetate with carboxylate anions and other bases (reaction IX).

coordinate the motion of bond 4 reverses itself and eventually HA_1 is re-formed. The derivation of eq 1 (or really of eq 9) was based on a monotonic motion of each bond, not on a reversal, and the relevant $\Delta F^{\circ\prime}$ for use in eq 1 is that for some hypothetical process, one in which reversal is absent. Equation 1 might then represent the behavior reasonably well except when reversal occurs before the barrier maximum is reached along the reaction coordinate. Accordingly, the effective $\Delta F^{\circ\prime}$ is again unknown to an additive constant. Related remarks apply to reaction XIII.[25]

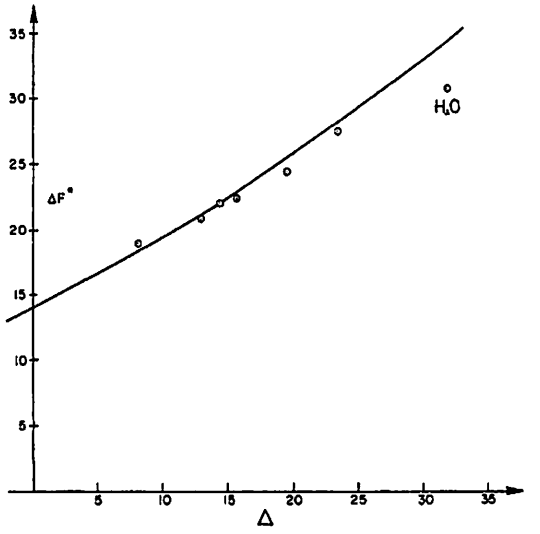


Figure 7. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for reaction of trimethoxybenzene with carboxylate anions and other bases (reaction X).

Table I: Quadratic Free Energy Relation for Proton Transfers

Reaction	Range of Δ, kcal/mol	λ, kcal/mol	Mean α	No. of points	Ref
III	−5–4	15.2	0.5	25	*a*
IV	−2–3	22	0.4	4	*a*
V	−6.6–30.5	46	0.7	89	*a, b*
VI	11–20	34	0.7	6	*c*
VII	7–10	58	0.6	4	*d*
VIII	−9–6	52	0.5	7	*a, b*
IX	0.2–10.5	52	0.5	8	*e*
X	8–32	56	0.6	7	*f*
XI	−2–22	24	0.7	33	*g, h*
XII	−2.6–18	56	0.55	48	*i*
XIII	−21–3	88	0.45	33	*j*

[a] Reference 17. [b] Reference 11. [c] Reference 12. [d] Reference 13. [e] Reference 15. [f] Reference 16. [g] Reference 1. [h] R. P. Bell and G. L. Wilson, *Trans. Faraday Soc.*, 46, 407 (1950); R. P. Bell and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1288 (1949); L. K. J. Tong and A. R. Olson, *J. Amer. Chem. Soc.*, 63, 3406 (1941); R. P. Bell and E. C. Baughan, *Proc. Roy. Soc.*, A158, 464 (1937); K. J. Pederson, *J. Chem. Phys.*, 38, 581 (1934); A. Voipio, *Ann. Acad. Sci. Fennicae, Ser. A*, No. 92 (1958); E. F. Caldin and J. Peacock, *Trans. Faraday Soc.*, 51, 1217 (1955); R. P. Bell, *Advan. Catal.*, 4, 151 (1952); see also ref 17. [i] See ref 19; compare M. Eigen, *Discussions Faraday Soc.*, 39, 7 (1965). [j] Reference 1b.

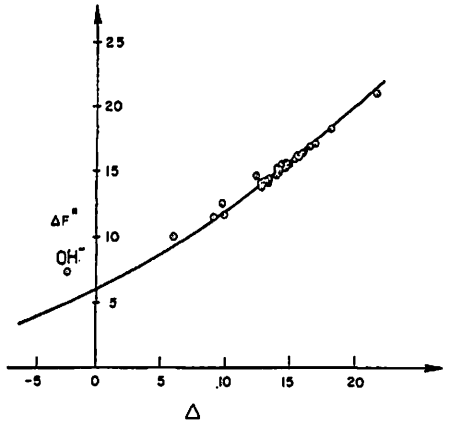


Figure 8. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for base-catalyzed decomposition of nitramide (reaction XI).

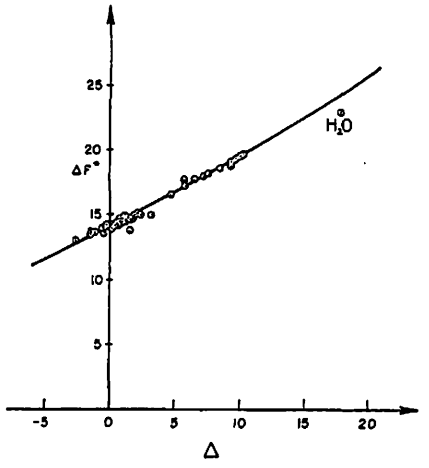


Figure 9. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for base-catalyzed dehydration of acetaldehyde (reaction XII).

Thus in the case of reactions XI–XIII we shall write

$$\Delta F^{\circ\prime} = \mp RT \ln K_i + B \qquad (7)$$

where the minus sign applies when $i = 1$, the plus sign when $i = 2$, and B is a constant chosen to give the best fit in each case (Figures 8–10). For reactions XI–XIII, $B = 20 \pm 5$, -4 ± 4, and 1 ± 4 kcal mol^{-1}, respectively,[26] and $\lambda = 6 \pm 3$, 14 ± 2, and 22 ± 2 kcal mol^{-1}, respectively.

(c) *Gas-Phase Atom Transfers.* Five gas-phase atom transfer reactions are also considered[3b,27-31]

$$CH_3 + RH \longrightarrow CH_4 + R \qquad (XV)$$

$$Na + RCl \longrightarrow NaCl + R \qquad (XVI)$$

$$CF_3 + RH \longrightarrow CF_3H + R \qquad (XVII)$$

$$RH + Cl \longrightarrow R + HCl \qquad (XVIII)$$

$$RH + Br \longrightarrow R + HBr \qquad (XIX)$$

Equation 4 was used for reactions XV–XIX. The results are given in Table II and Figures 11–13.[3b,27-32]

(d) *Kinetic Isotope Effect.* In Figure 14 kinetic isotope effect data (for proton transfer from ketones to bases) are compared with eq 6.[33]

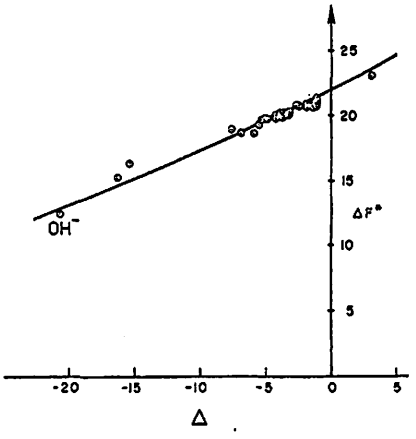


Figure 10. ΔF^* *vs.* $\Delta F^{\circ\prime}$ for acid-catalyzed mutarotation of glucose (reaction XIII).

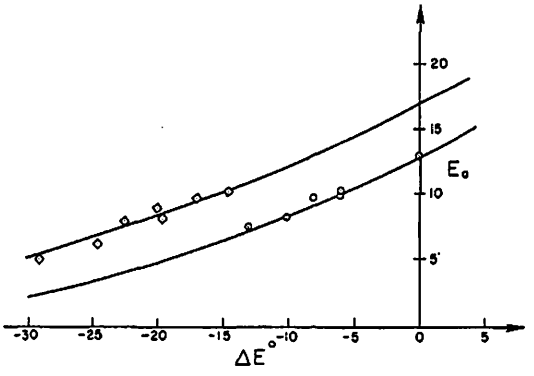


Figure 11. E_a *vs.* ΔE° for gas-phase hydrogen atom extraction from saturated hydrocarbons by methyl (⊙, reaction XV) and chlorine abstraction from alkyl chlorides by sodium atoms (◇, reaction XVI).

(26) In Figure 8, the actual B used was 19.6 kcal mol^{-1}.

(27) R. E. Dodd, *J. Chem. Phys.*, 26, 1353 (1957).

(28) H. Carmichael and H. S. Johnston, *ibid.*, 41, 1975 (1964).

(29) H. S. Johnston and C. Parr, *J. Amer. Chem. Soc.*, 85, 2544 (1963).

(30) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *Can. J. Chem.*, 38, 1643 (1960).

(31) H. S. Johnston and P. Goldfinger, *J. Chem. Phys.*, 37, 700 (1962).

(32) In reactions XV–XIX the substituents are the following: (XV) RH: CH_4, C_2H_6, C_3H_8, C_4H_{10}, i-C_4H_{10}, $(CH_3)_4C$; (XVI) RH: CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, C_2H_5Cl, C_3H_7Cl, t-C_4H_9Cl; (XVII) RH: CH_4, CHD_3, C_2H_6, C_3H_8, C_4H_{10}, CCl_3H; (XVIII) RH: CH_4, C_2H_6, various H's in C_3H_8 and C_4H_{10}, CH_3Cl, CH_2Cl_2, $CHCl_3$; (XIX) RH: CH_4, C_2H_6, various H's in C_3H_8 and C_4H_{10}.

Table II

Reaction	Range of ΔE°, kcal/mol	λ_E, kcal/mol	Mean α	No. of points	Ref
XV	0 to −14	52	0.45	6	*a*
XVI	−29 to 14.4	68	0.4	7	*b*
XVII	−14 to −2	44	0.45	7	*c*
XVIII	−13 to 10	24	~0.5	12	*d*

[a] Reference 27. [b] Reference 3b. [c] Reference 28. [d] References 29–31.

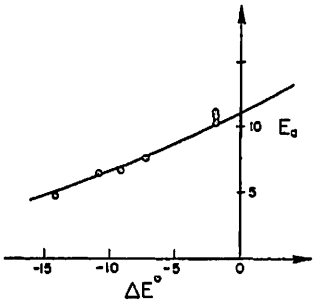


Figure 12. E_a *vs.* ΔE° for gas-phase hydrogen atom abstraction from saturated hydrocarbons by CF_3 (reaction XVII).

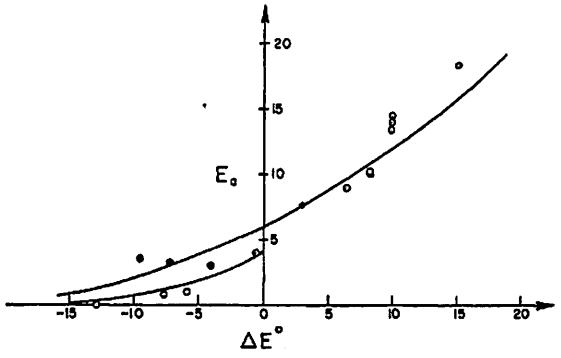


Figure 13. E_a *vs.* ΔE° for gas-phase hydrogen atom abstraction from saturated hydrocarbons by Cl (lower curve, reaction XVIII) or by Br (upper curve, reaction XIX). The filled circles refer to abstraction from chlorinated hydrocarbons by Cl.

Discussion

According to eq 1 (or to its counterpart for E_a), the sign of $\alpha - 1/2$ depends only on that of $\Delta F^{\circ\prime}$ (or, in the other case, ΔE°). In all cases in Figures 1–13 and Tables I and II the sign is seen to be that expected from that equation. (In the case of reactions XI–XIII the agreement was forced by choice of the unknown constant B in eq 7.) Except for reaction XIX perhaps, the data are consistent with eq 1 or its counterpart.

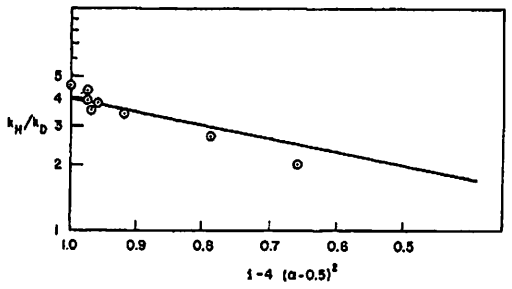


Figure 14. Kinetic isotope effect for proton transfer from ketones, compared with eq 6 (——).

When the data are sufficiently close to $\Delta F^{\circ\prime} = 0$ to permit λ (or λ^E) to be evaluated, the Brønsted slope α can be predicted from eq 5. In other cases, eq 1 can be regarded simply as a one-parameter equation, which compares in accuracy with the usual two-parameter equations in the literature. There is no assurance that λ should be constant for a reaction series in Figures 1–13, but the fit suggests that this one-parameter equation (1) suffices thus far. However, additional data could force a different view.

From the results in Tables I and II a series of intrinsic barriers is obtained, as in Tables III and IV. For some of the A_2 entries in Table III only representative compounds are given. The values in parentheses in Table III are not as certain as the others, since they depend on the use of the quantity B. The present analysis must be regarded as conjectural though supported by the approximate arguments in ref 7. If the analysis is valid, these intrinsic barriers become fundamental quantities in kinetics. They are also expected to obey an additivity property (eq 8) which can be tested, directly or indirectly, when sufficient data become available.

$$\lambda_{12} = {}^1/_2(\lambda_{11} + \lambda_{22}) \qquad (8)$$

where λ_{12} refers to the cross-reaction XX and λ_{ff} to the exchange reaction XXI.

$$A_1B + A_2 \longrightarrow A_1 + BA_2 \qquad (XX)$$

$$A_fB + A_f \longrightarrow A_f + BA_f \qquad (XXI)$$

Additivity might be expected to hold best if neither $\lambda_{11}/4$ nor $\lambda_{22}/4$ is near zero. An example where one λ_{ff} is near zero is the $\lambda_{Cl}/4$ in Table I, ref 7. If the λ's were additive, the minimum value for $\lambda_E/4$ in the first row of Table IV of the present paper would be 6.5 kcal/mol, as seen from the fourth row; the actual value is 4 kcal/mol.

(33) R. P. Bell and D. M. Goodall, *Discussions Faraday Soc.*, 39, 16 (1965). This paper also contains more extensive listings of kinetic isotope effect *vs.* pK_A such as that for nitro compounds and ketones. Figures 3 and 6, however, indicate that λ for NO_2 compounds is larger than for ketones, so that these data are not included.

Table III: Intrinsic Barriers for Proton Transfer in Solution, $\lambda/4$

A_1^-	A_2^-	$\lambda/4$, kcal/mol	Reaction
RNH_2	RCO_2^-, $C_6H_5O^-$	4	III
$RR'R''N$	$HO(CH_2)_2S^-$	5.5	IV
NO_2NH^-	RCO_2^-, OH^-, RNH_2	(6)	XI
$(CH_2)_4COC^-CO_2Et$	RCO_2^-	8.5	VI
CH_3COC^-RR'	RCO_2^-, $C_6H_5O^-$	11.5	V
CH_3COC^-RR'	OH^-, SH^-	13	VIII
$NO_2CH^-CO_2Et$	RCO_2^-	13	IX
$(CH_3O)_2C_6H_3$	RCO_2^-, OH^-, H_2O	14	X
$(CH_2)_5COC^-CO_2Et$	RCO_2^-	14.5	VII
$CH_3CH(OH)_2 + H_2O$	RCO_2^-, OH^-, $C_6H_5O^-$	(14)	XII
Glucose + H_2O	RCO_2^-, OH^-, H_2O	(22)	XIII

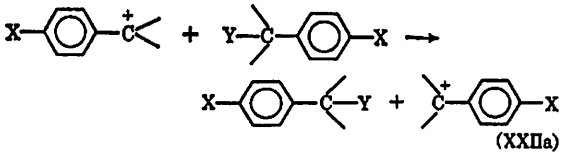
Table IV: Intrinsic Barriers for Gaseous Atom Transfers, $\lambda_E/4$

A_1	B	A_2	$\lambda_E/4$, kcal/mol	Reaction
C_nH_{2n+1}	H	Cl	4	XIX
C_nH_{2n+1}	H	Br	6	XVIII
C_nH_{2n+1}	H	CF_3	11	XVII
C_nH_{2n+1}	H	CH_3	13	XV
$C_nH_{2n+1-m}Cl_m$	Cl	Na	17	XVI

The point for H_2O has always been a well-known anomalous point in Brønsted plots. At first sight the anomaly, in the present terms, can either be ascribed to a difference $\lambda_{OH^-} - \lambda_{RCO_2^-}$ or to a possibility that the effective $\Delta F^{\circ\prime}$ for use in eq 1 is not that calculated from the usual acidity of water. The former possibility can be eliminated,[34] but further mechanistic analysis is needed to see if the latter one is appropriate.

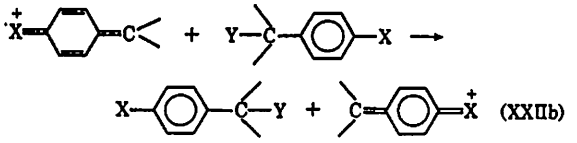
According to a bond energy–bond order equation, the λ for a reaction depends not only on the bond strengths but also on how rapidly the bond energies vary with bond order. Since the bond in HCl is stronger than that in HBr, the second of these two factors might be involved to account for the inversion of λ's in the first two rows of Table IV.

An example of how conjugation changes could affect a λ is seen as follows. Consider some exchange reaction of a *para*-substituted triphenylmethyl cation.[35]



(XXIIa)

If, for some substituent X, the cationic charge is centered instead on X, we have



(XXIIb)

The bond reorganization is greater in the second reaction than in the first, and so the latter should have a larger barrier, $\lambda/4$. Such λ differences would not disturb correlations involving equilibrium properties.[36]

An Alternative Equation

In the present paper the analysis of the various results is based on eq 1. In ref 7 an alternative relation was also derived from simple bond energy–bond order arguments. Instead of eq 1 one obtains[37]

$$\Delta F^*/\Delta F_0^* = 1 + {}^1/_2x + [\ln \cosh ({}^1/_2x \ln 2)]/(\ln 2) \quad (9)$$

where x is $\Delta F^{\circ\prime}/\Delta F_0^*$ and ΔF_0^* is the value of ΔF^* at $\Delta F^{\circ\prime} = 0$. At moderate to low x, this equation reduces to eq 1.[7] From eq 9 one obtains eq 10 instead of eq 5.[38]

$$\alpha = {}^1/_2[1 + \tanh ({}^1/_2x \ln 2)] \quad (10)$$

which again reduces to eq 5 at moderate to low x. Instead of eq 6 one finds

$$\ln (k_H/k_D) \cong \frac{\lambda_H - \lambda_D}{4RT}\{1 - (\alpha - {}^1/_2)x + [\ln \cosh ({}^1/_2x \ln 2)/\ln 2]\} \quad (11)$$

where α is given by eq 10. In ref 7, modifications of eq 1 and 5 were considered for the case where steric and work terms are included; we omit further discussion of that aspect.

A comparison of eq 1 and 9 is given in Figure 15. A comparison of the quantity which multiplies $(\lambda_H - \lambda_D)/4RT$ in eq 6 and 11 is given in Figure 16. (The quantity is $\partial\Delta F^*/\partial\Delta F_0^*$.) The two sets of equations are seen to be fairly similar. Related remarks apply to a comparison of eq 5 and 10 for α.[7] Evidently the apparent tendency for points at the higher $(\alpha - {}^1/_2)^2$

(34) Except for the mutarotation of glucose, the rates when OH^- is a base are low. (See reaction XI and also the differences of λ's of reactions V and VIII.) The rates are high when H_2O is an acid (reactions X and XII). Only if the rates were low (or high) in both cases could the anomaly be assigned to a λ difference. Thus the λ given in Tables I and III for reaction VIII is only an apparent λ.

(35) We are indebted to R. W. Taft for his very helpful remarks and for calling our attention to this reaction.

(36) These remarks were originally prompted by some results on hydrolysis of substituted triphenylmethyl cations by R. A. Diffenbach, K. Sano, and R. W. Taft, *J. Amer. Chem. Soc.*, 88, 4747 (1966), but the current experimental picture is somewhat uncertain (R. W. Taft, private communication).

(37) See R. A. Marcus, *J. Phys. Chem.* 72, 891 (1968), eq 20. The analog of eq 20 there is written here in terms of free energies, for convenience of comparison.

(38) R. A. Marcus, ref 37, eq 35.

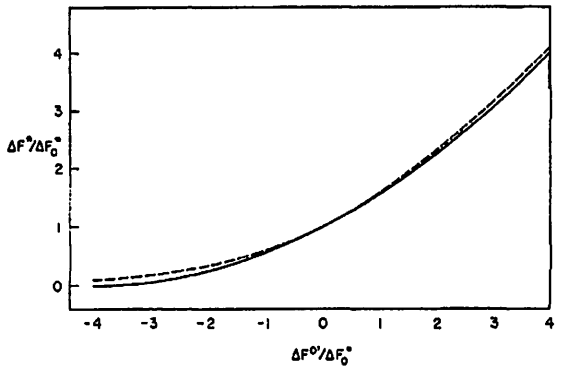


Figure 15. $\Delta F^*/\Delta F_0^*$ *vs.* $\Delta F^{\circ\prime}/\Delta F_0^*$ for eq 1 (——) and 9 (- - -).

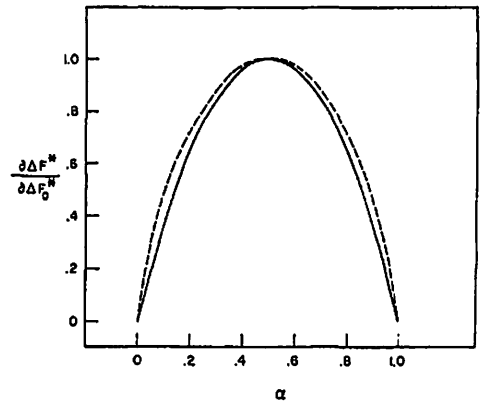


Figure 16. $\partial\Delta F^*/\partial\Delta F_0^*$ *vs.* α for eq 6 (——) and 11 (- - -). ($\partial\Delta F^*/\partial\Delta F_0^*$ is the coefficient of $(\lambda_H - \lambda_D)/4RT$ in those equations.)

to fall below the theoretical line in Figure 14 would not be reduced if eq 11 were used instead of eq 6.

Another application of eq 1 or 9 is to the calculation of the rate constants of cross-reactions (XX) from those of exchange reactions (XXI).[39] Extensive application has been made to inorganic electron transfers[40] and to several atom transfers in inorganic redox reactions.[41]

Concluding Remarks

The free energy plots considered above are consistent with eq 1 and 5 and lead to a table of intrinsic barriers, barriers freed from ΔF° contributions.

There are several precautionary notes to be considered, two of which have been mentioned already.

(1) Variation in a substituent causes variations in $\Delta F^{\circ\prime}$ but could also cause variations in λ. An example is the change in conjugation mentioned in an earlier section. The ultimate test for variation in λ would be measurement of the effect of substituents (*e.g.*, in A_1) on the ΔF^* for the exchange reaction XXI, $\lambda_{II}/4$. A variation in λ, unless corrected, leads to a misleading Brønsted slope, α.

(2) The additivity relation given by eq 8 is not yet established for atom or proton transfers, and indeed is dubious when one of the λ_{ii}'s vanishes.

(3) Equation 1 was derived for a reaction step whose potential energy function along the reaction coordinate possessed a single maximum. When there are several successive maxima and when the ΔF^* and ΔF° associated with any one maximum can be isolated (in theory or practice), eq 1 and 5 refer only to this isolated or isolable step.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This research was also supported by a grant from the National Science Foundation at the University of Illinois.

(39) R. A. Marcus, ref 37, eq 5, 24.

(40) N. Sutin, *Ann. Rev. Phys. Chem.*, 17, 119 (1966); R. A. Marcus, *ibid.*, 15, 155 (1964).

(41) N. Sutin, *ibid.*, 15, 154 (1964); N. Sutin, "Proceedings of the Symposium on Exchange Reactions, Upton, N. Y. 1965," International Atom Energy Agency, Vienna, 1965, p 7.; A. Haim and N. Sutin, *J. Amer. Chem. Soc.*, 88, 434 (1966).