limited by that of the detection photomultiplier (Philips XP-2020) to about 200 ps. Samples for single photon counting were carefully degassed.

Acknowledgment. We thank A. W. J. D. Dekkers and Professor W. N. Speckamp for providing the azadamantane derivatives (**1**) that gave incentive to the study described in this paper. Ing. D. Bebelaar provided essential technical assistance and support in measurement of the fluorescence lifetimes. Furthermore, the valuable discussion of the relevance of the present data for an understanding of the spectroscopic properties of other bichromophoric systems by Dr. K. A. Zachariasse and Professor F. C. de Schrijver is gratefully acknowledged. The present investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

Registry No. **1a**, 42949-28-0; **1b**, 42949-26-8; **1c**, 42949-32-6; **2a**, 82482-72-2; **2b**, 62702-79-8; **4**, 62702-82-3; **5b**, 82482-73-3; **5c**, 82482-74-4; **6a**, 62702-81-2; **6b**, 10292-84-9; **6c**, 62702-80-1; **6d**, 82482-75-5; **7c**, 63045-23-8; **8c**, 63045-24-9; **9c**, 82482-76-6; **10a**, 40203-74-5; **10b**, 55568-06-4; **10c**, 4354-73-8; **10d**, 3709-25-9; **11a**, 25220-06-8; **11b**, 25694-16-0; **11c**, 36317-36-9.

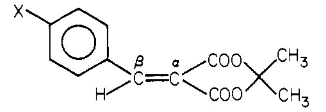
Nucleophilic Addition to Olefins. 6.[1] Structure–Reactivity Relationships in the Reactions of Substituted Benzylidene Meldrum's Acids with Water, Hydroxide Ion, and Aryl Oxide Ions

Claude F. Bernasconi* and Gianni D. Leonarduzzi

Contribution from the Thimann Laboratories of the University of California, Santa Cruz, California 95064. *Received October 26, 1981*

Abstract: The addition of water to *p*-methoxybenzylidene Meldrum's Acid (**1-OMe**), to form an adduct (T_{OH}^-), is subject to weak general base catalysis, just as water addition to carbocations studied by Ritchie. This implies a mechanism in which the base or a second water molecule removes the proton in concert with C–O bond formation. The same mechanism probably applies with the unsubstituted (**1-H**) and the *p*-nitro-substituted benzylidene Meldrum's acid (**1-NO$_2$**) even though general base catalysis was undetectable in these reactions because of experimental difficulties. Rates of water and of hydroxide ion addition to the substituted olefins correlate with σ^+ in the forward and with σ in the reverse direction. This implies an imbalanced transition state in which loss of conjugation is ahead of C–O bond formation. Rates of addition of phenoxide ion to the substituted olefins give a normalized ρ value of 0.56 while the rates of addition of substituted phenoxide ions to **1-NO$_2$** give a normalized $\beta_{nuc} = 0.39$. This result indicates another kind of transition-state imbalance in which negative charge development on the olefin as seen by the substituent in the olefin is larger than that seen by the substituent in the nucleophile. This imbalance can be explained if one assumes that in the transition state part of the negative charge tends to be localized in close proximity to the phenyl group while in the adduct T_{OH}^- the charge is essentially delocalized into the $(COO)_2C(CH_3)_2$ moiety. Our findings are further examples of a growing list of reported transition-state imbalances, and it is suggested that imbalanced transition states are probably the rule rather than the exception for a large variety of reactions. Problems arising from these imbalances in calculating Marcus intrinsic barriers in nucleophilic additions to olefins are discussed. Our data also permit us to estimate a $\rho \approx 1.2$ for the substituent effect on the C–H acidity constant of the carbon protonated OH$^-$ adducts (T_{OH}^0). This unusually high ρ value suggests that in the anion (T_{OH}^-) there is a strong intramolecular hydrogen bond from the OH group to the $(COO)_2C(CH_3)_2$ moiety.

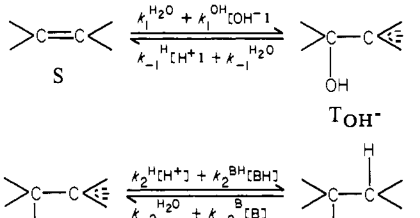
We recently reported a kinetic study of the nucleophilic addition of water, hydroxide ion, and aryl oxide ions to benzylidene Meldrum's acid (**1-H**)[2] and an investigation of the addition of piperidine and morpholine to **1-H**, **1-OMe**, and **1-NMe$_2$**.[3] The results of these studies raised a number of questions which the present and next paper[4] are meant to clarify. They are as follows.



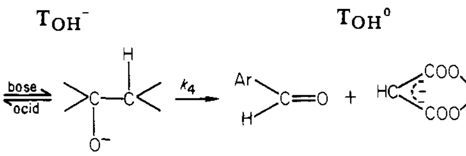
1-H (X = H) **1-NMe$_2$** (X = NMe$_2$)

1-OMe (X = OMe) **1-NO$_2$** (X = NO$_2$)

(1) Hydrolytic cleavage of **1-X**, to form the corresponding benzaldehyde and Meldrum's acid anion, involves the following steps.



(1)



(2)

(3)

---

(1) Part 5: Bernasconi, C. F.; Carré, D. J.; Kanavarioti, A. *J. Am. Chem. Soc.* **1981**, *103*, 4850.

(2) Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.* **1980**, *102*, 1361.

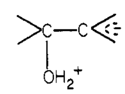
(3) Bernasconi, C. F.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 5329.

(4) Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.*, following article in this issue.

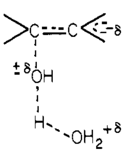
0002-7863/82/1504-5133$01.25/0

A detailed analysis of the hydrolysis rates, coupled with data on the separately measured reactions 1 and 2, led to the remarkable conclusion that k_4 must be in the order of 10^{10} s^{-1}.[2] In order to obtain a more definite value for k_4 from structure–reactivity relationships and to decide whether a preassociation mechanism might be involved,[5] we have now also studied the hydrolysis of **1-OMe** and **1-NO₂**.[4] In the present paper we report the results on steps 1 and 2 for **1-OMe** and **1-NO₂** which are needed for the analysis of the hydrolysis data.[4]

(2) The mechanism of water attack (eq 1) could either involve rate-limiting addition of a water molecule, to form $T_{OH}^{\pm}$, followed by rapid proton loss (Al mechanism in reverse direction), or it could involve removal of the proton by a second water molecule in concert with nucleophilic attack (**2**). In view of numerous precedents regarding water or alcohol additions to electrophiles,[5-14] this latter mechanism would seem more likely. The strongest evidence in favor of such a mechanism would be the observation of general base catalysis.[5-14] Our data on **1-H** were inconclusive in this respect, for the following reasons. (a) Catalysis, if present at all, appears to be very weak. (b) Rate measurements at low pH required that the equilibrium of reaction 1 be studied from right to left. Slight catalysis by carboxylic acids was observed, but it was not possible to distinguish it from a possible contribution by the rate of carbon protonation of T_{OH}^- (eq 2) which starts to compete with the k_{-1}^{H} [H⁺] step of reaction 1 at low pH. (c) With more basic buffers at higher pH nucleophilic attack by the buffer base made observation of base catalysis difficult.



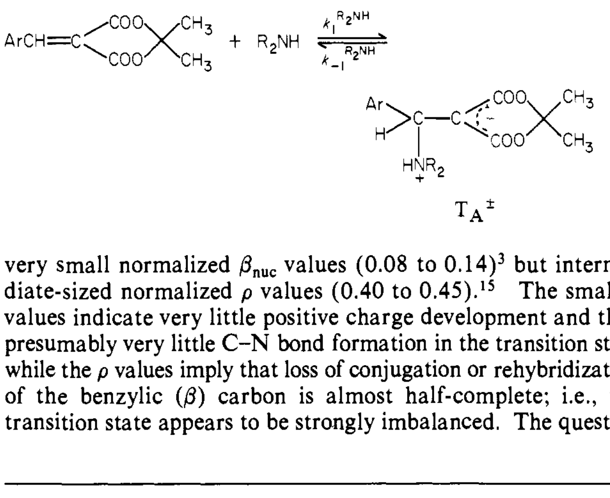
$T_{OH}^{\pm}$



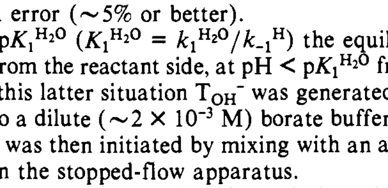
2

We hoped that by studying substituted benzylidene Meldrum's acids we might find a substrate where the mentioned adverse factors are less severe than for 1-H. We shall report that this is indeed the case for **1-OMe**.

(3) Nucleophilic attack by amines (eq 4) is characterized by very small normalized β_{nuc} values (0.08 to 0.14)[3] but intermediate-sized normalized ρ values (0.40 to 0.45).[15] The small β values indicate very little positive charge development and thus presumably very little C–N bond formation in the transition state while the ρ values imply that loss of conjugation or rehybridization of the benzylic (β) carbon is almost half-complete; i.e., the transition state appears to be strongly imbalanced. The question arises whether this imbalance is mainly observable with amine nucleophiles or whether it is a characteristic of the activating moiety in the olefin. To answer this question we have now studied the reaction of **1-NO₂** and **1-OMe** with phenoxide, *p*-bromophenoxide, and *p*-cyanophenoxide ion (eq 5).



(4)



(5)

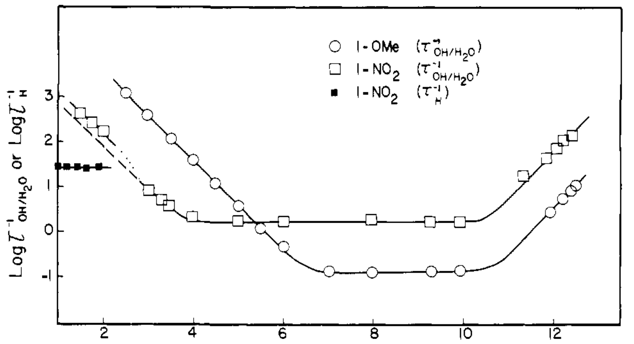


Figure 1. pH profiles for τ_{OH/H_2O}^{-1} and τ_H^{-1}.

Results

General Features. The general features of the reactions of **1-NO₂** and **1-OMe** are quite similar to those reported for **1-H** and will therefore be only briefly outlined here. All measurements refer to aqueous solutions at 25 °C, at an ionic strength of 0.5 M (KCl).

Rates of Reactions 1 and 5. Reaction 1 was monitored in the stopped-flow apparatus either at λ_{max} of the olefin (372 nm for **1-OMe**, 320 nm for **1-NO₂**) and/or at λ_{max} of T_{OH}^- (265 nm for **1-OMe**, 263 nm for **1-NO₂**). When the reactions were monitored at both wavelengths the observed rates were the same within experimental error (~5% or better).

At pH > $pK_1^{H_2O}$ ($K_1^{H_2O} = k_1^{H_2O}/k_{-1}^{H}$) the equilibrium was approached from the reactant side, at pH < $pK_1^{H_2O}$ from the side of T_{OH}^-. In this latter situation T_{OH}^- was generated by placing the olefin into a dilute (~2×10^{-3} M) borate buffer of pH ~9. The reaction was then initiated by mixing with an acidic buffer (pH-jump) in the stopped-flow apparatus.

Measurements were made in KOH solutions, in phenol, *p*-bromophenol, *p*-cyanophenol, phosphate, cacodylate, acetate, formate, and chloroacetate buffers. With **1-NO₂** either no buffer catalysis could be observed ($H_2PO_4^-$, formate), or the catalytic effect is too small to be unambiguous (chloroacetate) or there is even a slight decrease in rate (acetate).

With **1-OMe** somewhat stronger catalysis was observed with acetate and cacodylate buffers, but even here the rate increase at 0.2 to 0.3 M total buffer concentration was never more than 20–30%. Nevertheless, as will be shown in the Discussion these accelerations almost certainly represent authentic general acid–base catalysis.

The data, except for those in the phenol and substituted phenol buffers are summarized in Table I. They can be fitted to eq 6[16]

$$\tau_{OH/H_2O}^{-1} = k_1^{H_2O} + k_1^{OH}[OH^-] + k_{-1}^{H}[H^+] + k_{-1}^{H_2O} + k_B[B] + k_{BH}[BH] \quad (6)$$

where τ_{OH/H_2O}^{-1} is the reciprocal relaxation time (pseudo-first-order rate constant for equilibrium approach). Plots of τ_{OH/H_2O}^{-1}, ex-

---

(5) Jencks, W. P. *Acc. Chem. Res.* **1976**, *9*, 475; **1980**, *13*, 161.

(6) See, for example, Bell, R. P. *Adv. Phys. Org. Chem.* **1966**, *4*, 1, and ref 7–14.

(7) Gravitz, N.; Jencks, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 507.

(8) Capon, B.; Nimmo, K. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1113.

(9) (a) Ritchie, C. D. *J. Am. Chem. Soc.* **1975**, *97*, 1170; (b) Ritchie, C. D.; Wright, D. J.; Huang, D.; Kamego, A. *Ibid.* **1975**, *97*, 1163.

(10) Sayer, J. M.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 464.

(11) Funderburk, L. H.; Aldwin, L.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 5444.

(12) Bernasconi, C. F.; Gandler, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 8117.

(13) Bergstrom, R. G.; Cashen, M. J.; Chiang, Y.; Kresge, A. J. *J. Org. Chem.* **1979**, *44*, 1639.

(14) Palmer, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6466.

(15) The symbol $\alpha^n(k_1)$ was used for the normalized ρ value.[3]

(16) [H⁺] was calculated as a_{H^+}/γ_{H^+} where a_{H^+} is the activity measured with the glass electrode and $\gamma_{H^+} = 0.74$ at $\mu = 0.5$ M.[17a] [OH⁻] was calculated as $[OH^-] = K_w/[H^+]$ with $K_w = 1.87 \times 10^{-14}$ at $\mu = 0.5$ M.[17b]

(17) (a) Harned, H. S.; Robinson, R. A. In "Multicomponent Electrolyte Solutions"; Pergamon Press: Elmsford, N.Y., 1968; p 50. (b) Harned, H. S.; Owen, B. B. "The Physical Chemistry of Electrolyte Solutions"; Reinhold: New York, 1950; p 487.

Table I. τ_{OH/H_2O}^{-1} in KOH and in Phosphate, Cacodylate, Acetate, Formate, and Chloroacetate Buffers

buffer	$[B]_{tot}$,[a] M	$[B^-]:[BH]$	pH	τ_{OH/H_2O}^{-1}, s^{-1}
	A. **1-NO$_2$**			
KOH	4.38×10^{-2}		12.37	140
	2.96×10^{-2}		12.20	103
	2.10×10^{-2}		12.05	70.2
	1.27×10^{-2}		11.83	41.7
	3.73×10^{-3}		11.30	18.1
	5.91×10^{-4}		10.50	7.95
$H_2PO_4^-$	0.20	0.25	6.00	1.94
	0.10			1.89
	0.05			1.82
	0.025			1.87
AcO^-	0.25	2.70	5.00	1.75
	0.20			1.68
	0.125			1.84
	0.05			1.83
	0.25	0.27	4.00	2.20
	0.20			2.43
	0.125			2.55
	0.05			2.38
$HCOO^-$	0.25	0.91	3.50	4.13
	0.25	0.69	3.30	4.98
	0.25	0.35	3.00	8.46
	0.20			9.38
	0.15			9.38
	0.10			9.34
	0.05			8.97
$ClCH_2COO^-$	0.25	0.70	2.50	18.4
	0.20			17.9
	0.15			17.8
	0.10			18.1
	0.05			17.3
	B. **1-OMe**			
KOH	4.08×10^{-2}		12.47	10.61
	3.17×10^{-2}		12.36	8.29
	2.09×10^{-2}		12.18	5.77
	1.03×10^{-2}		11.87	2.88
$H_2PO_4^-$	0.084	2.51	7.00	0.145
	0.0084			0.153
	0.113	0.79	6.50	0.40
	0.0113			0.38
	0.15	0.25	6.00	0.74
	0.015			0.81
$ClCH_2COO^-$ [c]	0.30	2800	6.10	0.595[d]
	0.20			0.587[d]
	0.10			0.570[d]
	0.0			0.557[d]
$Me_2AsO_2^-$	0.268	0.79	6.00	0.71
	0.161			0.64
	0.107			0.59
	0.0536			0.56
	0[b]			0.52[b]
AcO^-	0.276	8.51	5.50	1.64
	0.162			1.54
	0.114			1.46
	0.057			1.43
	0[b]			1.36[b]
	0.343	2.69	5.00	5.08
	0.151			4.71
	0.103			4.48
	0.0187			4.26
	0[b]			4.20[b]
	0.434	0.85	4.50	15.5
	0.216			13.8
	0.111			13.6
	0.0425			13.4
	0[b]			12.9[b]
	0.94	0.27	4.00	46.4
	0.47			43.7
	0.23			41.1
	0.089			40.6
	0[b]			39.9[b]
$HCOO^-$	0.38	1.1	3.50	112
	0.19			108
	0.095			110
	0.038			113
	0[b]			113[b]
	0.077	0.347	3.00	403
	0.039			397

[a] Total buffer concentration. [b] Extrapolated to zero buffer concentration. [c] In the presence of $Me_2AsO_2^-$ buffer of 0.2 M total concentration and $[B^-]:[BH] = 1.0$. Experiments designed to test for salt effects; see Discussion. [d] Average of three to four determinations, estimated error ±1%.

trapolated to zero buffer concentration for the reaction of **1-OMe**, vs. pH are shown in Figure 1. It should be noted that for **1-NO$_2$**, the validity of eq 6 breaks down at pH <3, but not for **1-OMe**. The reasons for this will be discussed below.

The various rate constants were evaluated as follows. k_1^{OH} was obtained at high pH where $k_1^{OH}[OH^-]$ is dominant, k_{-1}^{H} at low pH where the $k_{-1}^{H}[H^+]$ term is dominant. From the pH-independent range $k_1^{H_2O}$ can be obtained directly because $k_1^{H_2O} \gg k_{-1}^{H_2O}$; this also yields $K_1^{H_2O} = k_1^{H_2O}/k_{-1}^{H}$. $k_{-1}^{H_2O}$ can be calculated from k_1^{OH} and $K_1^{OH} = K_1^{H_2O}/K_w$ where $K_1^{OH} = k_1^{OH}/k_{-1}^{H_2O}$. k_B and k_{BH} were obtained from the slopes of the buffer plots by standard procedures. The rate constants are summarized in Table II.

In the presence of phenol buffers τ_{OH/H_2O}^{-1} decreases with increasing buffer concentration as shown in Table III. This decrease is caused by reaction 5 which acts as a rapid preequilibrium with respect to reaction 1. As a consequence τ_{OH/H_2O}^{-1} is reduced according to

$$\tau_{OH/H_2O}^{-1} = \frac{k_1^{H_2O} + k_1^{OH}[OH^-] + k_{OAr}[ArO^-]}{1 + K_1^{OAr}[ArO^-]} \qquad (7)$$

Note that in eq 7 only terms in the forward direction are included since at the pH values investigated the equilibrium greatly favors T_{OH}^-. Note also that k_{OAr} refers to possible catalysis by ArO^- while $K_1^{OAr} = k_1^{OAr}/k_{-1}^{OAr}$ refers to nucleophilic attack.

A more direct manifestation of reaction 5 is that an additional relaxation time is observed. It is much shorter than τ_{OH/H_2O} and obeys

$$\tau_{OAr}^{-1} = k_1^{OAr}[ArO^-] + k_{-1}^{OAr} \qquad (8)$$

The data on τ_{OAr}^{-1} are included in Table III. For the reaction of the strongest nucleophile (phenoxide ion) with the strongest electrophile (**1-NO$_2$**) the equilibrium of eq 5 can be driven almost completely to the right without having to use such high phenoxide ion concentrations as to interfere with the measurement of the spectrum of T_{OAr}^-. This spectrum is, as one would expect, almost identical with that of T_{OH}^-. The similarity between these spectra and the favorable equilibrium position also explains why no good data on τ_{OH/H_2O}^{-1} could be obtained for **1-NO$_2$** in the concentration range of phenoxide ion reported in Table III. At these concentrations the equilibrium of reaction 5 strongly favors T_{OAr}^- so that the τ_{OH/H_2O}^{-1} process essentially corresponds to a conversion of

Table II. Rate and Equilibrium Constants for Water and Hydroxide Ion Addition to **1-X** (Reaction 1)

constant	1-OMe	1-H[a]	1-NO$_2$
$k_1^{\mathrm{H_2O}}$, s^{-1}	0.118	0.55	1.75
k_{-1}^{H}, M^{-1} s^{-1}	3.54×10^5	1.47×10^5	5.10×10^3
$K_1^{\mathrm{H_2O}} = k_1^{\mathrm{H_2O}}/k_{-1}^{\mathrm{H}}$ (p$K_1^{\mathrm{H_2O}}$), M	3.33×10^{-7} (6.48)	3.75×10^{-6} (5.43)	3.43×10^{-4} (3.46)
p$K_1^{\mathrm{H_2O}}$ (spectrophot.)[e]	6.60	5.37	3.48
k_1^{OH}, M^{-1} s^{-1}	2.51×10^2	7.45×10^2	3.11×10^3
$k_{-1}^{\mathrm{H_2O}} = k_1^{\mathrm{OH}}/K_1^{\mathrm{OH}}$, s^{-1}	1.41×10^{-5}	3.73×10^{-6}	1.70×10^{-7}
$K_1^{\mathrm{OH}} = K_1^{\mathrm{H_2O}\,b}/K_{\mathrm{w}}^{\,c}$, M^{-1}	1.78×10^7	2.00×10^8	1.83×10^{10}
$k_{\mathrm{Me_2AsO_2^-}}$,[d,g] M^{-1} s^{-1}	0.45		
$k_{\mathrm{Me_2AsO_2H}}$,[d,g] M^{-1} s^{-1}	1.07		
$k_{\mathrm{AcO^-}}$,[d,g] M^{-1} s^{-1}	0.120		
k_{AcOH},[d,g] M^{-1} s^{-1}	9.73		
$k_{\mathrm{ClCH_2COO^-}}$,[f,g]	$\approx 4.0 \times 10^{-2}$		
$k_{\mathrm{ClCH_2COOH}}$,[f,g] M^{-1} s^{-1}	$\approx 2.7 \times 10^{-2}$		

[a] Data from ref 2. [b] Kinetic $K_1^{\mathrm{H_2O}}$ was used. [c] $K_{\mathrm{w}} = 1.87 \times 10^{-14}$ M^2 at $\mu = 0.5$ M, ref 16. [d] From buffer dependence of $\tau_{\mathrm{OH/H_2O}}^{-1}$, assuming that it represents general acid-base catalysis. [e] From ref 4. [f] From chloroacetate ion dependence at pH 6.1; see Discussion. [g] pK_a (Me$_2$AsO$_2$H) = 6.10, pK_a (AcOH) = 4.57, pK_a (ClCH$_2$COOH) = 2.50 at $\mu = 0.5$ M.

Table III. $\tau_{\mathrm{OH/H_2O}}^{-1}$ and τ_{OAr}^{-1} in Phenol, *p*-Bromophenol, and *p*-Cyanophenol Buffers

ArO$^-$	10^2[ArO$^-$],[a] M	pH	$\tau_{\mathrm{OH/H_2O}}^{-1}$, s^{-1}	τ_{OAr}^{-1}, s^{-1}
	A.	1-NO$_2$		
C$_6$H$_5$O$^-$	0.30	9.90		390
	0.20			301
	0.10			149
	0.05			81
p-BrC$_6$H$_4$O$^-$	0.40	9.25	0.128	340
	0.30		0.164	270
	0.20		0.243	200
	0.15		0.294	148
	0.10		0.46	107
	0.05		0.62	56
	0[b]		1.73[b]	
p-CNC$_6$H$_4$O$^-$	1.00	7.95	0.705	365
	0.80		0.85	330
	0.50		1.09	
	0.40		1.25	243
	0.375		1.29	238
	0.25		1.38	213
	0.20		1.56	197
	0.125		1.71	
	0[b]		2.20[b]	
	B.	1-OMe		
C$_6$H$_5$O$^-$	1.50	9.90	0.098	216
	1.00		0.108	191
	0.75		0.121	181
	0.50		0.129	161
	0.25		0.147	154
	0.125		0.156	
	0[b]		0.160[b]	
p-BrC$_6$H$_4$O$^-$	1.25	9.25	0.123	
	1.00		0.127	
	0.50		0.134	
	0.25		0.141	
	0[b]		0.144[b]	
p-CNC$_6$H$_4$O$^-$	1.0	7.95	0.130	
	0.75		0.133	
	0.50		0.135	
	0.25		0.135	
	0[b]		0.135[b]	

[a] [ArO$^-$]:[ArOH] = 1:1. [b] Extrapolated to zero concentration according to eq 9.

T$_{\mathrm{OAr}}^-$ into T$_{\mathrm{OH}}^-$ via S, with S being present at a very low concentration. Hence monitoring the reaction at $\lambda_{\max}$ of T$_{\mathrm{OH}}^-$ or T$_{\mathrm{OAr}}^-$ produces no measurable ΔOD since the two extinction coefficients are very similar, while monitoring at $\lambda_{\max}$ of S is unfavorable because of its low concentration.

In the reaction of the weakest electrophile (**1-OMe**) with the two weakest nucleophiles (*p*-bromo- and *p*-cyanophenoxide ion), the equilibrium of reaction 5 never lies very far to the right; furthermore, k_{-1}^{OAr} is so high that τ_{OAr}^{-1} could not be measured by the stopped-flow technique.

The data in Table III were analyzed as follows. Inversion of eq 7 affords

$$\tau_{\mathrm{OH/H_2O}} = \frac{1}{k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}[\mathrm{OH^-}] + k_{\mathrm{OAr}}[\mathrm{ArO^-}]} + \frac{K_1^{\mathrm{OAr}}[\mathrm{ArO^-}]}{k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}[\mathrm{OH^-}] + k_{\mathrm{OAr}}[\mathrm{ArO^-}]} \qquad (9)$$

Plots (not shown) of $\tau_{\mathrm{OH/H_2O}}$ vs. [ArO$^-$] are linear, indicating that catalysis by ArO$^-$ (k_{OAr}[ArO$^-$] term) is not significant in the concentration range ($\leq 1.5 \times 10^{-2}$ M) used. From the slope and intercepts of such plots K_1^{OAr} and $k_1^{\mathrm{H_2O}} + k_1^{\mathrm{OH}}$[OH$^-$] can be evaluated. These latter fit very well with the data obtained for $\tau_{\mathrm{OH/H_2O}}^{-1}$ in the other buffers and are included in Figure 1.

From τ_{OAr}^{-1} k_1^{OAr} and k_{-1}^{OAr} were evaluated according to eq 8. In the reaction of **1-NO$_2$** with phenoxide ion k_{-1}^{OAr} is very small compared to τ_{OAr}^{-1} and could not be evaluated accurately. A more reliable k_{-1}^{OAr} was obtained from pH-jump experiments in which a solution containing T$_{\mathrm{OAr}}^-$ at pH ~10 was mixed with an acetate buffer at pH 4.75 or with an HCl solution (pH 3.35 and 2.28). These different experiments all yielded the same k_{-1}^{OAr} value, showing that the reaction is not subject to measurable acid catalysis.

The rate and equilibrium constants of reaction 5 are summarized in Table IV. In those cases where K_1^{OAr} could be determined both from τ_{OAr}^{-1} ($k_1^{\mathrm{OAr}}/k_{-1}^{\mathrm{OAr}}$) and $\tau_{\mathrm{OH/H_2O}}^{-1}$, the agreement between the two values is very good except for the reaction of **1-NO$_2$** with *p*-cyanophenoxide ion where there is a discrepancy of ~60%. This higher error is probably due to the fact that the equilibrium of reaction 5 is relatively unfavorable, making its measurement difficult.

Rates of Reaction 2. When reaction 1 for **1-NO$_2$** was studied in HCl solution at pH ≤ 2 (pH-jump experiments), an additional kinetic process with the relaxation time τ_{H} was observed at $\lambda_{\max}$ of the olefin but not at $\lambda_{\max}$ of T$_{\mathrm{OH}}^-$. $\tau_{\mathrm{OH/H_2O}}^{-1}$ and τ_{H}^{-1} are summarized in Table V. τ_{H}^{-1} is pH independent while $\tau_{\mathrm{OH/H_2O}}^{-1}$ increases strongly with [H$^+$] and becomes too high for the stopped-flow method at pH <1.50. If one places $\tau_{\mathrm{OH/H_2O}}^{-1}$ obtained in these very acidic solutions on the pH profile of Figure 1, one notices an approximately 2.5-fold positive deviation from the line defined by the data at pH ≥ 3.0.

These observations are similar to the ones made with **1-H** and can be explained by the formation of measurable quantities of T$_{\mathrm{OH}}^0$ (eq 2) in these highly acidic media.[2] This leads to a coupling of reactions 1 and 2 as shown in eq 10 ($k_{-1}^{\mathrm{H_2O}}$, $k_1^{\mathrm{H_2O}}$, and k_1^{OH}-

$$\mathrm{S} \xleftarrow{k_{-1}^{\mathrm{H}}[\mathrm{H^+}]} \mathrm{T_{OH}}^- \underset{k_{-2}^{\mathrm{H_2O}} + k_{-2}^{\mathrm{B}}[\mathrm{B}]}{\overset{k_2^{\mathrm{H}}[\mathrm{H^+}] + k_2^{\mathrm{BH}}[\mathrm{BH}]}{\rightleftharpoons}} \mathrm{T_{OH}}^0 \qquad (10)$$

[OH$^-$] are negligible at these pH values) and two relaxation times

Table IV. Rate and Equilibrium Constants for Aryl Oxide Addition to 1-**X** (Reaction 5)

	$C_6H_5O^-$ (pK_a = 9.9)[a]	*p*-$BrC_6H_4O^-$ (pK_a = 9.25)[a]	*p*-$CNC_6H_4O^-$ (pK_a = 7.95)[a]
	1-OMe		
k_1^{OAr}, $M^{-1}\ s^{-1}$	5.11×10^3		
k_{-1}^{OAr}, s^{-1}	140		
$K_1^{OAr} = k_1^{OAr}/k_{-1}^{OAr}$, M^{-1}	36.5		
K_1^{OAr} (from τ_{OH/H_2O}^{-1}), M^{-1}	45.0	13.8	
	1-H[b]		
k_1^{OAr}, $M^{-1}\ s^{-1}$	1.81×10^4	9.11×10^3	
k_{-1}^{OAr}, s^{-1}	33	127	
$K_1^{OAr} = k_1^{OAr}/k_{-1}^{OAr}$, M^{-1}	550	72	
K_1^{OAr} (from τ_{OH/H_2O}^{-1}), M^{-1}	490	83	3.12
	1-NO_2		
k_1^{OAr}, $M^{-1}\ s^{-1}$	1.26×10^5	8.07×10^4	2.09×10^4
k_{-1}^{OAr}, s^{-1}	8.63	25.6	159
$K_1^{OAr} = k_1^{OAr}/k_{-1}^{OAr}$, M^{-1}	1.46×10^4	3.15×10^3	132
K_1^{OAr} (from τ_{OH/H_2O}^{-1}), M^{-1}		3.13×10^3	209

[a] pK_a determined potentiometrically at $\mu = 0.5$ M. [b] From ref 2.

Table V. τ_{OH/H_2O}^{-} and τ_H^{-1} for 1-NO_2 in HCl Solution

pH	τ_{OH/H_2O}^{-1}, s^{-1}	τ_H^{-1}, s^{-1}
2.00	184	27.3
1.75	252	28.5
1.50	417	29.4
1.25	*a*	28.5
1.00	*a*	27.6
0.75	*a*	27.4

[a] Too fast for the stopped-flow method.

should be observed. For the general case these two relaxation times are given by[18a]

$$\tau_{OH/H_2O}^{-1} \text{ or } \tau_H^{-1} = \frac{1}{2}(a_{11} + a_{22}) \pm \sqrt{\left(\frac{a_{11} + a_{22}}{2}\right)^2 + a_{12}a_{21} - a_{11}a_{22}} \quad (11)$$

with

$$a_{11} = k_{-1}^{H}[H^+] \quad (12)$$

$$a_{12} = k_{-1}^{H}[H^+] \quad (13)$$

$$a_{21} = k_2^{H}[H^+] + k_2^{BH}[BH] \quad (14)$$

$$a_{22} = k_2^{H}[H^+] + k_2^{BH}[BH] + k_{-2}^{H_2O} + k_{-2}^{B}[B] \quad (15)$$

If one assumes that, in the absence of buffer, $(k_{-1}^{H} + k_2^{H})[H^+] \gg k_{-2}^{H_2O}$, eq 11 simplifies to

$$\tau_{OH/H_2O}^{-1} = (k_{-1}^{H} + k_2^{H})[H^+] \quad (16)$$

$$\tau_H^{-1} = k_{-2}^{H_2O}k_{-1}^{H}/(k_{-1}^{H} + k_2^{H}) \quad (17)$$

Mechanistically this means that the τ_{OH/H_2O}^{-1} process is the reaction of T_{OH}^- with hydronium ion to form a mixture of S and T_{OH}^0; it can be monitored either at λ_{max} of S or λ_{max} of T_{OH}^- (T_{OH}^0 does not absorb[2]). At the end of this process most of the material is in the S and T_{OH}^0 form, with very little T_{OH}^- left. The τ_H^{-1} process then corresponds to the conversion of T_{OH}^0 into the thermodynamically more stable S via T_{OH}^- which now is a steady-state intermediate. This is consistent with the fact that τ_H^{-1} can only be monitored at λ_{max} of S but not at λ_{max} of T_{OH}^-.

Table VI. Rate and Equilibrium Constants for Reaction 2 (Proton Transfer to and from Carbon)

constant	1-OMe	**1**-H[b]	1-NO_2
k_2^{H}, $M^{-1}\ s^{-1}$	3.72×10^4 [a]	2.40×10^4	7.75×10^3
$k_{-2}^{H_2O}$, s^{-1}	19.1[a]	27.2	69.7
$k_{-2}^{H_2O}/k_2^{H} = K_a^{CH}$, M	5.13×10^{-4} [a]	1.12×10^{-3}	9.23×10^{-3}
pK_a^{CH}	3.29[a]	2.95	2.04

[a] From Hammett plot defined by 1-H and 1-NO_2, $\rho(K_a^{CH}) = 1.20$; see text. [b] From ref 2.

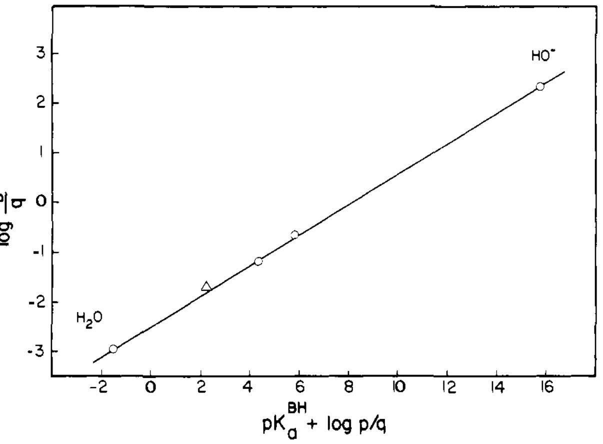


Figure 2. Brønsted plot for acetate and cacodylate ion catalyzed water addition to **1-OMe**, including the water and OH^--reactions. Δ refers to chloroacetate ion; see Discussion.

From an analysis according to eq 16 and 17 and using $k_{-1}^{H} = 5.10 \times 10^3\ M^{-1}\ s^{-1}$ (Table II) one obtains $k_2^{H} = 7.75 \times 10^3\ M^{-1}\ s^{-1}$ and $k_{-2}^{H_2O} = 69.7$. These numbers show that $(k_1^{H} + k_2^{H})[H^+] \gg k_{-2}^{H_2O}$ is indeed a good approximation at pH ≤1.25.

In principle, the same behavior would be expected for **1-OMe**. There is, in fact, evidence for the τ_H process, but the OD change is so small that no meaningful τ_H^{-1} values could be obtained. This is because for **1-OMe** $k_{-1}^{H} \gg k_2^{H}$ so that very little T_{OH}^0 is formed during the τ_{OH/H_2O}^{-1} process. This interpretation is also consistent with τ_{OH/H_2O}^{-1} not deviating measurably from the line defined at higher pH (Figure 1). An estimate of k_2^{H} and $k_{-2}^{H_2O}$ based on a Hammett $\sigma\rho$ relationship for **1-H** and **1-NO₂** confirms this analysis: $k_2^{H} \approx 3.72 \times 10^4$ while $k_{-1}^{H} \approx 2.95 \times 10^5\ M^{-1}\ s^{-1}$. The various rate and equilibrium constants for reaction 2 are summarized in Table VI; incidentially $\rho = 1.20$ for $K_a^{CH} = k_{-2}^{H_2O}/k_2^{H}$.

Discussion

Mechanism of Water and OH⁻ Addition. Buffer catalysis of water addition to the olefin (eq 1) was not measurable for **1-NO₂**, just as for **1-H**,[2] but in the case of **1-OMe**, catalysis by acetate and cacodylate buffers, although still weak, seems to be real and outside experimental error. Rate constants k_{BH} and k_B (eq 6), calculated on the assumption that they represent authentic acid-base catalysis, are included in Table II.

The following points argue in favor of authentic catalysis and against an interpretation of the rate enhancement in terms of either a "contamination" of τ_{OH/H_2O}^{-1} by reaction 2, a differential salt effect by the buffer base (at constant ionic strength), or a medium effect by the buffer acid.

(1) The rate constants for acetate and cacodylate ion catalysis, together with those for OH⁻ and water attack ($k_1^{H_2O}/55.5$), define a Brønsted plot of slope $\beta = 0.31$ as shown in Figure 2.[19] This is reminiscent of general base catalyzed water addition to Malachite Green[20a] and to tris-*p*-methoxyphenylmethyl cation.[20b]

---

[18] Bernasconi, C. F. "Relaxation Kinetics," Academic Press: New York, 1976: (a) Chapter 3; (b) Chapter 9.

[19] For water the statistical factors $p = 3$ and $q = 2$ were used. See: Gold, V.; Waterman, D. C. A. *J. Chem. Soc. B* **1968**, 839.

Table VII. Calculated and Observed τ_{OH/H_2O}^{-1} Values for 1-OMe in Acetate Buffers

pH	$[B]_{tot}$, M	τ_{OH/H_2O}^{-1}, s^{-1} calcd[a]	$\Delta\%$[c]	τ_{OH/H_2O}^{-1}, obsd	$\Delta\%$[c]	τ_H^{-1}, s^{-1} calcd[b]
5.50	0.057	1.51		1.43		117
	0.276	1.51	0	1.64	14.7	492
5.00	0.0187	4.69		4.26		46.3
	0.343	4.70	0.25	5.08	19.2	504
4.50	0.0425	13.8		13.4		62.1
	0.434	14.2	2.9	15.5	15.7	423
4.00	0.089	31.6		40.6		79.3
	0.94	39.1	24.0	46.4	14.3	485

[a] Equation 11 with negative square root. [b] Equation 11 with positive square root. [c] Percent increase in τ_{OH/H_2O}^{-1} from low to high buffer concentration.

(2) As shown in the Results section and in contrast to the situation with **1-H** and **1-NO$_2$**, contamination by reaction 2 is never very pronounced with **1-OMe**, even at very low pH where eq 16 holds. This is because $k_{-1}^{H} \gg k_2^{H}$ (Tables II and VI). Nevertheless, in the presence of a buffer a slight contamination by reaction 2 which could enhance τ_{OH/H_2O}^{-1} by say 10 to 20% is a real possibility which needs to be considered. In order to assess this hypothesis we have calculated the effect of acetate buffer concentration on τ_{OH/H_2O}^{-1} using the general equation 11 which is devoid of any approximations. We used k_{-1}^{H}, k_2^{H}, and $k_{-2}^{H_2O}$ from Tables II and VI, respectively, while $k_2^{BH} = 10^2$ and $k_{-2}^{B} = 1.90 \times 10^3$ were estimated from a Brønsted plot referring to reaction 2 for **1-H**.[4] The results of these calculations for a few typical reaction conditions reported in Table I are summarized in Table VII; the table also includes τ_H^{-1} values calculated in a similar way from eq 11.

The following conclusions emerge. At pH 5.5, 5.0, and 4.5 the percent increase in the calculated τ_{OH/H_2O}^{-1} in going from the lowest to the highest buffer concentration in negligible ($\Delta\%$ column) compared to the catalytic effect on the observed τ_{OH/H_2O}^{-1}. Hence the observed catalysis cannot be attributed to contamination by reaction 2. This can be understood in qualitative terms by realizing that at these pH values the equilibrium of reaction 2 strongly favors T_{OH}^- ($pK_a^{CH} = 3.29$), implying that eq 6 is a very good approximation. On the other hand, at pH 4.0 T_{OH}^- is favored only about fivefold over T_{OH}^0, contamination becomes significant ($\Delta = 24\%$) and appears to account for more than the entire observed ($\Delta = 14.3\%$) catalysis. In view of the conclusion drawn from the results at higher pH, one wonders why the observed catalytic effect is not ≈38%, namely, ≈24% for contamination plus ≈14% for catalysis. The reason is that at low buffer concentration the observed τ_{OH/H_2O}^{-1} is somewhat too high because it differs only ≈ threefold from τ_H^{-1}. When two relaxation times are that close, one can observe only one, with a value which is the amplitude-weighted average of the two.[18b] This will tend to enhance the observed τ_{OH/H_2O}^{-1} at low but not at high buffer concentration since at high concentration $\tau_H^{-1} \gg \tau_{OH/H_2O}^{-1}$. At pH 4.5, a similar though less acute problem seems to exist. However, here the amplitude of τ_H^{-1} is so small (equilibrium favors T_{OH}^- strongly over T_{OH}^0) that the amplitude-weighted average of τ_{OH/H_2O}^{-1} and τ_H^{-1} would hardly be distinguishable from τ_{OH/H_2O}^{-1}. On the other hand, at pH 3.5 and 3.0 the situation is even worse than at pH 4.0 and prevents observation of a catalytic effect by formate buffer altogether.

(3) With respect to a possible medium effect by the buffer acid, we note that acetate buffer catalysis was studied at four different buffer ratios, spanning a range from 8.51 (pH 5.50) to 0.27 (pH 4.00). In this pH range the equilibrium of reaction 1 strongly favors the olefin, and hence catalysis, if authentic, would mainly refer to the $k_{BH}[BH]$ term in eq 6. Even discounting the data at pH 4.0 for the reasons mentioned above, the values obtained for k_{BH} at three different pH values are remarkably consistent (8.40, 9.90, and 10.9 $M^{-1}\ s^{-1}$ at pH 5.5, 5.0, and 4.5, respectively, for an average $k_{BH} = 9.73\ M^{-1}\ s^{-1}$). Since the concentration of the acid varied widely (highest [AcOH = 0.029 M at pH 5.5, 0.235 M at pH 4.5) but the relative acceleration at the highest [AcOH] was always about the same (22% at pH 5.5, 21% at pH 5.0, 20% at pH 4.5), catalysis cannot be due to a medium effect caused by the acid.

(4) If acetate buffer catalysis were due to a salt effect induced by replacing the chloride ion by the acetate ion, one would expect that the chloroacetate ion leads to a similar rate acceleration. In order to test this hypothesis we studied the effect of potassium chloroacetate in a 1:1 cacodylate buffer at pH 6.1. At this pH τ_{OH/H_2O}^{-1} is still dominated by the $k_{-1}^{H}[H^+]$ term; i.e., we are dealing with the same reaction as in the acetate buffer experiments. The results show that there is indeed a small acceleration amounting to a 6.5% increase in τ_{OH/H_2O}^{-1} at 0.3 M. This is much less than the 20% accelerations observed for comparable or smaller acetate ion concentrations and suggests that, if part of the acetate buffer catalysis were due to a salt effect, it would only be a small fraction of the total.

However, the small acceleration induced by chloroacetate is probably not even due to a salt effect. If one evaluates the catalytic effect according to eq 6, one obtains the k_B and k_{BH} values listed in Table II. It turns out that k_B lies very close to the Brønsted line of Figure 2 (triangle) which is probably no coincidence but indicates general acid–base catalysis.

The most likely mechanism for buffer catalysis is a concerted one, with a transition state like **2**, except that the second water molecule is replaced by B. Such catalysis is quite common in reactions of electrophiles with water;[5-14,20] Calmon's[21] observation in the hydrolysis of benzylideneacetylacetone probably represents the same phenomenon.

The fact that $k_1^{H_2O}/55.5$ for the water reaction lies on the same Brønsted line as k_B for the buffer bases (Figure 2) suggests that the water reaction proceeds by the same mechanism (**2**) and not via $T_{OH}^{\pm}$. Interestingly, even k_1^{OH} for hydroxide ion attack lies on the same Brønsted line. A possible interpretation of this finding is that hydroxide ion acts as a base catalyst for water addition rather than as a nucleophile.[9a] Our observation is consistent with similar findings in the hydroxide ion addition to carbocations;[20] possible reasons why catalysis of water addition might be a more favorable process than direct nucleophilic attack have been discussed by Ritchie.[9a]

The fact that catalysis could only be observed with **1-OMe** but not with **1-H** or **1-NO$_2$** calls for some comment. Even with **1-OMe** catalysis is weak. We can see now that this must be due to the smallness of $\beta = 0.31$ which makes it difficult to detect catalysis against the background of the water and hydroxide ion reactions.[22] Assuming the same mechanism for **1-H** and **1-NO$_2$** one can calculate Brønsted β values based on $k_1^{H_2O}/55.5$ and k_1^{OH}. One obtains 0.30 for **1-H**, 0.31 for **1-NO$_2$**; i.e., they are, within experimental error, the same as for **1-OMe**. Hence a similar catalytic effect should have been observed for **1-H** and **1-NO$_2$**. The absence of such an effect must therefore be attributed to the reasons mentioned in the introduction, i.e., competing nucleophilic attack with the more basic buffers (acetate) which is expected to be more pronounced with the more reactive **1-H** and **1-NO$_2$**, and, with the more acidic buffers, complications of the sort discussed for **1-OMe** at pH 4.0 due to coupling with reaction 2. The slight *decrease* in τ_{OH/H_2O}^{-1} with increasing acetate buffer concentrations for **1-NO$_2$** (Table I) which is similar to the effect of phenol buffers (eq 7) is probably a direct manifestation of the first factor while the data at very low pH show that coupling with reaction 2 is indeed more pronounced for **1-H** and **1-NO$_2$** than for **1-OMe**.

The independence of β (or α in the reverse direction) on the phenyl substituent, indicating that $p_{xy} = \partial\alpha/\partial\sigma = -\partial\beta/\partial\sigma = 0$,[23] is noteworthy. According to considerations based on structure–

---

(20) (a) Ritchie, C. D. *J. Am. Chem. Soc.* **1972**, *94*, 3275. (b) Ride, J. N.; Wyatt, P. A. H.; Zochowski, Z. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1188.

(21) Calmon, M.; Calmon, J.-P. *Bull. Soc. Chim. Fr.* **1974**, *977*.

(22) Jencks, W. P. "Catalysis in Chemistry and Enzymology"; McGraw-Hill: New York, 1969; p 174.

Table **VIII.** Structure-Reactivity Parameters for Nucleophilic Additions to the 1-**X**

nucleophile	H_2O	OH^-	ArO^-	morpholine[a]	piperidine[a]
$\rho(k_1)$	≈ 0.70 (ρ^+)	≈ 0.68 (ρ^+)	1.12^d ($\rho^{(+)}$)[b]		
$\rho(k_{-1})$	-1.82 (ρ)	-1.85 (ρ)	-0.78 (ρ^+)		
$\rho(K_1)$	2.53^c ($\rho^{(+)}$)[b]	2.53^c ($\rho^{(+)}$)[b]	1.90^e ($\rho^{(+)}$)[b]	~1.26-1.70^f ($\rho^{(+)}$)[b]	~1.46-1.70^f ($\rho^{(+)}$)[b]
$\rho_n(k_1) = \rho(k_1)/\rho(K_1)$	0.28	0.27	0.59	0.45	0.40
$\rho_n(k_{-1}) = \rho(k_{-1})/\rho(K_1)$	-0.72	-0.73	-0.41	-0.55	0.60
$\beta_{nuc}(k_1)$			0.41^g	0.07^h	0.07^h
$\beta_{lg}(k_{-1})$			-0.63^g	-0.80^h	-0.80^h
$\beta_{eq}(K_1)$			1.04^g	0.87^h	0.87^h
$\beta_{nuc}{}^n(k_1) = \beta_{nuc}(k_1)/\beta_{eq}(K_1)$			0.39^g	0.08^h	0.08^h
$\beta_{lg}{}^n(k_{-1}) = \beta_{lg}(k_{-1})/\beta_{eq}(K_1)$			-0.61^g	-0.92^h	-0.92^h

[a] Reference 3. [b] $\rho^{(+)}$ means that correlation is with σ_{MeO} between σ and σ^+. [c] Based on $\sigma_{MeO} = -0.52$; see text. [d] Based on $\sigma_{MeO} = -0.49$. [e] Based on $\sigma_{MeO} = -0.65$. [f] Lower number based on σ^+ correlation for 1-H and **1**-NMe$_2$ ($\sigma^+_{Me_2N} = -1.67$, ref 28), higher number based on correlation of 1-H and 1-OMe with $\sigma_{MeO} = -0.65$ as for aryl oxide addition. [g] Based on **1**-NO$_2$. [h] Based on 1-H.

reactivity surfaces,[23-25] one would have expected a decrease in β (increase in α) for a change to a more electron-withdrawing substituent, corresponding to a positive p_{xy} coefficient.[23] Such positive p_{xy} coefficients have indeed been observed in the hydrolysis of substituted benzaldehyde methyl phenyl acetals[8] and in the breakdown of Meisenheimer complexes.[12] On the other hand, in the dehydration of carbinolamines derived from the reaction of substituted benzaldehydes with a variety of amines $p_{xy} = 0$[26,27] as in the present reaction. The reason why these seemingly similar reactions show different behavior with respect to p_{xy} is at present not clear.

Structure-Reactivity Relationships. A. Reaction 1. $k_1^{H_2O}$ and k_1^{OH} for water and hydroxide ion addition to the olefins correlate fairly well with σ^+,[28] giving $\rho^+ \approx 0.70$ for $k_1^{H_2O}$, $\rho^+ \approx 0.68$ for k_1^{OH}. On the other hand, in the reverse direction the correlation is much better with the normal σ values, giving $\rho = -1.82$ for k_{-1}^{H} and $\rho = -1.85$ for $k_{-1}^{H_2O}$. Thus $K_1^{H_2O}$ or K_1^{OH} correlate with neither σ or σ^+ but give a linear Hammett plot if $\sigma_{MeO} = -0.42$ (spectrophotometric K's[4]) or $\sigma_{MeO} = -0.52$ (kinetic K's) is chosen. With the former $\rho = 2.43$, with the latter $\rho = 2.53$.

The poor correlation of $K_1^{H_2O}$ with either σ or σ^+ has been noticed before in 10,[29] 80,[30] and 99%[30] aqueous methanol and has other precedents in nucleophilic additions to olefins.[31] It indicates that there is *some* resonance interaction between the phenyl substituent and the highly polarized double bond, but it is weaker than in those systems used to define σ^+.[32]

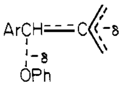
Normalized ρ values, defined as $\rho_n(k_1) = \rho(k_1)/\rho(K_1)$, etc., are summarized in Table VIII. In the forward direction the normalized ρ values are a measure of the combined effect of how much negative charge has been transferred from the nucleophile to the substrate and how much of the resonance interaction has been lost in the transition state, as seen by the phenyl substituent. In the reverse direction they measure how much charge has been lost and how much resonance interaction has been built up in the transition state. The fact that the rates correlate with σ^+ in the forward but with σ in the reverse direction indicates that a large fraction, and perhaps all, of the resonance interaction is lost in the transition state. This implies that the fractional negative charge transferred to the olefin in the transition state is considerably less than $\rho_n(k_1)$ and therefore quite small.

These considerations suggest then that the transition state is imbalanced in the sense that loss of resonance, and with it presumably $sp^2 \rightarrow sp^3$ rehybridization of the β carbon, has made much more progress than negative charge transfer and with it presumably C–O bond formation.[33] Based on similar evidence Funderburk and Jencks[27] have reached essentially the same conclusions for the transition state of the dehydration of carbinol amines derived from substituted benzaldehydes and semicarbazide.

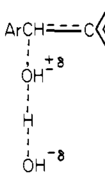
B. Reaction 5. k_1^{OAr} for phenoxide ion attack on the substituted olefin does not correlate very well with either σ^+ or σ but, nevertheless, correlates better with σ^+ than with σ; a straight Hammett plot is obtained with $\sigma_{MeO} = -0.49$, yielding $\rho = 1.12$. In the reverse direction k_{-1}^{OAr} gives an excellent correlation with σ^+ and yields $\rho^+ = -0.78$. The correlation for the equilibrium constants K_1^{OAr} gives $\rho = 1.80$ with $\sigma_{MeO} = -0.65$ which is quite close to $\sigma_{MeO}{}^+ = -0.79$. The various ρ values and their normalized values are summarized in Table VIII.

The fact that in these reactions it is the reverse process (k_{-1}^{OAr}) which correlates well with σ^+ while k_1^{OAr} does not correlate as well with σ^+ indicates that loss of resonance interaction has made slightly less than 50% progress in the transition state. Since $\rho_n(k_1) = 0.59$ suggests that the combined progress made by charge transfer and resonance loss is slightly *more* than 50%, one may conclude that charge transfer is slightly ahead of resonance loss.

These considerations show that the imbalance seen for the water and hydroxide ion reactions seems to reverse itself in the aryl oxide reactions. This change in behavior can probably be related, at least in part, to an electrostatic effect. The phenyl substituent in the substrate does not only respond to the negative charge which has been transferred from the nucleophile to the olefin but also to the negative charge *remaining* on the nucleophile. In the transition state for aryl oxide ion attack (**3**) this remaining charge is quite close to the substituent and thus is strongly felt. In the transition state for water attack (**2**) there is essentially no such



3



4

---

(23) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948.

(24) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274.

(25) Jencks, W. P. *Chem. Rev.* **1972**, *72*, 705.

(26) Sayer, J. M.; De Pecol, M. *J. Am. Chem. Soc.* **1977**, *99*, 2665.

(27) Funderburk, L. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1978**, *100*, 6708.

(28) $\sigma^+_{MeO} = -0.79$ from Hine, J. "Structural Effects on Equilibria in Organic Chemistry"; Wiley-Interscience: New York, 1975; p 72.

(29) Margaretha, P.; Schuster, P.; Polanski, O. E. *Tetrahedron* **1971**, *27*, 71.

(30) Schuster, P.; Polanski, O. E.; Wessely, F. *Tetrahedron, Suppl. 8* **1966**, II, 463.

(31) Rappoport, Z.; Ladkani, D. *Chem. Scripta* **1974**, *5*, 124.

(32) See, e.g., ref 28, p 70.

(33) This conclusion is also consistent with secondary α kinetic and equilibrium deuterium isotope effects for water addition to **1-OMe**: $(k_1^{H_2O})_H/(k_1^{H_2O})_D = 0.93 \pm 0.02$ while $(K_1^{H_2O})_H/(K_1^{H_2O})_D = 0.89 \pm 0.03$.[4] If one accepts the notion that the kinetic isotope effect is a measure of the extent of rehybridization in the transition state,[34] comparison between the kinetic and the equilibrium isotope effect suggests that this rehybridization has made more than 50% progress in the transition state. We do not want to put too much emphasis on these isotope effects, though, because of some experimental difficulties in obtaining reliable data[4] and because of recent observations which indicate that secondary α kinetic deuterium isotope may not be a reliable indicator of transition state hybridization.[35]

(34) See, e.g.: (a) Palmer, J. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6472. (b) Shiner, V. J., Jr. "Isotope Effects in Chemical Reactions," Collins, C. J., Bowman, N. S., Eds.; Van Nostrand-Reinhold: New York, 1970; p 90. (c) do Amaral, L.; Bastos, M. P.; Bull, H. G.; Cordes, E. H. *J. Am. Chem. Soc.* **1973**, *95*, 7369. (d) Young, P. R.; McMahon, P. E. *Ibid.* **1979**, *101*, 4678. (e) Bilkadi, Z.; de Lorimier, R.; Kirsch, J. F. *Ibid.* **1975**, *97*, 3417.

(35) (a) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789. (b) Pohl, E. R.; Hupe, D. J. *Ibid.* **1980**, *102*, 2763.

charge. Similarly, if in the hydroxide ion reaction the nucleophile acts as a base catalyst (**4**), the remaining negative charge would be far removed from the substituent and be only weakly felt. Thus the relative contribution to $\rho_n(k_1)$ which relates to negative charge stabilization should be larger for the aryl oxide reactions, as observed. Young and Jencks'[36] observations in the reaction of sulfite ion with substituted benzophenones seem to support this interpretation. They found that negative charge development in the transition state is considerably ahead of resonance loss; the large amount of charge seen in the transition state by the phenyl substituents was attributed to the large remaining negative charge on the nucleophile which is a dianion.

It should be pointed out that the above electrostatic effect (**3**) operates only in the transition state but not in the adduct T_{OAr}^-. Hence $\rho(K_1^{OAr})$ should not be larger than $\rho(K_1^{H_2O})$ or $\rho(K_1^{OH})$ for water and OH^- addition. The observed $\rho(K_1^{OAr}) = 1.90$ is, in fact, *smaller* than $\rho(K_1^{H_2O}) = \rho(K_1^{OH}) = 2.53$. This may, in part, be due to the stronger electron-withdrawing effect of the phenoxy compared to the hydroxyl group which helps stabilize part of the negative charge in the adduct. Intramolecular hydrogen bonding between the OH group and the $(COO)_2C(CH_3)_2$ moiety in the hydroxide ion adduct has been suggested by a referee as an additional, and perhaps the main, factor which might be responsible for the higher $\rho(K_1^{OH})$ value. This is an attractive suggestion, it is supported by the high ρ value associated with the pK_a^{CH} values which we attribute to the same kind of intramolecular hydrogen bonding as discussed in more detail below. As pointed out by the same referee, if development of such hydrogen bonding were to lag behind C–O bond formation, this might account for part (but not all) of the small size of $\rho_n(k_1^{OH})$ relative to $\rho_n(k_1^{OAr})$.[37]

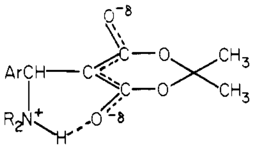
Another kind of transition-state imbalance is indicated by comparing the normalized ρ values with $\beta_{nuc}(k_1^{OAr}) = 0.41 \pm 0.03$ and $\beta_{lg}(k_{-1}^{OAr}) = -0.63 \pm 0.03$ for the reaction of aryl oxide ions with **1-NO$_2$**. These latter parameters result from a correlation of the rates with the pK_a of the phenols; one also obtains $\beta_{eq}(K_1^{OAr}) = 1.04 \pm 0.06$. Incidentally, this latter value shows that, within experimental error, the substituent effects on the carbon basicity of the aryl oxide ions are the same as on their proton basicity.

The β and the normalized-β values are summarized in Table VIII. $\beta_{nuc}^n(k_1^{OAr})$ is a measure of how much charge has been transferred from the nucleophile to the olefin in the transition state, as seen by the substituent in the nucleophile. Its value of 0.39 implies that this process is 39% complete. This result contrasts with $\rho_n(k_1^{OAr}) = 0.59$ which indicates that charge transfer is at least (see above) 59% complete. It appears that the degree of charge transfer seen by the substituent in the olefin is larger than that seen by the substituent in the nucleophile. Since we have shown above that loss of resonance is not ahead of negative charge development (it even lags slightly behind), this imbalance must have a different origin. A possible explanation of this imbalance is that in the transition state some of the negative charge on the attacking nucleophile might tend to be localized on either the α or β carbon and/or be delocalized into the benzene ring of the olefin[38] while in the adduct (T_{OAr}^-) most of this charge is delocalized into the $(COO)_2C(CH_3)_2$ moiety. Thus, in the transition state the charge is closer to the substituent than in the adduct, and hence the substituent's response to that charge is relatively stronger which leads to an exalted $\rho_n(k_1^{OAr})$ value. An additional factor contributing to a disproportionately high $\rho_n(k_1^{OAr})$ value is the negative charge which remains on the aryloxy oxygen and which, as pointed out before, is also close to the substituent.

This interpretation of the imbalance might imply that it is only $\rho_n(k_1^{OAr})$ which is abnormal. This is, of course, not the case. If part of the transferred charge remains in close vicinity of the nucleophile, this charge will also still be seen to some extent by the substituent in the *nucleophile* and reduce $\beta_{nuc}^n(k_1^{OAr})$ accordingly. Hence we realize that the imbalance is the result of both an exaltation of ρ_n and an attenuation of β_{nuc}^n, and therefore neither parameter gives an accurate account of the extent of charge transfer or bond formation.

An even larger imbalance of the same kind was observed in the addition of piperidine and morpholine to **1-H**, **1-OMe**, and **1-NMe$_2$** (Table VIII) as indicated by the large difference between $\rho_n(k_1^{Mor}) = 0.45$ or $\rho_n(k_1^{Pip}) = 0.40$ and $\beta_{nuc}^n(k_1^{R_2NH}) = 0.08$ (**1-H**). This increase in the imbalance is probably of electrostatic origin: the incipient positive charge on nitrogen helps stabilize the incipient negative charge on the olefin, thereby keeping this latter in close proximity of the phenyl group. If everything else is equal, the result is a further increase in ρ_n and a further decrease in β_{nuc}^n which increases the difference between the two.[39]

Whether the effect is purely electrostatic or whether intramolecular hydrogen bonding to an oxygen of the $(COO)_2C(CH_3)_2$ moiety plays a role is difficult to say. Such hydrogen bonding is probably more important in the *adduct* **5** where most of the negative charge has been shifted into the $(COO)_2C(CH_3)_2$ moiety and where the acidity of the NH proton is enhanced. The fact that $\beta_{eq}(K_1^A)$ and $\rho(K_1^A)$[40] for the amine reactions are smaller than $\beta_{eq}(K_1^{OAr})$ and $\rho(K_1^{OAr})$ for the aryl oxide ion reactions is a direct manifestation of the hydrogen-bonding and/or electrostatic effect in the adduct.



5

C. Reaction 2. We shall focus our attention on the pK_a^{CH} values of T_{OH}^0 which are summarized in Table VI; the *rates* of carbon protonation/deprotonation will be discussed in the next paper.[4]

We note that the pK_a^{CH} values are all significantly lower than $pK_a = 4.83$ of Meldrum's acid,[41] showing the electron-withdrawing effect of the ArCH(OH) moiety. The effect of the phenyl substituent is reflected in $\rho = 1.20$ for K_a^{CH}. Even though this ρ value is based on two points only (**1-H** and **1-NO$_2$**) and may therefore not be very accurate, its remarkably large magnitude seems surprising. Since the high acidity of Meldrum's acid and of T_{OH}^0 implies that in the anion there is an exceedingly strong delocalization of the negative charge into the $(COO)_2C(CH_3)_2$ moiety, a much smaller ρ value should have been expected. For example, $\rho = 0.40$ for the ionization constants of $ArCH_2CH(CH_3)NO_2$ in 50% aqueous methanol[42] which reflects the strong delocalization of the negative charge into the nitro group; ρ values being notoriously larger in nonaqueous solvents,[43] the above value would

---

(36) Young, P. R.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 3288.

(37) Another hypothesis by the referee is that a π-complex-type interaction between the aromatic substrate and the aryl oxide nucleophile in the transition state could have an influence on $\rho(k_1^{OAr})$. The suggestion of a π-complex-type interaction was offered as a possible rationalization of why nucleophilic attack by the aryl oxide ions is so much faster than attack by hydroxide ion. We have currently no evidence which could either support or refute this idea.

(38) It is difficult to be more precise about the location of this negative charge. Whether there is any on the α carbon may depend on whether it will remain completely sp^2-hybridized or whether it might acquire some sp^3 character.

(39) As seen in Table VIII the value of $\rho_n(k_1^{R_2NH})$ is actually *smaller* than $\rho_n(k_1^{OAr})$. This is because everything is *not* equal; i.e., ρ_n also depends on the extent of bond formation which is apparently smaller in the amine reactions and which reduces ρ_n. But the smaller extent of bond formation also reduces β_{nuc}^n, a decrease which is on top of the decrease produced by the electrostatic effect. Thus the net result of the electrostatic effect is again seen to increase the *difference* between ρ_n and β_{nuc}^n while the absolute values of ρ_n and β_{nuc}^n depend on the extent of bond formation.

(40) The fact that the reduction of $\rho(K_1^A)$ is not more dramatic or that $\rho(K_1^A)$ is not negative is perhaps surprising since the positive charge on the nitrogen is much closer to the phenyl substituent than the strongly delocalized negative charge. This shows that the major factor which determines ρ is not the negative charge but the loss of conjugation in the olefin as pointed out before.[3,30]

(41) Eigen, M.; Ilgenfritz, G.; Kruse, W. *Chem. Ber.* **1965**, *98*, 1623.

(42) Bordwell, F. G.; Boyle, W. J., Jr.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5926.

(43) Exner, O. In "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds., Plenum Press: New York, 1972; p 1.

Table IX. Standard Free Energies of Reaction, Marcus Intrinsic Barriers, and Marcus α_M Values for the Reactions of Nucleophiles with **1**-X[a]

	1-NO$_2$			**1**-H			**1**-OMe			**1**-NMe$_2$		
nucleophile	ΔG^0	$\Delta G_0^\ddagger$	α_M	ΔG^0	$\Delta G_0^\ddagger$	α_M	ΔG^0	$\Delta G_0^\ddagger$	α_M	ΔG^0	$\Delta G_0^\ddagger$	α_M
OH^-	−13.9	19.0	0.41	−11.3	18.7	0.42	−9.86	18.7	0.43			
H_2O	+7.07	15.7	0.56	+9.75	14.8	0.58	+11.2	14.9	0.59			
$C_6H_5O^-$	−5.66	13.1	0.44	−3.72	13.4	0.47	−2.12	13.4	0.48			
p-$BrC_6H_4O^-$	−4.76	13.0	0.45	−2.52	13.2	0.48						
p-$CNC_6H_4O^-$	−2.88	12.9	0.47									
piperidine				−9.80	14.5	0.42	−8.63	14.3	0.43	−5.93	14.3	0.45
morpholine				−6.72	13.4	0.44	−5.44	13.2	0.45	−2.86	13.4	0.47

[a] In kcal/mol; $\Delta G_0^\ddagger$ calculated from eq 18, α_M from eq 19.

Table X. Standard Free Energies of Reaction, Marcus Intrinsic Barriers, and Marcus α_M Values for the Reactions of Nucleophiles with Alkoxycarbonyl-, Nitro-, and Cyano-Activated Olefins[a]

	$PhCH{=}C(COO)_2C(CH_3)_2$ [b]			$PhCH{=}CHNO_2$ [c]			$PhCH{=}C(CN)_2$ [d]		
nucleophile	ΔG^0	$\Delta G_0^\ddagger$	α_M	ΔG^0	$\Delta G_0^\ddagger$	α_M	ΔG^0	$\Delta G_0^\ddagger$	α_M
OH^-	−11.3	18.7	0.42				−3.37	16.2	0.47
H_2O	+9.75	14.8	0.58				+18.0	14.1	0.66
piperidine	−9.80	14.5	0.42	−2.04	14.2	0.48	−1.61	11.0	0.48
morpholine	−6.72	13.4	0.44	+0.90	13.8	0.51	+0.87	10.7	0.51

[a] Same as in Table IX. [b] Amine reactions, ref 3. [c] Bernasconi, C. F.; Carré, D. J.; Fox, J. P. In "Techniques and Applications of Fast Reactions in Solution", Gettins, W. J., Wyn-Jones, E., Eds.; Reidel: Dordrecht, Holland, 1979; p 453. [d] Amine reactions, ref 68, OH^- and H_2O reactions based on preliminary data: Bernasconi, C. F.; Fox, J. P.; Howard, K. A., to be submitted for publication.

probably be lower still in pure water. Even the ρ values for the ionization of acids where no charge delocalization is possible are usually smaller than for T_{OH}^0, e.g., $\rho = 1.01$ for $ArCH(OH)CF_3$,[44] 1.05 for $ArAsO(OH)_2$,[45] and 0.76 for $ArPO(OH)_2$.[45]

Intramolecular hydrogen-bonding in the anion T_{OH}^-, similar to that postulated for $T_A^\pm$ (**5**), is probably responsible for the large ρ value. According to this view an electron-withdrawing substituent would stabilize the negative charge not only by the usual polar effect but also by enhancing the acidity of the OH group, thereby making it a better hydrogen-bond donor. The strength of this hydrogen bond might be comparable to or, owing to the negative charge, even greater than that in the enol form of acetylacetone since the pK difference between donor and acceptor is probably roughly comparable[46] and the geometries of the six-membered cycle are similar. The stability constant of the intramolecularly bound enol form of acetylacetone is 500, based on the 500-fold reduction below the diffusion-controlled level of the rate of deprotonation of the enol by hydroxide ion.[49] This stability constant implies the hydrogen-bonding interaction is indeed quite large.

Imbalanced Transition States: Rule or Exception? As the transition state of an increasing number of reactions is being probed by multiple structure–reactivity relationships it becomes more and more apparent that imbalanced transition states are a common phenomenon.[10,12,23,27,36,50–57] It is time to ask whether they might be the rule rather than the exception.

For reactions with very complex transition states such as concerted E2 eliminations[58] or concerted type n and e reactions,[5] there is such a multitude of events which have to take place before the transition state is reached that imbalances are not surprising. Most reports indeed refer to these types of reaction. But even in a slightly simpler reaction like ours there are many processes which need to have made some progress in the transition state.[59] They include approach and desolvation of the nucleophile, rehybridization of the β carbon with a concomitant change in bond angles and geometry, forming a bond to the β carbon, breaking the double bond, delocalization of the negative charge, and solvation of this negative charge as well as other, less well-defined solvational changes. This is quite overwhelming, and one wonders whether a transition state where all these processes have occurred in total synchrony could ever be found.

What about "simple" reactions? Proton transfers are often thought of as "simple" but here too imbalanced transition states are common. The nitroalkane anomaly[23,52–55] is the most prominent example but every proton transfer for which α (variation of rate with pK_a of acid) and β (variation of rate with pK_a of base) are not equal has, by definition, an imbalanced transition state.

The combination of an anion with a cation is an even simpler reaction than a proton transfer since it only involves the formation of one bond and the breaking of none. But even here an imbalanced transition state has been reported by Ritchie and Gandler.[56] It appears then that imbalances are indeed the rule rather than the exception.

Relation to Marcus Theory. Marcus theory has become fashionable in relating rate–equilibrium data not only for electron[60] and proton transfer reactions[61] but more recently also for nucleophilic substitution[62] and addition[63–65] reactions. Albery has reviewed the subject recently.[65]

---

(44) Stewart, R.; Van der Linden, R. *Can. J. Chem.* **1960**, *38*, 399.

(45) Jaffé, H. H. *Chem. Rev.* **1953**, *53*, 191.

(46) In the absence of hydrogen bonding the pK_a of the enol form of acetylacetone is estimated to be 5.5[47] while the carbonyl group pK must be $\lesssim -9$, based on pK values around −7 for simple ketones without an additional electron-withdrawing group such as acetyl.[48] Thus $|\Delta pK| \leq 14.5$. For T_{OH}^0 (**1**-H) we estimate a p$K_a \approx 15$ for the OH group while the pK_a of the enol form of T_{OH}^0 must be ≈ 0.7. This latter estimate is based on the findings that there is about 0.5% enol form in an aqueous solution of Meldrum's acid[41] or T_{OH}^0. Thus again $|\Delta pK| \approx 14.3$.

(47) The actual pK is 8.2; the value of 5.5 is based on the ≈500-fold reduction below the diffusion-controlled limit of the rate of deprotonation by hydroxide ion.[49]

(48) Palm, V. A.; Haldna, U. L.; Talvik, A. J. In "The Chemistry of the Carbonyl Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1966; p 421.

(49) Eigen, M.; Kruse, W.; Maass, G.; DeMaeyer, L. *Prog. React. Kinet.* **1964**, *2*, 287.

(50) Hupe, D. J.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 451.

(51) Gilbert, H. F.; Jencks, W. P. *J. Am. Chem. Soc.* **1979**, *101*, 5774.

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

(53) Bordwell, F. G.; Boyle, W. J. *J. Am. Chem. Soc.* **1975**, *97*, 3447.

(54) Bordwell, F. G.; Bartmess, J. E.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3107.

(55) Kresge, A. J. *Can. J. Chem.* **1974**, *52*, 1897.

(56) Ritchie, C. D.; Gandler, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 7318.

(57) (a) Bell, R. P.; Sørensen, P. E. *J. Chem. Soc., Perkin Trans. 2* 1976, 1594. (b) Arora, H.; Cox, B. G.; Sørensen, P. E. *Ibid.* **1979**, 103.

(58) Saunders, W. H., Jr.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley-Interscience: New York, 1973.

(59) See also discussion by Maggiora, G. M.; Schowen, R. L. In "Bioorganic Chemistry"; van Tamelen, E. E., Ed.; Academic Press: New York, 1977; Vol. 1, p 173.

(60) (a) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966. (b) Marcus, R. A. *Ibid.* **1957**, *26*, 872. (c) Marcus, R. A. *J. Phys. Chem.* **1963**, *67*, 853. (d) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679.

(61) (a) Marcus, R. A. *J. Phys. Chem.* **1968**, *72*, 891. (b) Cohen, A. O.; Marcus, R. A. *Ibid.* **1968**, *72*, 4249. (c) Marcus, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 7224. (d) Marcus, R. A. *Faraday Symp. Chem. Soc.* **1975**, *10*, 60.

In its simplest version the Marcus equation is of the form

$$\Delta G^{\ddagger} = \Delta G_0^{\ddagger} + \frac{1}{2}\Delta G^0 + [(\Delta G^0)^2/16\Delta G_0^{\ddagger}] \qquad (18)$$

where $\Delta G^{\ddagger}$ is the free energy of activation, ΔG^0 the standard free energy of the reaction, and $\Delta G_0^{\ddagger}$ is the intrinsic barrier, equivalent to $\Delta G^{\ddagger}$ when $\Delta G^0 = 0$.

Since structure–reactivity parameters such as α and β in proton transfer, or normalized β_{nuc}, β_{lg}, and ρ values in nucleophilic additions, are defined as the derivative $\text{d}\Delta G^{\ddagger}/\text{d}\Delta G^0$, it has been common practice to relate them to α_{M}[66] obtained by differentiating eq 18 with respect to ΔG^0.

$$\frac{\text{d}\Delta G^{\ddagger}}{\text{d}\Delta G^0} = \alpha_{\text{M}} = \frac{1}{2}\left(1 + \frac{\Delta G^0}{4\Delta G_0^{\ddagger}}\right) \qquad (19)$$

However, as already pointed out by Marcus in 1969,[61c] eq 19 is only justified if $\Delta G_0^{\ddagger}$ is not itself subject to substituent effects. Thus, whenever the observed structure–reactivity parameters do not coincide with α_{M} the implication is that $\Delta G_0^{\ddagger}$ is substituent dependent and eq 19 cannot be valid. This will always be the case in a situation where the observed structure–reactivity parameters imply an imbalanced transition state.[67] Since imbalances seem to be the rule, one needs to be very cautious in using eq 19 as well as in interpreting the meaning of $\Delta G_0^{\ddagger}$ which is calculated via eq 18. The problem is illustrated with some numerical examples in Tables IX and X.

For the addition of aryl oxide ions to **1-H**, **1-NO$_2$**, and **1-OMe** application of eq 18 yields $\Delta G_0^{\ddagger}$ values ranging from 12.9 to 13.4 kcal/mol (Table IX). The variation is quite small because, even though $\rho_n(k_1^{\text{OAr}}) = 0.59$ and $\beta_{\text{nuc}}^{n}(k_1^{\text{OAr}}) = 0.39$ are not equal, they are not far apart from each other and the α_{M} values obtained via eq 19 (Table IX) lie about half-way between ρ_n and β_{nuc}^{n}. Thus $\Delta G_0^{\ddagger}$ is only slightly substituent dependent and the average value of 13.15 ± 0.25 kcal/mol would seem to give a reasonable account of the intrinsic barrier of aryl oxide ion addition to substituted benzylidene Meldrum's acids. Incidentally, if one bypasses eq 18 and calculates $\Delta G_0^{\ddagger}$ by linearly extrapolating a plot of $\Delta G^{\ddagger}$ vs. ΔG^0 to $\Delta G^0 = 0$, one obtains $\Delta G_0^{\ddagger} = 13.5$ for the reaction of phenoxide ion with the three olefins, and $\Delta G_0^{\ddagger} = 12.7$ for the reaction of **1-NO$_2$** with the three aryl oxide ions.

The spread from 13.2 to 14.5 kcal/mol in $\Delta G_0^{\ddagger}$ calculated via eq 18 is much larger in the case of the amine reactions (Table IX). This is because α_{M} and β_{nuc}^{n} are very different from each other. If one calculates $\Delta G_0^{\ddagger}$ by extrapolating $\Delta G^{\ddagger}$ vs. ΔG^0 plots, the spread is even larger: for the reaction of **1-H**, **1-OMe**, and **1-NMe$_2$** with morpholine $\Delta G_0^{\ddagger} = 14.1$, with piperidine $\Delta G_0^{\ddagger} = 13.3$; for the reaction of the two amines with **1-NMe$_2$** $\Delta G_0^{\ddagger} = 12.4$, with **1-OMe** $\Delta G_0^{\ddagger} = 11.2$, and with **1-H** $\Delta G_0^{\ddagger} = 10.9$.

The above considerations show that the intrinsic barrier is only going to be a useful concept in discussing the factors which make certain reactions intrinsically fast and others slow as long as the uncertainties in $\Delta G_0^{\ddagger}$ are smaller than the effects to be discussed. A case in point is the comparison of intrinsic reactivities of nitro-, alkoxycarbonyl-, and cyano-activated olefins toward nucleophilic attack by amines. In a recent paper[68] we calculated $\Delta G_0^{\ddagger}$ values by extrapolating two-point plots (piperidine and morpholine) of $\Delta G^{\ddagger}$ vs. ΔG^0 and found $\Delta G_0^{\ddagger} = 10.5$ for $PhCH{=}C(CN)_2$,[69] 12.4 for **1-NMe$_2$**, and 13.9 for $PhCH{=}CHNO_2$.[69] We argued that the trend in $\Delta G_0^{\ddagger}$ reflects the greater structural and solvational reorganization involved in the reaction when the activating substituent becomes more effective in delocalizing the negative charge ($(CN)_2 < (COO)_2C(CH_3)_2 < NO_2$), just as in proton transfers of the corresponding C–H acids.

We have now calculated the Marcus intrinsic barrier (eq 18) for these reactions (Table X). For $PhCH{=}C(CN)_2$ and $PhCH{=}CHNO_2$ the Marcus $\Delta G_0^{\ddagger}$ values and those obtained by linear extrapolation are very similar. They are probably a fairly reliable measure of the intrinsic reactivities of these two olefins toward piperidine and morpholine, and the earlier conclusions[68] remain unchanged. For $ArCH{=}C(COO)_2C(CH_3)_2$ there is a problem. From the Marcus treatment one would conclude that the intrinsic barrier is similar to that for $PhCH{=}CHNO_2$. From our earlier treatment in which we used the dimethylamino derivative one concludes that the barrier is about half-way between that for NO_2 and $(CN)_2$ activation. If $\Delta G_0^{\ddagger}$ for the unsubstituted benzylidene Meldrum's acid is determined from a $\Delta G^{\ddagger}$ vs. ΔG^0 plot the obtained $\Delta G_0^{\ddagger} = 11.0$ is close to that for $(CN)_2$ activation. It is apparent that a definite answer as to the rank of the $(COO)_2C(CH_3)_2$ group cannot be given because the barrier depends too strongly on the phenyl substituent.

A similar problem may exist for the water and hydroxide ion addition. Even though the Marcus treatment suggests that the barrier is higher for $PhCH{=}C(COO)_2C(CH_3)_2$ than for $PhCH{=}C(CN)_2$ (Table X), in view of the strong substituent dependence of $\Delta G_0^{\ddagger}$ in the amine reactions we cannot be sure whether this represents the true rank of $(COO)_2C(CH_3)_2$ vs. $(CN)_2$ activation.

Experimental Section

Materials. **1-NO$_2$**, mp 216 °C (lit.[70] mp 217 °C) was prepared by the condensation of Meldrum's acid with *p*-nitrobenzaldehyde as described by Schuster et al.[70] while **1-OMe** was available from a previous study.[3] The other materials were reagent grade and were used without further purification.

Kinetic Experiments. The procedures were essentially the same as reported before.[2]

Acknowledgment. This research was supported by Grants CHE77-27998 and CHE80-24261 from the National Science Foundation. We also thank Professor William P. Jencks for criticism of the manuscript.

Registry No. **1-OMe**, 15795-54-7; **1-NO$_2$**, 15795-62-7; **1-H**, 1214-54-6; **1-NMe$_2$**, 15795-57-0.

---

(62) (a) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87. (b) Albery, W. J. *Pure Appl. Chem.* **1979**, *51*, 949. (c) Lewis, E. S.; Kukes, S.; Slater, C. D. *J. Am. Chem. Soc.* **1980**, *102*, 1619.

(63) Hine, J. *J. Am. Chem. Soc.* **1971**, *93*, 3701.

(64) Guthrie, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 5892.

(65) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

(66) We prefer the symbol α_{M} in order to distinguish it from experimentally determined Brønsted α values.

(67) It will also be the case for a balanced transition state if α_{M} is not equal to the observed parameter.

(68) Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 2810.

(69) In 50% Me_2SO–50% water at 20 °C. The slightly different reaction conditions are not expected to affect $\Delta G_0^{\ddagger}$ greatly.[68]

(70) Schuster, P.; Polanski, O. E.; Wessely, F. *Monatsh. Chem.* **1964**, *95*, 53.