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The Use of Variable Intrinsic Barriers for the Prediction of Brønsted Slopes for the Deprotonation of Carbon Acids

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Abstract: Extensive sets of experimental data for the deprotonation of carbon acids by a variety of bases in aqueous solution have been analyzed in terms of a variable intrinsic barrier ($\Delta G_0^\ddagger = A + B\Delta G^\circ$) in the Marcus equation. It is shown that this empirically deduced two-parameter relationship accurately reproduces both Brønsted α values and Brønsted β values over a wide range of reactivities. This treatment is shown to be equally applicable to both normal and "abnormal" carbon acids, with Brønsted $\alpha > 1$ in the latter cases being a natural outcome when the variable intrinsic barrier shows a pronounced dependence upon ΔG°.

The application of the simplest form of the Marcus relationship (eq 1) has recently been examined[1] for the hydroxide ion catalyzed deprotonation of four series of benzylic ketones (**1**).

$$\Delta G^\ddagger = \Delta G_0^\ddagger(1 + \Delta G^\circ/4\Delta G_0^\ddagger)^2 \qquad (1)$$

$XC_6H_4CH_2COPy$
1

(Py = 3-pyridyl, 4-pyridyl, and their *N*-methyl cations)

It was found that the intrinsic barrier ($\Delta G_0^\ddagger$) was not constant when substituents (X) were varied within each of these series. However, within each series of ketones, the substituent effect upon the intrinsic barrier could be expressed[2] as a linear function of the free energy of reaction (eq 2), which leads to the modified form of the Marcus equation that is given in eq 3.

$$\Delta G_0^\ddagger = A + B\Delta G^\circ \qquad (2)$$

$$\Delta G^\ddagger = (A + B\Delta G^\circ)(1 + \Delta G^\circ/4(A + B\Delta G^\circ))^2 \qquad (3)$$

In a report[3a] that closely followed our own work,[1] Yamataka and Nagase have deduced a variable intrinsic barrier which depends upon the free energy of reaction from ab initio molecular orbital calculations of hydrogen atom transfer reactions. These workers showed that linear relations similar to eq 2 above emerge from these calculations, and they also extended this observation to several selected sets of literature data for solution reactions. Rose and Stuehr[3b] have also shown that the emprical relationship of eq 2 is applicable to proton transfers from intramolecularly hydrogen bonded phenols. These observations, and in particular the success of eq 2 and 3 as descriptions of substituent effects upon the hydroxide ion catalyzed deprotonation of benzylic ketones, suggest that this approach may be generally applicable to the quantitative description of rate–equilibrium relationships for carbon acid deprotonations. The current work reports an investigation of the applicability of these equations to literature data for reactions corresponding to eq 4 and 8 in aqueous solution.

Cohen and Marcus[4] first applied eq 1 to various reactions involving proton transfers in aqueous solution. Kresge[5] subsequently reviewed the relationship between the Marcus treatment and the Brønsted equation and elaborated upon the assumptions inherent in its use and the limitations to be expected. The Brønsted α value ($= d(\Delta G^\ddagger)/d(\Delta G^\circ)$) for the deprotonation of a series of substituted carbon acids by a common base (eq 4) is defined as the first derivative of eq 1 or 3. Differentiation of eq 1 and 3 gives eq 5 and 6, respectively.

$$XCH + B \rightleftharpoons XC^- + BH^+ \qquad (4)$$

$$\alpha = 0.5[1 + \Delta G^\circ/4\Delta G_0^\ddagger] \qquad (5)$$

$$\alpha = 0.5[1 + \Delta G^\circ/4(A + B\Delta G^\circ)] + \mathrm{B}[1 - [\Delta G^\circ/4(A + B\Delta \mathrm{G}^\circ)]^2] \qquad (6)$$

In an early application of eq 1 to deprotonation reactions of carbon acids, Marcus recognized[6] the possibility of substituent dependent intrinsic barriers and expressed this concept in the form of eq 7, where $\beta_1 = d(\Delta G_0^\ddagger)/d(\Delta G^\circ)$. However, further evaluation of β_1 was not attempted since no analytical expression was suggested for $\Delta G_0^\ddagger = f(\Delta G^\circ)$.

$$\alpha = 0.5[1 + \Delta G^\circ/4\Delta G_0^\ddagger] + \beta_1[1 - (\Delta G^\circ/4\Delta G_0^\ddagger)^2] \qquad (7)$$

Such a function is now available in the empirically deduced eq 2. Substitution of eq 2 and its derivative, $\beta_1 = B$, into eq 7, generates eq 6. Thus the empirically deduced eq 3 and its derivative, eq 6, are exactly consistent with Marcus' eq 7.

Analogous ideas to those presented above are also applicable to the reaction of eq 8, which describes the deprotonation of a carbon acid by a series of substituted bases. This latter reaction is represented by a Brønsted β value ($= d(\Delta G^\ddagger)/d(\Delta G^\circ)$) to which the formalisms of eq 5 and 6 are also applicable upon simply substituting β for α, i.e. eq 9 and 10.

$$CH + YB \rightleftharpoons C^- + YBH^+ \qquad (8)$$

$$\beta = 0.5[1 + \Delta G^\circ/4\Delta G_0^\ddagger] \qquad (9)$$

$$\beta = 0.5[1 + \Delta G^\circ/4(A + B\Delta G^\circ)] + B[1 - [\Delta G^\circ/4(A + B\Delta G^\circ)]^2] \qquad (10)$$

The intrinsic barrier ($\Delta G_0^\ddagger$) may be calculated from eq 1 for any reaction for which both the rate and equilibrium constants are known. For such a reaction, ΔG° ($= -RT \ln K$) and $\Delta G^\ddagger$ (from the Eyring equation) are readily evaluated and $\Delta G_0^\ddagger$ can then be obtained by the solution of the quadratic equation 11, which is derived from eq 1. In general, the appropriate root of eq 11 is given by eq 12. The other root, which is either negative (for $\Delta G^\circ < 0$) or very small (for $\Delta G^\circ > 0$), has no physical significance.

$$(\Delta G_0^\ddagger)^2 + \Delta G_0^\ddagger\,(0.5\Delta G^\circ - \Delta G^\ddagger) + (\Delta G^\circ)^2/16 = 0 \qquad (11)$$

$$\Delta G_0^\ddagger = 0.5\,\Delta G^\ddagger\,[1 + (1 - \Delta G^\circ/\Delta G^\ddagger)^{0.5}] - \Delta G^\circ/4 \qquad (12)$$

Table I shows a compilation of the Brønsted α values that have been located in the literature for carbon acid deprotonations in aqueous solution. Many of these are the "anomalous" $\alpha > 1$ measured by Bordwell and co-workers[7] for deprotonation of

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[1] Bunting J. W.; Stefanidis, D. *J. Am. Chem. Soc.* **1988**, *110*, 4008.

[2] Equation 3 is only applicable to X substituents which do not stabilize the enolate ion conjugate base of **1** via resonance interactions. Thus, substituents such as 4-NO_2, 4-CN, and 4-OCH_3 show[1] significant deviations from eq 2.

[3] (a) Yamataka, H.; Nagase, S. *J. Org. Chem.* **1988**, *53*, 3232. (b) Rose, M. C.; Stuehr, J. *J. Am. Chem. Soc.* **1971**, *93*, 4350.

[4] Cohen, A. H.; Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 4249.

[5] Kresge, A. J. *Chem. Soc. Rev.* **1973**, *2*, 475.

[6] Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224.

0002-7863/89/1511-5834$01.50/0

Table I. Analysis of Rate–Equilibrium Data for Reactions of Eq 4 via Eq 1 and 5

acid (XCH)	base	α(exptl)[a]	$\Delta G°$ (X = H)	$\Delta G_0^{\ddagger}$ (X = H)	α(calcd)[b]
$XPhCH_2NO_2$	HO^-	1.54[7]	-9.7	19.0	0.44
	morpholine	1.28[7]	-2.5	18.7	0.48
	2,4-lutidine	1.30[7]	+0.3	18.7	0.50
$XPhCH(CH_3)NO_2$	HO^-	1.14[7]	-9.0	20.6	0.45
	piperidine	0.98[7]	-5.2	20.4	0.47
	diethylamine	0.96[7]	-5.1	20.8	0.47
	piperazine	0.89[7]	-3.5	20.3	0.48
	morpholine	0.92[7]	-1.8	20.6	0.49
$XPhCH_2CO(3\text{-}C_5H_4N)$	HO^-	0.66[1]	-1.0	15.8	0.49
$XPhCH_2CO(4\text{-}C_5H_4N)$	HO^-	0.68[1]	-2.4	16.2	0.48
$XPhCH_2CO(3\text{-}C_5H_4N^+CH_3)$	HO^-	0.73[1]	-5.0	16.0	0.46
$XPhCH_2CO(4\text{-}C_5H_4N^+CH_3)$	HO^-	0.76[1]	-6.8	16.7	0.45
$XPhCH_2CH(COMe)CO_2Et$	$CH_3CO_2^-$	0.76[8]	+9.6	14.8	0.58
$XPhCH_2CH(COMe)_2$	$CH_3CO_2^-$	0.51[8c]	+7.8	15.3	0.57

[a] Superscripts indicate references from which the data have been obtained. Brønsted α values based[8] upon detritiation data are not analyzable by the current method in the absence of accurate tritium isotope effects for these reactions. [b] Calculated from eq 5 using the $\Delta G°$ (for X = H) and $\Delta G_0^{\ddagger}$ values listed in this table. [c] Reference 6 gives σ = 0.58; however, recalculation of the original data gives α = 0.51.

Table II. Analysis of Rate–Equilibrium Data for Reactions of Eq 4 via Eq 3 and 6

acid	base	*A*, kcal/mol	*B*	α(calcd)[a]	Δα[b]
$XPhCH_2NO_2$	HO^-	29.9 (±0.07)	1.12 (±0.07)	1.54	0.00
	morpholine	20.6 (±0.3)	0.80 (±0.09)	1.28	0.00
	2,4-lutidine	18.3 (±0.1)	0.79 (±0.09)	1.29	0.01
$XPhCH(CH_3)NO_2$	HO^-	26.8 (±0.3)	0.68 (±0.03)	1.12	0.02
	piperidine	23.1 (±0.2)	0.52 (±0.03)	0.99	-0.01
	diethylamine	23.3 (±0.1)	0.50 (±0.01)	0.97	-0.01
	piperazine	21.7 (±0.1)	0.42 (±0.02)	0.90	-0.01
	morpholine	21.4 (±0.1)	0.44 (±0.01)	0.93	-0.01
$XPhCH_2CO(3\text{-}C_5H_4N)$	HO^-	16.0[c]	0.18	0.67	-0.01
$XPhCH_2CO(4\text{-}C_5H_4N)$	HO^-	16.7[c]	0.22	0.70	-0.01
$XPhCH_2CO(3\text{-}C_5H_4N^+CH_3)$	HO^-	17.4[c]	0.28	0.74	-0.01
$XPhCH_2CO(4\text{-}C_5H_4N^+CH_3)$	HO^-	18.9[c]	0.32	0.77	-0.01
$XPhCH_2CH(COMe)CO_2Et$	$CH_3CO_2^-$	13.4 (±0.3)	0.15 (±0.03)	0.73	0.03
$XPhCH_2CH(COCH_3)_2$	$CH_3CO_2^-$	15.8 (±0.3)	-0.05 (±0.04)	0.51	0.00

[a] Calculated from eq 6 using A and B from this table, and $\Delta G°$ for (X = H) from Table I. [b] α(exptl) − α(calcd). [c] Data from ref 1.

ring-substituted phenylnitromethanes. According to eq 5, α is predicted to be <0.5 when $\Delta G° < 0$. Thus, in terms of Marcus theory (eq 1), any α > 0.5 is "anomalous" if $\Delta G° < 0$. On this basis, most of the experimentally determined α values in Table I must be considered "anomalous"! The magnitudes of these anomalies are obvious if one compares these experimental α values with values of α calculated from eq 5 with $\Delta G°$ and $\Delta G_0^{\ddagger}$ (calculated from eq 12) for the unsubstituted carbon acid (X = H) in each reaction series (see Table I). One can only conclude that the simple form (eq 1) of the Marcus relationship is not applicable to the description of the data for the reactions of Table I.

Intrinsic barriers ($\Delta G_0^{\ddagger}$) have been calculated from eq 12 for every substituent for each of the reactions of Table I. Some of these data are shown graphically in Figure 1. The linear dependence of $\Delta G_0^{\ddagger}$ upon $\Delta G°$ that was previously described[1] by eq 2 for benzylic ketones appears to be a general phenomenon. Values of *A* and *B* have been evaluated from the linear dependence of $\Delta G_0^{\ddagger}$ upon $\Delta G°$ for each of the reactions in Table I. These parameters are listed in Table II. This latter table also contains α values calculated from eq 6 with *A*, *B*, and $\Delta G°$ for X = H in each series. In general, there is excellent agreement between the calculated α values of Table II and the experimental values of Table I.

Experimental measurements of Brønsted β values relevant to eq 8 are far more numerous than are the available data on Brønsted α values for eq 4. At the present time, the investigation of the applicability of eq 2 and 3 to the reaction of eq 8 has been limited to an analysis of the extensive compilations[9-11] of data for the deprotonation of an enormous variety of carbon acids by substituted carboxylate ion bases.

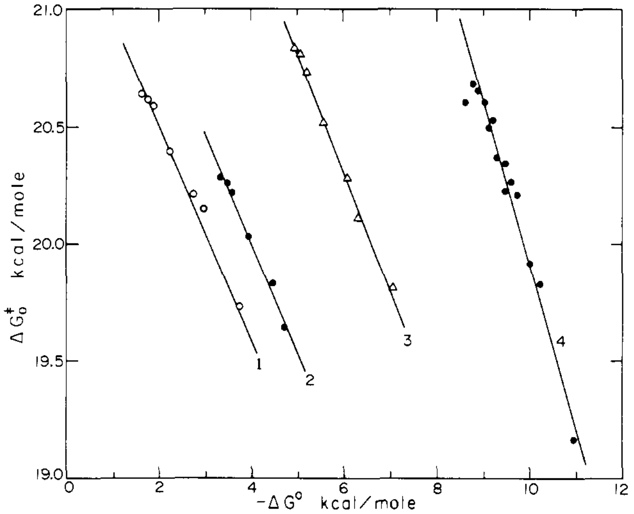

Figure 1. Dependence of $\Delta G_0^{\ddagger}$ upon $\Delta G°$ for the deprotonation of $XC_6H_4CHMeNO_2$ by (1) morpholine, (2) piperazine, (3) diethylamine, and (4) hydroxide ion. The original experimental data are from ref 7.

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(7) Bordwell, F. G.; Boyle, W. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907.

(8) Bell, R. P.; Grainger, S. *J. Chem. Soc., Perkin Trans. 2*, 1976, 1367.

(9) Guthrie, J. P. *Can. J. Chem.* **1979**, *57*, 1177.

(10) Argile, A.; Carey, A. R. E.; Fukata, G.; Harcourt, M.; More-O'-Ferrall, R. A.; Murphy, M. G. *Isr. J. Chem.* **1985**, *26*, 303.

(11) (a) Bordwell, F. G.; Hughes, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 4737. (b) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1982**, *47*, 3224.

(12) Bell, R. P.; Lidwell, O. M. *Proc. R. Soc. London, A* **1940**, *176*, 88.

(13) Bell, R. P.; Cox, B. G. *J. Chem. Soc. B* **1971**, 652.

(14) Bell, R. P.; Hillier, G. R.; Manfield, J. W.; Street, D. G. *J. Chem. Soc. B* **1967**, 827.

(15) Bell, R. P.; Barnes, D. J. *Proc. R. Soc. London, A* **1970**, *318*, 421.

(16) Bell, R. P.; Everett, D. H.; Longuet-Higgins, H. C. *Proc. R. Soc. London, A* **1946**, *186*, 433.

(17) Hibbert, F.; Long, F. A.; Walters, E. A. *J. Am. Chem. Soc.* **1971**, *93*, 2829.

(18) Bell, R. P.; Crooks, J. E. *Proc. R. Soc. London, A* **1965**, *286*, 285.

Table III. Analysis of Rate–Equilibrium Data for the Deprotonation of Carbon Acids by Carboxylate Anions (Eq 8) via Eq 1 and 9[a]

acid	pK_a	β(exptl)[b]	log k_4	$\Delta G°$	$\Delta G_0^‡$	β(calcd)[c]
CH_3COCH_3	20.0	0.88[12]	-8.06	21.8	15.6	0.67
$(EtSO_2)_2CHMe$	14.56	0.73[13]	-2.57	14.4	12.7	0.64
$CO(CH_2SO_3^-)_2$	14.45	0.67[14]	-3.90	14.3	14.8	0.62
$MeCOCH_2SO_3^-$	13.90	0.74[15]	-4.31	13.5	15.9	0.61
$CH_2(CO_2Et)_2$	13.60	0.80[16]	-2.58	13.1	13.6	0.62
$Me_3CCH(CN)_2$	12.87	0.97[17]	-1.13	12.1	12.2	0.62
$MeCOCH(Me)CO_2Et$	12.70	0.62[18]	-2.86	11.9	14.8	0.60
$PhCH_2CH(COMe)CO_2Et$	11.81	0.44[8]	-2.17	10.7	14.6	0.59
$PhCH_2CH(CN)_2$	11.80	1.00[8]	0.09	10.6	11.4	0.62
$MeCOCH_2CO_2Et$	10.98	0.57[19]	-1.03	9.5	13.7	0.57
2-$(EtO_2C)C_6H_9O$[d]	10.94	0.65[20]	-2.77	9.5	16.2	0.57
2-$(MeO_2C)C_5H_7O$[e]	10.52	0.58[20]	-0.60	8.9	13.5	0.58
9-(MeCO)fluorene	9.95	0.50[10]	-1.17	8.1	14.7	0.57
$MeCOCH_2COMe$	9.41	0.57[21]	-0.18	7.4	13.8	0.57
HCN	9.0	0.82[28]	3.80	6.8	8.9	0.60
$PhCOCH_2COMe$	8.82	0.55[19]	-0.08	6.6	14.1	0.56
$PhCOCH_2Q^+H$[f]	7.84	0.45[10]	0.28	5.2	14.3	0.55
$CH(CO_2Me)_3$	7.80	0.54[15]	0.34	5.2	14.3	0.55
$MeCH(NO_2)_2$	5.24	0.65[22]	-0.16	1.7	16.8	0.51
$EtQ^+CH_2Q^+Et$[g]	4.31	0.49[23]	1.46	0.4	15.3	0.50
$C_8H_{14}N^+$[h]	4.05	0.49[29]	1.73	0.1	15.1	0.50
3-(NO_2)camphor	3.54	0.47[24]	1.35	-0.6	15.9	0.50
$NO_2C_5H_5$[i]	3.25	0.44[25]	0.98	-1.0	16.6	0.49
2-$(PhCOCH_2)C_4H_3N_2$[j]	2.75	0.41[10]	2.48	-1.7	14.9	0.49
$C_{10}H_9^+$[k]	-1.46	0.39[10,26]	3.52	-7.5	16.2	0.44
$(MeO)_3C_6H_4^+$[l]	-5.40	0.41[10,27]	5.98	-12.8	15.0	0.39

[a] All rate and equilibrium data have been statistically corrected for the number of equivalent acidic hydrogen atoms in each carbon acid; log k_4 and $\Delta G°$ refer to deprotonation by a carboxylate ion of pK_a = 4 (see the text); $\Delta G°$ and $\Delta G_0^‡$ are in kcal/mol; k_4 in M^{-1} s^{-1}. [b] Superscripts indicate the reference from which the data have been obtained. [c] Calculated from eq 9 with the $\Delta G°$ and $\Delta G_0^‡$ values in this table. [d] 2-(Ethoxycarbonyl)cyclohexanone. [e] 2-(Methoxycarbonyl)cyclopentanone. [f] 4-Phenacylquinolinium cation. [g] *N,N'*-Diethyldi-2-quinolinylmethane dication. [h] C-5 protonated 2,4-dimethyl-3-ethylpyrrole. [i] 5-Nitro-1,3-cyclopentadiene. [j] 2-Phenacylpyrazine. [k] Azulenium cation. [l] C-2 protonated 1,3,5-trimethoxybenzene.

Table IV. Analysis of Rate–Equilibrium Data for the Deprotonation of Carbon Acids by Carboxylate Anions (Eq 8) via Eq 3 and 10[a]

acid[b]	*A*, kcal/mol	*B*	β(calcd)[c]	$\Delta\beta$[d]
CH_3COCH_3	10.7 (±0.4)	0.23 (±0.02)	0.88	0.00
$(EtSO_2)_2CHMe$	11.3 (±0.7)	0.10 (±0.06)	0.73	0.00
$CO(CH_2SO_3^-)_2$	14.5 (±0.1)	0.06 (±0.01)	0.67	0.00
$MeCOCH_2SO_3^-$	12.8 (±0.9)	0.19 (±0.06)	0.79	-0.05
$CH_2(CO_2Et)_2$	11.5 (±0.4)	0.19 (±0.03)	0.80	0.00
$Me_3CCH(CN)_2$	7.7 (±0.1)	0.37 (±0.01)	0.97	0.00
$MeCOCH(Me)CO_2Et$	14.8 (±0.4)	0.01 (±0.03)	0.61	0.01
$PhCH_2CH(COMe)CO_2Et$	16.3 (±0.1)	-0.16 (±0.01)	0.44	0.00
$PhCH_2CH(CN)_2$	7.1 (±0.4)	0.41 (±0.04)	1.00	0.00
$MeCOCH_2CO_2Et$	13.7 (±0.3)	0.00 (±0.03)	0.59	-0.02
2-$(EtO_2C)C_6H_9O$	14.9 (±0.2)	0.07 (±0.02)	0.64	0.01
2-$(MeO_2C)C_5H_7O$	13.5 (±0.2)	0.00 (±0.02)	0.58	0.00
9-(MeCO)fluorene	15.3 (±0.1)	-0.08 (±0.02)	0.49	0.01
$MeCOCH_2COMe$	13.9 (±0.2)	-0.01 (±0.02)	0.56	0.01
HCN	7.0 (±0.2)	0.23 (±0.03)	0.82	0.00
$PhCOCH_2COMe$	13.6 (±0.3)	-0.03 (±0.05)	0.53	0.02
$PhCOCH_2Q^+H$	15.2 (±0.4)	-0.10 (±0.07)	0.45	0.00
$CH(CO_2Me)_3$	14.0 (±0.4)	0.01 (±0.07)	0.56	-0.02
$MeCH(NO_2)_2$	16.6 (±0.1)	0.13 (±0.03)	0.64	0.01
$EtQ^+CH_2Q^+Et$	15.3 (±0.1)	-0.02 (±0.05)	0.48	0.01
$C_8H_{14}N^+$	15.1 (±0.1)	-0.03 (±0.03)	0.47	0.00
3-(NO_2)camphor	15.9 (±0.1)	-0.04 (±0.03)	0.46	0.01
$NO_2C_5H_5$	16.4 (±0.1)	-0.06 (±0.05)	0.43	0.01
2-$(PhCOCH_2)C_4H_3N_2$	14.8 (±0.1)	-0.09 (±0.04)	0.40	0.01
$C_{10}H_9^+$	15.7 (±0.5)	-0.06 (±0.07)	0.38	0.01
$(MeO)_3C_6H_4^+$	15.1 (±0.7)	0.01 (±0.06)	0.40	0.01

[a] All rate and equilibrium data have been statistically corrected for the number of equivalent acidic hydrogen atoms in each carbon acid. [b] Structural details for some acids are given in Table III. [c] Calculated from eq 10. [d] β(exptl) - β(calcd).

Tables III and IV summarize the analyses of literature data for the deprotonation of 26 different carbon acids by carboxylate ions in aqueous solutions. In Table III, k_4 represents the second-order rate constant for deprotonation of each carbon acid by the carboxylate anion of a hypothetical carboxylic acid of pK_a = 4. Values of k_4 were obtained by interpolation on the Brønsted plot for carboxylate ions reacting with each carbon acid. The

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(19) Bell, R. P.; Gelles, E.; Miller, E. *Proc. R. Soc. London, A* **1949**, *198*, 310.

(20) Bell, R. P.; Goldsmith, M. C. *Proc. R. Soc. London, A* **1952**, *216*, 322.

(21) Bernasconi, C. F.; Bunnell, R. D. *Isr. J. Chem.* **1985**, *26*, 420.

(22) Bell, R. P.; Tranter, R. L. *Proc. R. Soc. London, A* **1974**, *337*, 517.

(23) Dynes, P. J.; Chapman, G. S.; Kebede, E.; Schneider, F. W. *J. Am. Chem. Soc.* **1972**, *94*, 6356.

(24) Bell, R. P.; Grainger, S. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1606.

(25) Okuyama, T.; Ikenouchi, Y.; Fueno, T. *J. Am. Chem. Soc.* **1978**, *100*, 6162.

(26) Thomas, R. J.; Long, F. A. *J. Am. Chem. Soc.* **1964**, *86*, 4770.

(27) Kresge, A. J.; Chen, H. J.; Hakka, L. E.; Kouba, J. E. *J. Am. Chem. Soc.* **1971**, *93*, 6174.

(28) Bednar, R. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1985**, *107*, 7117.

(29) Terrier, F. G.; Debleds, F. L.; Verchere, J. F.; Chatrousse, A. P. *J. Am. Chem. Soc.* **1985**, *107*, 307.

intrinsic barrier ($\Delta G_0^\ddagger$) for deprotonation of the carbon acid by this carboxylate ion was then calculated from eq 12. Brønsted β values were then calculated from eq 9, and these calculated parameters are listed in the last column of Table III. There is reasonable agreement between the calculated and experimental β values for the most acidic carbon acids listed toward the bottom of this table. However, there is little correspondence between the calculated and experimental β values for the weaker carbon acids toward the top of the table for which $\beta > 0.5$.

Values of A and B for the carboxylate ion catalyzed deprotonations of these 26 carbon acids are listed in Table IV, along with β values calculated using these parameters and eq 10, again for the conjugate base of a hypothetical carboxylic acid of $pK_a = 4$. There is excellent agreement between these calculated β values in Table IV and the experimental values of Table III. It is clear that the modified form of the Marcus relationship given by eq 3 and its derivative (eq 10) provide an excellent description of the data for these 26 carbon acids, although it should be noted that $B \simeq 0$ and $A \simeq \Delta G_0^\ddagger$, for the most acidic carbon acids toward the bottom of this table. This description is particularly impressive when one notes that the equilibrium acidities of these carbon acids vary over a range greater than 10^{25} in K_a and the rate constants vary by a factor greater than 10^{14} in k_4.

There are two significant differences between the Brønsted coefficients defined by eq 5 and 6. Equation 5 predicts that $\alpha = 0.5$ at $\Delta G^\circ = 0$, while eq 6 leads to $\alpha = (0.5 + B)$ for this condition. As was indicated above, the prediction from eq 5 is incompatible with $\alpha > 0.5$ for $\Delta G^\circ < 0$, which is commonly observed (Table I). Secondly, while both eq 5 and 6 predict nonlinear Brønsted relationships, different curvatures are predicted for these nonlinear relationships. These curvatures are given by the first derivatives of eq 5 or 6, i.e. by eq 13 and 14, respectively. Equation 13 predicts constant curvature throughout the Brønsted plot ($d^2\alpha/d(\Delta G^\circ)^2 = 0$), while eq 14 predicts a dependence of curvature upon ΔG°.

$$d\alpha/d(\Delta G^\circ) = 1/8\Delta G_0^\ddagger \tag{13}$$

$$d\alpha/d(\Delta G^\circ) = A^2/8(A + B\Delta G^\circ)^3 \tag{14}$$

Despite these theoretical predictions of nonlinear Brønsted plots, experimental observations lead to apparently linear Brønsted relationships over the very limited ΔG° ranges (i.e. pK_a ranges of XCH) that are experimentally accessible. To illustrate this point, eq 13 and 14 may be rewritten as eq 15 and 16, respectively.

$$d\alpha/d(pK_{CH}) = (RT \ln 10)/8\Delta G_0^\ddagger \tag{15}$$

$$d\alpha/d(pK_{CH}) = (RT \ln 10)A^2/8(A + B\Delta G^\circ)^3 \tag{16}$$

Typical values of $\Delta G_0^\ddagger$, A, and B from the recent study[1] on benzylic ketones may be used to illustrate the expected variation in α with K_{CH}. This variation in α is of the order of 0.01 per pK_{CH} unit. Such variation is less than the experimental error in the determination of α. Nonlinearity in Brønsted plots for reactions corresponding to eq 4 will not usually be experimentally demonstrable, since the accessible range of pK_{CH} that is obtainable by variation in remote X substituents is usually less than 3 pK_{CH} units in aqueous solutions. Kresge[5] has discussed this phenomenon in some detail. Note that a simple linear extrapolation of the Brønsted plots to $\Delta pK_a = 0$ would give intrinsic barriers much larger than those of Tables I and III.

Equations 13–16 have exact analogies for $d\beta/d(\Delta G^\circ)$. These may be deduced from eq 9 and 10. Brønsted plots for the influence of Y substituents upon eq 8 are similarly predicted to be nonlinear, although this nonlinearity will usually not be experimentally observable over the limited range of pK_{BH^+} that is accessible for remote Y substituents within any single series of structurally related bases.

The present study shows that eq 3 and its first derivatives, eq 6 and 10, give excellent descriptions of the rate–equilibrium correlations for the deprotonation of a reasonable range of carbon acids by a variety of bases in aqueous solution. The parameters A and B are defined in a purely empirical manner. It should be noted that A plays the same role in eq 3 that $\Delta G_0^\ddagger$ has in eq 1, i.e. A represents the free energy of activation at $\Delta G^\circ = 0$. In general, A is not equal to $\Delta G_0^\ddagger$ (except when $B = 0$). The difference between these two parameters is determined both by B and by ΔG°. This latter factor is particularly important, in that it determines the length of the formal extrapolation (to $\Delta G^\circ = 0$) that is inherent in the evaluation of either A or $\Delta G_0^\ddagger$ from the experimental data.

There have been numerous explorations[4–6,9,10,30–38] of the Marcus relationship in the context of proton-transfer reactions since Marcus' original work[39] in this area. Related applications of this theory to hydride-transfer[40] and methyl-transfer[41] processes are also currently under vigorous investigation. While the concept of a variable intrinsic barrier has received consideration in some of these studies, the usual approach has been based upon a theoretical derivation from an assumed model, followed by a fit to experimental data. In the current work, we have taken an alternative approach which justifies the variable barrier of eq 2 in a purely empirical manner.

The A and B parameters of eq 3 must contain contributions from the work terms (for encounter complex formation and product separation) which are introduced in more sophisticated applications of Marcus theory to deprotonation reactions.[5,37a,39] The expansion of the reaction of eq 4 to show such work terms (w^r and w^p for encounter complex formation from reactant and product species, respectively) is displayed in eq 17.

$$\mathrm{XCH} + \mathrm{B} \overset{w^r}{\rightleftharpoons} \mathrm{XCH{\cdot}B} \xrightleftharpoons{\Delta G_c^\circ} \mathrm{XC^-{\cdot}BH^+} \underset{w^p}{\rightleftharpoons} \mathrm{XC^-} + \mathrm{BH^+} \tag{17}$$

The algebraic consequences of these work terms lead to the modification of eq 1 as indicated in eq 18, which is stated in terms of the experimentally measured $\Delta G^\ddagger$ and ΔG° but has $\Delta G_0^\ddagger$ defined in terms of the intrinsic barrier to proton transfer within the encounter complexes.

$$\Delta G^\ddagger = w^r + \Delta G_0^\ddagger\,[1 + (\Delta G^\circ - w^r + w^p)/(4\Delta G_0^\ddagger)]^2 \tag{18}$$

Equation 18 may be expressed as a quadratic equation in ΔG° (eq 19), which may be used to evaluate both the work terms and the intrinsic barrier from experimental data when significant curvature is observable in a Brønsted relationship. A number of analyses of this type have been presented;[5,30,31,38] however, the case for nonlinear rather than linear Brønsted relationships in these studies is rarely persuasive. Invariably, drastic structural variations in the general-base catalysts are required in order to span a significant range of ΔG°. Since different Brønsted relationships are often observed[11,21,28,42] for different chemical types of gen-

$$\Delta G^\ddagger = (\Delta G^\circ)^2/(16\Delta G_0^\ddagger) + \Delta G^\circ[0.5 - (w^r - w^p)/(8\Delta G_0^\ddagger)] + 0.5(w^r + w^p) + \Delta G_0^\ddagger + (w^r - w^p)^2/(16\Delta G_0^\ddagger) \tag{19}$$

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(30) Kreevoy, M. M.; Konasewich, D. E. *Adv. Chem. Phys.* **1971**, *21*, 241.

(31) Kreevoy, M. M.; Oh, S. W. *J. Am. Chem. Soc.* **1973**, *95*, 4805.

(32) (a) Bell, R. P. *The Proton in Chemistry*, 2nd ed.; Chapman and Hall: London, 1973; Chapter 11. (b) Bell, R. P. *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; Chapter 2.

(33) Albery, W. J.; Campbell-Crawford, A. N.; Curran, J. A. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 2206.

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

(35) Hibbert, F. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 1289.

(36) Lewis, E. S.; More-O'Ferrall, R. A. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1084.

(37) (a) Kreevoy, M. M.; Truhlar, D. G. *Techniques of Chemistry*, Part I, 4th ed.; C. F. Bernasconi, Ed.; Wiley-Interscience: New York, 1986; Vol VI, Chapter I. (b) Keefe, J. R.; Kresge, A. J. ref 37a, Chapter XI.

(38) (a) Pruszynski, P.; Chiang, Y.; Kresge, A. J.; Schepp, N. P.; Walsh, P. A. *J. Phys. Chem.* **1986**, *90*, 3760. (b) Chiang, Y.; Kresge, A. J.; Santaballa, J. A.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 5506.

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

(40) (a) Kreevoy, M. M.; Lee, I. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550. (b) Kreevoy, M. M.; Ostovic, D.; Lee, I. H.; Binder, D. A.; King, G. W. *J. Am. Chem. Soc.* **1988**, *110*, 524. (c) Lee, I. H.; Ostovic, D.; Kreevoy, M. *J. Am. Chem. Soc.* **1988**, *110*, 3989.

(41) (a) Albery, J. A.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) Lewis, E. S.; Hu, D. D. *J. Am. Chem. Soc.* **1984**, *106*, 3292. (c) Lewis, E. S. *J. Phys. Chem.* **1986**, *90*, 3756.

eral-base catalysts, it is usually unclear whether a perceived curvature in a Brønsted relationship is truly of the type expressed in eq 19 or whether it is only an apparent curvature that is produced by smoothing the data for two (or more) slightly different linear Brønsted relationships.[10,11b,32b] While the nonlinearity of the Brønsted relationship can be dramatized by the inclusion of remote data points for solvent-derived acid and base species, such approaches are really not particularly convincing. Even if one accepts the description of the data according to eq 19, in most cases any realistic evaluation of the standard errors of the fit leads to quite large uncertainties in the values of the three parameters in eq 18.[38]

The empirical modification to the Marcus relationship that we have suggested in eq 3, may be expanded as shown in eq 20.

$$\Delta G^{\ddagger} = (\Delta G^{\circ})^2/[16(A + B\Delta G^{\circ})] + \Delta G^{\circ}(B + 0.5) + A \quad (20)$$

Any application of eq 19 or 20 to the many linear Brønsted relationships represented by the data in Tables I and III requires that $\Delta G^{\ddagger}$ be linear in ΔG°. Consequently, eq 19 and 20 must be approximated by eq 21 and 22, respectively. Equation 21 is readily

$$\Delta G^{\ddagger} = \Delta G^{\circ}[0.5 - (w^{r} - w^{p})/(8\Delta G_0^{\ddagger})] + 0.5(w^{r} + w^{p}) + \Delta G_0^{\ddagger} + (w^{r} - w^{p})^2/(16\Delta G_0^{\ddagger}) \quad (21)$$

$$\Delta G^{\ddagger} = \Delta G^{\circ}(B + 0.5) + A \quad (22)$$

justified by the requirement that $(\Delta G^{\circ})^2/(16\Delta G_0^{\ddagger})$ in eq 19 must be insignificant when linearity is experimentally observed. The approximation of eq 20 by eq 22 is less obvious; however, we have shown arithmetically using the parameters from Tables I and II that, for the four series of ketones **1** in Table I, $(\Delta G^{\circ})^2/[16(A + B\Delta G^{\circ})]$ never contributes more than 1.3% to $\Delta G^{\ddagger}$.

Equations 21 and 22 now allow a direct evaluation of the contribution of the work terms for the reaction in eq 17 to the empirically derived parameters of eq 3. Thus, the coefficients of ΔG° in eq 21 and 22 require the relationship of eq 23, while the constant terms require eq 24.

$$B = (w^{p} - w^{r})/(8\Delta G_0^{\ddagger}) \quad (23)$$

$$A = 0.5\,(w^{r} + w^{p}) + \Delta G_0^{\ddagger} + (w^{r} - w^{p})^2/(16\Delta G_0^{\ddagger}) \quad (24)$$

Thus in general, both A and B are complex functions of w^{r}, w^{p}, and $\Delta G_0^{\ddagger}$. These latter three parameters are not readily evaluated for any individual reaction for which A and B are given in Tables II and IV. However, some insights via eq 23 and 24 are available in special cases. Thus, the often observed B $\approx$ 0 in Table IV must be a reflection of $w^{r} \approx w^{p}$ in these cases. This condition in turn leads to $A \approx (w^{r} + \Delta G_0^{\ddagger})$ according to eq 24 (when $B \approx 0$).

It is also possible to combine eq 23 and 24 as in eq 25:

$$A = 0.5(w^{r} + w^{p}) + \Delta G_0^{\ddagger} + 4B^2\Delta G_0^{\ddagger} \quad (25)$$

Equation 25 suggests a linear relationship between A and B^2 for closely related series of reactions. In fact, such a linear relationship is approximated for the hydroxide ion catalyzed deprotonation of the four series of ketones **1** in Table II. The slope of this linear relationship allows the calculation of $\Delta G_0^{\ddagger} = 10 \pm 1$ kcal/mol for the intrinsic barrier for intracomplex proton transfer in these series of ketones. From the ordinate intercept of 14.7 ± 0.4 kcal/mol, one can calculate $(w^{r} + w^{p}) = 10 \pm 3$ kcal/mol. When this sum and eq 23 are solved as simultaneous equations using individual values of B from Table II, values of w^{r} are obtained in the range -2 to -7 kcal/mol, while w^{p} varies between 12 and 17 kcal/mol for the deprotonation of **1** by hydroxide ion. An analogous treatment of the data in Table II for the deprotonation of the 1-nitro-1-phenylethanes by the four secondary amines leads to $\Delta G_0^{\ddagger} = 5 \pm 1$ kcal/mol, $(w^{r} + w^{p}) = 26 \pm 5$ kcal/mol, w^{r} = 2–4 kcal/mol, and w^{p} = 24–22 kcal/mol.

While the values of these work and intrinsic barrier parameters are algebraically determined within the above mathematical formalisms for the scheme of eq 17, the absolute interpretation of these parameters in physical and chemical terms is a matter of considerable uncertainty. In this regard, the meaning of the negative w^{r} terms calculated above is particularly obscure. The above treatment seems to imply a common intrinsic barrier for the hydroxide ion deprotonation of the four series of ketones **1**, with the distinctly different Brønsted relationships which are observed for these four series of ketones being attributable to differences in the work terms for encounter complex formation. Albery and co-workers[33] arrived at an analogous result (variable work terms but approximately constant intrinsic barrier) from their analysis of data for the general-acid-catalyzed protonation of several diazo derivatives.

Since ionic species are involved as reactants and/or products in all of these acid–base reactions, the question of the role of the solvent reorganization within the scheme of eq 17 is extremely important, but it is undefined by such a simple scheme. Kresge[5] and Albery[33] have explored this problem in some detail without reaching any definite conclusions. Kreevoy and Oh[31] concluded that the magnitudes of the work terms that they evaluated based upon eq 19 require that "the heavy-atom and solvent reorganization that accompanies a proton transfer precedes or follows the rate-determining step". Consistent with this observation, the large values for w^{p} quoted above seem to require a massive solvent reorganization upon dissociation of the product species encounter complex. Transition-state imbalances between bond making and bond breaking, electron delocalization, charge accumulation, and solvent reorganization, which Bernasconi[43] has expressed in terms of a Principle of Nonperfect Synchronization, also suggest that the chemical basis for the interpretation of work terms will remain problematical even in those cases in which these work terms can be accurately evaluated from experimental data.

It is also of interest to consider the current empirical modification (eq 3) to the Marcus relationship in the context of Kreevoy's approach,[37a,38b] which uses eq 26 to define the Brønsted α parameter in terms of a tightness parameter, τ, which is the sum of the bond orders to the proton being transferred.

$$\alpha = 0.5[1 + \Delta G^{\circ}/(4\Delta G_0^{\ddagger})] + 0.5(1 - \tau) \quad (26)$$

Equation 26 can be compared with eq 6, which is obtained as the first derivative of eq 3. For the particular case of $\Delta G^{\circ} = 0$, a particularly simple relationship is apparent between τ and the B parameter of eq 3:

$$\tau = 1 - 2B \text{ for } \Delta G^{\circ} = 0 \quad (27)$$

Thus for $B = 0$, $\tau = 1$ and the in flight hydrogen atom bears no net charge. For $0 < B < 0.5$, eq 27 requires $1 > \tau > 0$, which requires a fractional positive charge upon the transferred proton in the transition state. The conditions $B > 0.5$ ($\tau < 0$) and $B < 0$ ($\tau > 1$) have no obvious physical significance, although the latter condition may be interpreted as implying fractional negative charge upon the hydrogen atom in the transition state.

When $\Delta G^{\circ} \neq 0$, the relationships between eq 6 and 26 may be approximated by eq 28. This equation suggests that in general τ is a function of ΔG°, which does not seem an unreasonble result.

$$\tau = 1 - 2B\,[1 - [\Delta G^{\circ}/(4(A + B\Delta G^{\circ}))^2]] \quad (28)$$

The complexities discussed above do not detract from the usefulness of eq 6 and 10 as empirical relationships that predict the experimentally observed Brønsted α and β parameters over a wide range of structural variations in both the acid and base species of the reactions in eq 4 and 8. A particular strength of the current treatment, using a variable intrinsic barrier according to eq 2, lies in the fact that it makes no distinction between normal carbon acids and so-called "abnormal" carbon acids for which $\alpha > 1$. The observation of $\alpha > 1$ is a natural outcome of eq 6 for those reactions in which the parameter B is large, i.e. for those reactions in which $\Delta G_0^{\ddagger}$ shows a strong dependence upon ΔG°.

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(42) (a) Walters, E. A.; Long, F. A. *J. Am. Chem. Soc.* **1969**, *91*, 3733. (b) Bruice, P. Y. *J. Am. Chem. Soc.* **1984**, *106*, 5959.

(43) (a) Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335. (b) Bernasconi, C. F. *Tetrahedron* **1985**, *41*, 3219. (c) Bernasconi, C. F. *Acc. Chem. Res.* **1987**, *20*, 301.

As noted above, $\alpha > 0.5$ is actually "anomalous" for any reaction having $\Delta G° < 0$ if one assumes a constant intrinsic barrier, but such reactions may be readily reconciled with a nonzero B parameter in the variable intrinsic barrier of eq 2. In this sense, Bordwell's conjecture[44] —that the deprotonation of ketones may resemble nitroalkane deprotonations in having unusual Brønsted α values—is fulfilled, since hydroxide ion catalyzed deprotonations of such ketones display B values in the range 0.18–0.32 (Table II) even though α is not greater than 1 as is found for phenylnitromethanes.

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[44] Bordwell, F. G.; Boyle, W. J., Jr.; Hautala, J. A.; Yee, K. C. *J. Am. Chem. Soc.* **1969**, *91*, 4002.

Thermal Decomposition of Allylbenzene Ozonide

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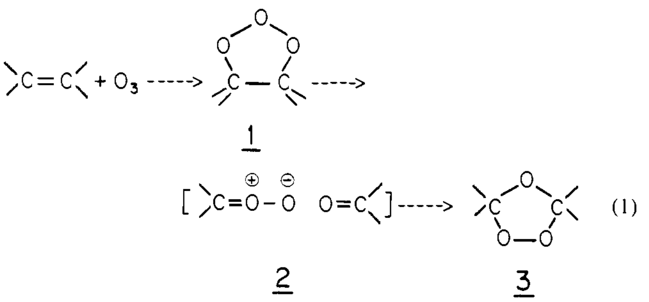
Abstract: Thermal decomposition of allylbenzene ozonide (ABO) at 98 °C in the liquid phase yields toluene, bibenzyl, phenylacetaldehyde, formic acid, and (benzyloxy)methyl formate as major products; benzyl chloride is formed when chlorinated solvents are employed. These products, as well as benzyl formate, are formed when ABO is decomposed at 37 °C. When the decomposition of ABO is carried out in the presence of 1-butanethiol, the product distribution changes: yields of toluene increase, no bibenzyl is formed, and decreases in yields of (benzyloxy)methyl formate, phenylacetaldehyde, and benzyl chloride are observed. The decomposition of 1-octene ozonide (OTO) also was studied for comparison. The activation parameters for both ABO and OTO are similar (28.2 kcal/mol, log A = 13.6 and 26.6 kcal/mol, log A = 12.5, respectively); these data suggest that ozonides decompose by homolysis of the O–O bond, rather than by an alternative synchronous two-bond scission process. When ABO is decomposed at 37 °C in the presence of the spin traps 5,5-dimethyl-1-pyrroline N-oxide (DMPO) or 3,3,5,5-tetramethyl-1-pyrroline N-oxide (M_4PO), ESR signals are observed that are consistent with the trapping of benzyl and other carbon- and oxygen-centered radicals. A mechanism for the thermal decomposition of ABO that involves peroxide bond homolysis and subsequent β-scission is proposed. Thus, Criegee ozonides decompose to give free radicals at quite modest temperatures.

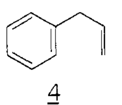
The reaction of ozone with olefins has been the subject of intense study.[1] The generally accepted mechanism for the ozonation of simple olefins in the liquid phase is that proposed by Criegee[2] and modified by others.[3] It involves the formation of a 1,2,3-trioxolane, **1**, which undergoes rapid scission to give a carbonyl oxide,



(1)

2, and a carbonyl compound. In the absence of a protic solvent, **2** reacts rapidly with a carbonyl compound to yield a 1,2,4-trioxolane, **3**; **3** is commonly called the Criegee ozonide.[1] Even though this mechanism does not involve free radicals, evidence collected over recent years implicates radicals as reactive intermediates in the ozonation of some olefins.[1,4]

Our efforts have been aimed at elucidating the mechanism(s) by which ozone, a nonradical, reacts with olefins to produce radicals.[4d-h] As part of this study we have examined the reaction of ozone with polyunsaturated fatty acids (PUFA) and model PUFA compounds.[4d-h] We recently utilized allylbenzene, **4** as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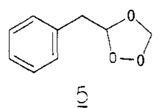
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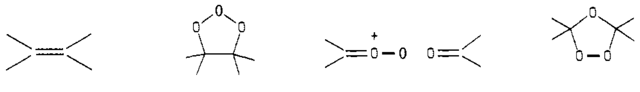

a PUFA model and showed that allylbenzene ozonide (ABO), **5**, initiates the autoxidation of methyl linoleate (18:2ME) at 37 °C.[5]

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(1) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol I.

(2) (a) Criegee, R. *Liebigs Ann. Chem.* **1953**, *583*, 1–36. (b) Criegee, R. In *Peroxide Reaction Mechanisms*; Edwards, J. D., Ed.; Wiley-Interscience: New York, 1962.

(3) (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565–598. (b) Greenwood, F. L.; Rubenstein, H. *J. Org. Chem.* **1969**, *32*, 3369–3374.

(4) (a) Pryor, W. A.; Dooley, M. M.; Church, D. F. In *The Biomedical Effects of Ozone and Related Photochemical Oxidants*; Lee, S. D., Mustafa, M. G., Mehlman, M. A., Eds.; Princeton Scientific Publishers: Princeton, NJ, 1982; pp 7–19. (b) Menzel, D. B. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1976; Vol. II, pp 181–202. (c) Pryor W. A. In *Free Radicals in Biology*; Pryor, W. A., Ed.; Academic Press: New York, 1982; Vol. I, pp 1–49. (d) Pryor, W. A.; Stanley, J. P.; Blair, E.; Cullen, G. B. *Arch. Environ. Health* **1976**, *31*, 201–210. (e) Pryor, W. A.; Prier, D. G.; Church, D. F. *Environ. Res.* **1981**, *24*, 42–52. (f) Pryor, W. A.; Prier, D. G.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 2883–2888. (g) Pryor, W. A.; Gu, J.; Church, D. F. *J. Org. Chem.* **1985**, *50*, 185–189. (h) Pryor, W. A.; Ohto, N.; Church, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 3614–3622.

(5) (a) Ewing, J. C.; Cosgrove, J. P.; Giamalva, D. G.; Church, D. F.; Pryor, W. A. *Lipids*, in press. (b) Ewing, J. C. Ph.D. Dissertation, Louisiana State University, 1988; pp 1–78.

0002-7863/89/1511-5839$01.50/0