(21), 146 (2), 116 (16), 115 (15), 89 (54), 88 (100), 87 (19), 86 (11), 76 (22), 75 (29), 74 (21), 73 (18), 72 (18).

Anal. Calcd for $C_8H_9D_5O_2$: D, 35.71. Found: D, 34.65.

Methyl Cyclohexanecarboxylate-d_6 (IV). Deuterium (99.97%) was used as received from Baker Chemical Co., Phillipsburg, N. J. Acetic acid-d_1 was prepared as described[22] and used directly for the deuterations. A Parr apparatus was prepared for deuterium by alternately purging with nitrogen and evacuation. After a final evacuation at 0.1 mm the tank was charged with deuterium to 50 psi.

Methyl benzoate (5 g), 1.0 g of 5% rhodium on alumina catalyst, and 50 ml of acetic acid-d_1 were placed in a bottle under nitrogen. The bottle was then attached to the apparatus and evacuated. Nitrogen was admitted through a three-way stopcock and evacuated three times to purge the system. The theoretical volume of deuterium was consumed within 2 hr and the product was isolated as described for II in quantitative yield by distillation: ir (CCl_4), 2164 (CD), 1735 (C=O), 1251 (OCH_3) and 1072 cm^{-1} (OCH_3); nmr (see Figure 2); mass spectrum (10 eV) *m/e* (rel intensity) 149 (5), 148 (12.4), 147 (6), 118 (6.0), 117 (14.9), 116 (16.2), 115 (11.0), 91 (16.2), 90 (61.5), 89 (100), 88 (24.4), 87 (16.2), 77 (17.6), 76 (38.4), 75 (32.5).

Anal. Calcd for $C_8H_8D_6O_2$: D, 42.86. Found: D, 43.70.

Methyl *cis*-4-*t*-Butylcyclohexanecarboxylate-d_6 (VI). Methyl 4-*t*-butylbenzoate (V) was exhaustively deuterated similarly to IV to give a quantitative yield of products; 78% *cis* (VI) and 22% *trans* (VII). The *cis* isomer (VI) was isolated in 99% purity by careful fractionation on a Nester-Faust Annular Teflon spinning band column in 50% yield based on V, bp 62-63° (0.1 mm).

Anal. Calcd for $C_{12}H_{16}D_6O_2$: D, 27.27. Found: D, 24.80.

Methyl *trans*-4-*t*-Butylcyclohexanecarboxylate-d_5 (IX). VI (40 g) was refluxed for 15 hr with 250 ml of 5% sodium methoxide in methanol under nitrogen. The methanol was then removed *in vacuo* and the same procedure was repeated twice more with fresh methanol. After work-up the mixture consisted of 17% *cis* (VIII) and 83% *trans* (IX) isomers. IX (18 g) was isolated in 99% purity by distillation on a spinning band column. A forerun of 20.5 g of a mixture of isomers could be treated with base and reprocessed ultimately leading to high yields (>90%) of IX.

Anal. Calcd for $C_{12}H_{17}D_5O_2$: D, 22.73. Found: D, 21.60.

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[22] G. Binsch and J. D. Roberts, *J. Amer. Chem. Soc.*, **87**, 5158 (1965).

Equilibrium and Kinetic Acidities of Nitroalkanes and Their Relationship to Transition State Structures[1]

F. G. Bordwell, William J. Boyle, Jr.,[2] and K. C. Yee

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Abstract: The rates of deprotonation by base in 50% (v/v) H_2O–MeOH and the pK_a's in this solvent have been determined for $ArCH_2CHMeNO_2$ (13 substituents) and for $ArCHMeNO_2$ (12 substituents). Log-log plots for one series against the other gave excellent lines showing that the relative influence of the substituents is the same in each series, despite the possibility of direct conjugative effects operating in one series but not the other. Although direct resonance effects for *p*-NO_2, *p*-CF_3, *p*-Cl, *p*-F, *p*-Me, and *p*-MeO groups are absent, indirect resonance effects, relayed by induction, are shown to be operative in each series. Substituents affect the rates of the forward (deprotonation) and reverse (protonation) reactions in the *same* manner. As a consequence the ρ's are smaller for the equilibria (0.395 and 1.07) than for the forward rates (0.665 and 1.44). This leads to the unprecedented observation of Brønsted coefficients larger than one (1.61 and 1.37). The Brønsted coefficients for the reverse (protonation) reactions are negative (−0.61 and −0.37) because here the substituent effects are opposite in direction to those prevailing in the equilibria. Evidence concerning the structure of the transition state in the deprotonation of nitroalkanes by hydroxide ion is reviewed and the conclusion is drawn that the transition state is *not* product-like. The evidence points to a transition state in which there is about equal O-H bond making and H-C bond breaking, but with very little delocalization of the developing negative charge to the oxygen atoms of the nitro group.

In order to elucidate the effect of substituents on the rates of proton abstraction by bases from nitroalkanes and on the stereochemistry of the protonation of the corresponding nitronate ions with acids[3] it became necessary to learn more about the nature of the transition state for these reactions. Considerable attention has been given to this question, but various approaches have led to quite different conclusions. Hammond pointed out that the rough parallelism between acidity and the rates of proton removal by bases from weak pseudoacids (nitroalkanes and ketones are implied by the referencing) to form carbanions is explicable on the basis of a carbanion-like transition state "since these reactions are rather highly endothermic."[4] Similarly, for the reverse reaction, protonation of the nitronate ion, the transition state has been assumed to resemble the nitronate ion (carbanion) in structure.[5] It was also concluded that the transition state must be product-like for the reaction of hydroxide ion with nitroethane on the basis of a large negative entropy of activation (−15.5 eu) which corresponded closely to the equilibrium entropy (−18.3 eu) for this reaction.[6] On the other hand, consideration of solvent deuterium isotope effects (k_{H_2O}/k_{D_2O}) on the rate of proton abstraction by hydroxide ion from nitromethane led Swain and Rosenberg to conclude that the transition state is

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[1] For a preliminary account of this work see F. G. Bordwell, W. J. Boyle, Jr., J. A. Hautala, and K. C. Yee, *J. Amer. Chem. Soc.*, **91**, 4002 (1969).

[2] National Institutes of Health Predoctoral Fellow, 1967–1970.

[3] F. G. Bordwell and M. M. Vestling, *J. Amer. Chem. Soc.*, **89**, 3906 (1967).

[4] G. S. Hammond, *ibid.*, 77, 334 (1955).

[5] H. E. Zimmerman, "Molecular Rearrangements," Vol. I., P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 346.

[6] L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 16 (1963).

Table I. Equilibrium and Kinetic Acidities of $ArCH_2CHMeNO_2$ in 50% (v/v) H_2O–MeOH and in MeOH

Substituent	pK_a[a]	k,[b] M^{-1} sec^{-1}	k,[c] M^{-1} sec^{-1}
p-MeO	9.20 ± 0.01	(7.80 ± 0.13) × 10^{-1}	(3.87 ± 0.01) × 10^{-1}
p-Me	9.20 ± 0.03	(8.01 ± 0.30) × 10^{-1}	(4.09 ± 0.03) × 10^{-1}
m-Me	9.18 ± 0.03	(8.37 ± 0.40) × 10^{-1}	(4.30 ± 0.03) × 10^{-1}
H	9.13 ± 0.03	(9.42 ± 0.56) × 10^{-1}	(5.14 ± 0.05) × 10^{-1}
p-F	9.06 ± 0.01	1.20 ± 0.04	(7.47 ± 0.06) × 10^{-1}
m-MeO	9.09 ± 0.02	1.04 ± 0.03	(5.09 ± 0.08) × 10^{-1}
p-Cl	9.05 ± 0.03	1.45 ± 0.04	(9.77 ± 0.09) × 10^{-1}
m-F	9.03 ± 0.01	1.69 ± 0.07	1.03 ± 0.00
m-Cl	9.00 ± 0.02	1.71 ± 0.11	1.15 ± 0.01
m-CF_3	9.02 ± 0.03	1.96 ± 0.10	1.49 ± 0.01
p-CF_3	8.94 ± 0.03	2.10 ± 0.07	1.52 ± 0.01
m-NO_2	8.85 ± 0.02	3.17 ± 0.13	2.39 ± 0.01
p-NO_2	8.76 ± 0.01	3.65 ± 0.07	2.75 ± 0.01

[a] In 50% (v/v) H_2O–MeOH at room temperature (23 ± 1°); average of two runs. [b] In 50% (v/v) H_2O–MeOH at 25°; average of three to four runs. [c] In MeOH at 25°; average of three runs.

only "slightly closer to products than the symmetrical one."[7] (For the reaction of water with nitromethane, however, "the transition state is close to hydronium ion and anion."[7]) Bell and Goodall have shown that the k_H/k_D ratio for the reaction of a series of bases with nitromethane depends on the base strength: H_2O (3.8), $ClCH_2CO_2^-$ (4.3), $CH_3CO_2^-$ (6.5), and HO^- (9.6).[8] Evidence was presented in their paper to show that k_H/k_D for a variety of bases reacting with nitroalkanes and ketones probably goes through a maximum when ΔpK_a for the carbon acid and the conjugate acid of the attacking base is near zero. If we adopt the generally held view that the maximum k_H/k_D ratio will occur at the most symmetrical transition state,[9] this would place the transition state for the reaction of hydroxide ion with nitromethane (pK_a = 10.2) slightly on the reactant side of the maximum,[10] and the transition states for the reactions of the weaker bases $CH_3CO_2^-$, $ClCH_2CO_2^-$, and water progressively on the product side. The transition states for proton abstraction from the more acidic nitroalkanes, nitroethane (pK_a = 8.6), and 2-nitropropane (pK_a = 7.7) by hydroxide ion would be progressively more on the reactant side. This conclusion corresponds reasonably well with that arrived at on the basis of a Brønsted coefficient of *ca.* 0.5 for the reaction of a variety of amine bases with nitroethane.[11] The nearness of the Brønsted coefficient, β, to zero or one is commonly used as a guide to the position of the transition state along the reaction coordinate.[12] Thus the conclusion is reached that the transition states for the reactions of amines with nitroethane are at about the midpoint between reactants and products and that "any effect operating on the ground state of either products or reactants should be observable."[11] Since, as a general rule, the transition state bears the "greater resemblance to the less stable of the species (reactants or products) of a chemical equilibrium,"[12,13] one would then expect the transition state for the reaction of nitroethane with hydroxide ion to be more reactant-like. It is somewhat disturbing in this respect to find that the hydroxide point fits on the line defined for primary amines.[11,14]

To summarize, it would appear (a) from the Hammond postulate and entropy considerations that the transition state for the reaction of hydroxide ion with nitromethane is product-like in structure, (b) from k_{H_2O}/k_{D_2O} values that it is near the midpoint, but slightly closer to products, (c) from the usual interpretation of k_H/k_D values that it is near the midpoint, but slightly closer to reactants,[10] and (d) from the Brønsted β value (for amines) that it is somewhere near reactants. It was the purpose of the present study to examine further the use of the Brønsted relationship with respect to determining the structure of the transition state.

Results

1-Aryl-2-nitropropanes. The pK_a values for $ArCH_2CHMeNO_2$ (13 substituents) were measured in 50% (v/v) H_2O–MeOH at room temperature. A Hammett plot of log K_a *vs.* σ gave ρ_K = 0.395 ± 0.031 (correlation coefficient, r = 0.967).

The rates of proton abstraction by methoxide (or hydroxide) ion were measured in methanol and in 50% (v/v) H_2O–MeOH. The latter rates were 1.3–2.0-fold faster.[15] Hammett plots of log k *vs.* σ gave ρ_k values of 0.868 (r = 0.979) and 0.665 (r = 0.986) in MeOH and in 50% (v/v) H_2O–MeOH, respectively. The lower ρ value in water is not unexpected, since the lower dielectric constant of methanol allows the polar effect of the substituent to be transmitted more effectively.[16]

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(7) C. G. Swain and A. S. Rosenberg, *J. Amer. Chem. Soc.*, **83**, 2154 (1961).

(8) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc., Ser. A*, **294**, 273 (1966).

(9) (a) F. H. Westheimer, *Chem. Rev.*, **61**, 265 (1961); (b) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1964, pp 351–363; (c) R. A. More O'Ferrall and J. Kouba, *J. Chem. Soc. B*, 985 (1967); (d) R. P. Bell, *Discuss. Faraday Soc.*, **39**, 16 (1965), discusses the limitations of this method as a criterion for transition state structure.

(10) A contrary view is held, however, by H. Shechter and coworkers, *J. Amer. Chem. Soc.*, **91**, 2797 (1969), who have interpreted a near maximum isotope effect in the reaction of hydroxide ion with nitrocycloalkanes to mean that "the reacting carbon–hydrogen bond is highly broken and that between hydroxide and the removable proton is weakly developed." If this interpretation is adopted, the transition state would be product-like, at least insofar as the nitroalkane is concerned.

(11) M. J. Gregory and T. C. Bruice, *ibid.*, **89**, 2327 (1967).

(12) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 156–161, 235–242.

(13) J. E. Leffler, *Science*, **117**, 340 (1953).

(14) The hydroxide point would be expected to lie on a line for stronger bases which would have a smaller slope. It is, of course, possible that the positioning on the primary amine line is fortuitous, the lines happening to cross at this point.

(15) P. Jones, J. L. Longride, and W. F. K. Wynne-Jones, *J. Chem. Soc.*, 3606 (1965), have observed a similar solvent effect in deprotonation of nitroethane in H_2O–MeOH and H_2O–EtOH.

(16) L. P. Hammett, *J. Amer. Chem. Soc.*, **59**, 96 (1937); J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, Chapter 4.

The equilibrium and kinetic data are summarized in Table I.

The Brønsted α value determined from the slope of a plot of log K_a *vs.* log k in 50% (v/v) H_2O–MeOH was +1.61 ($r = 0.977$; standard deviation = 0.11), that calculated from $\alpha = \rho_k/\rho_K$ was +1.68. Using only *meta* points, $\alpha = 1.88$ ($r = 0.972$).

1-Arylnitroethanes. The pK_a values for $ArCHMeNO_2$ (twelve substituents) were measured in 50% (v/v) H_2O–MeOH at room temperature (23 ± 1°). A Hammett plot gave $\rho_K = 1.07$ ($r = 0.957$). The rates were determined in 50% (v/v) H_2O–MeOH at 15°. A Hammett plot of log k *vs.* σ gave $\rho_k = 1.44$ ($r = 0.983$). The data are summarized in Table II.

Table II. Equilibrium and Kinetic Acidities of $ArCHMeNO_2$ in 50% (v/v) H_2O–MeOH

Substituent	pK_a[a]	k,[b] M^{-1} sec^{-1}
p-MeO	*c*	2.28 ± 0.06
p-Me	(8.55)[c]	2.36 ± 0.05
m-Me	8.62 ± 0.03	2.54 ± 0.06
H	(8.52)[c]	3.53 ± 0.05
m-MeO	8.48 ± 0.02	4.36 ± 0.17
p-F	8.36 ± 0.02	5.76 ± 0.17
p-Cl	8.23 ± 0.01	8.64 ± 0.47
m-F	8.22 ± 0.01	10.4 ± 0.3
m-Cl	8.20 ± 0.01	12.2 ± 0.4
m-CF_3	8.12 ± 0.01	17.0 ± 0.4
p-CF_3	8.05 ± 0.01	18.5 ± 0.8
m-NO_2	7.73 ± 0.01	43.3 ± 0.7
p-NO_2	7.49 ± 0.01	72.5 ± 1.4

[a] Average of two or more determinations at 23 ± 1°. [b] Average of three to nine runs at 15°. [c] Uncertain due to sample decomposition.

The Bronsted α value determined from the slope of a plot of log K_a *vs.* log k was +1.37 ($r = 0.987$, standard deviation = 0.07), that calculated from $\alpha = \rho_k/\rho_K$ was +1.35. Using only *meta* points, $\alpha = 1.42$ ($r = 0.993$).

Discussion

Resonance Effects in *para* Substituents. The 1-aryl-2-nitropropanes are the carbon acid analogs of benzoic acids with respect to the distance between the ring substituents and the acidic hydrogen atoms, while the 1-aryl-1-nitroethanes are the carbon acid analogs of phenols. It was anticipated that the 1-aryl-2-nitropropane series might serve as a better model for evaluating substituent effects than the benzoic acids because direct resonance effects, which lead to the variations observed in *para* Hammett σ constants, are absent. The expectation was not realized for two reasons. First, substituents were found to produce much smaller effects on the equilibrium acidities of 1-aryl-2-nitropropanes than of benzoic acids ($\rho = 0.395$ in 50% (v/v) H_2O–MeOH for $ArCH_2CHMeNO_2$ *vs.* $\rho = 1.1$ for $ArCO_2H$ in this solvent), and the measurements are less accurate for the carbon acids. Second, much to our surprise, the substituent effect for the $ArCH_2CHMeNO_2$ series paralleled that in the $ArCHMeNO_2$ series, despite the fact that direct conjugative effects are possible in one series, but not in the other. The parallelism of the substituent effects in the two series is brought out by the fact that a plot of log (K/K_0) for 1-aryl-2-nitropropanes *vs.* log (K/K_0) for 1-aryl-1-nitroethanes gave a reasonably good line ($r = 0.977$; slope = 0.38).

The parallelism between effects of *para* substituents in the $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ series was brought out further by preparing a Hammett plot using only *meta* substituents,[17] and using this line to calculate the *para* σ's (Table III). Similar calculations were made for the effect of substituents on the deprotonation rates, and these were also included in Table III.[18]

Table III. σ Constants Calculated from the Equilibrium Constants and from the Rates of Deprotonation of *meta*-Substituted 1-Aryl-2-nitropropanes and 1-Aryl-1-nitroethanes in 50% (v/v) H_2O–MeOH

Sub-	$ArCH_2CHMeNO_2$		$ArCHMeNO_2$			
stituent	σ_K	σ_k	σ_K	σ_k	σ	σ^0
p-MeO	−0.13	−0.094		−0.095	−0.27	−0.12
p-Me	−0.18	−0.078	+0.018	−0.085	−0.17	−0.15
p-F	+0.23	+0.15	+0.19	−0.16	+0.06	+0.17
p-Cl	+0.26	+0.26	+0.31	+0.27	+0.23	+0.27
p-CF_3	+0.55	+0.48	+0.47	+0.48	+0.54	
p-NO_2	+1.02	+0.79	+0.98	+0.86	+0.78	+0.82

The calculated σ values for the two series (Table III) do not differ greatly in most instances from one another and are in good agreement with Taft σ^0 values.[18] For substituents capable of conjugative electron release (*p*-MeO, *p*-Me, *p*-F, and *p*-Cl) the calculated σ values show much better agreement with Taft σ^0 than with Hammett σ constants, which is understandable since the latter were derived for benzoic acids where, unlike either of the present series, direct resonance effects are possible. Indirect resonance effects, presumably relayed by induction,[19] are apparently still operative, however, judging from the relative magnitude of the *para* and *meta* σ constants.

Direct conjugation between the functions is possible in the *p*-$F_3CC_6H_4CMe{=}NO_2^-$ ion, but $\sigma_{p\text{-}CF_3}$ is not exalted as it is for phenols ($\sigma^- = +0.74$[20]). The calculated σ value of +0.98 for *p*-NO_2 in the $ArCHMeNO_2$ series suggests some direct conjugation but this conclusion is negated by the equally large value (+1.02) in the $ArCH_2CHMeNO_2$ series where direct resonance is impossible. The existence of a resonance parameter in these interactions is indicated by the larger value observed for *para* relative to *meta* substituents.[21]

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(17) The correlation coefficients for these plots were improved considerably ($r = 0.980$ for $ArCH_2CHMeNO_2$ *vs.* 0.967, and 0.990 for $ArCHMeNO_2$ *vs.* 0.947) as would be expected, since the Hammett *para* σ's contain resonance parameters which will differ in magnitude from those in the $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ series.

(18) This is comparable to the method used by R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960), to derive σ^0 values for *para* substituents.

(19) Indirect inductive relay of resonance effects for *meta* substituents on the benzene ring is well known: see, *e.g.*, R. W. Taft, Jr., and I. C. Lewis, *J. Amer. Chem. Soc.*, **80**, 2436 (1958), and C. G. Swain and L. C. Lupton, Jr., *ibid.*, **90**, 4328 (1968). Transmission of conjugative effects through methylene groups is also indicated by the linearity of the plot for log (K/K_0) for $ArCH_2CO_2H$ *vs.* log (K/K_0) for $ArCO_2H$ (K. B. Wiberg, ref 9b, p 278). Here the *p*-MeO and *p*-Me points fall off the line because with $ArCO_2H$ the resonance effects are direct, whereas with $ArCH_2CO_2H$ they only indirect.

(20) J. D. Roberts, R. A. Clement, and J. J. Drysdale, *J. Amer. Chem. Soc.*, **73**, 2181 (1951).

(21) The alternative view, that the inductive effect is greater from *para* than from *meta* positions [O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966)] appears untenable because the Me_3N^+ group, which has no resonance contributor, has been shown in at least five

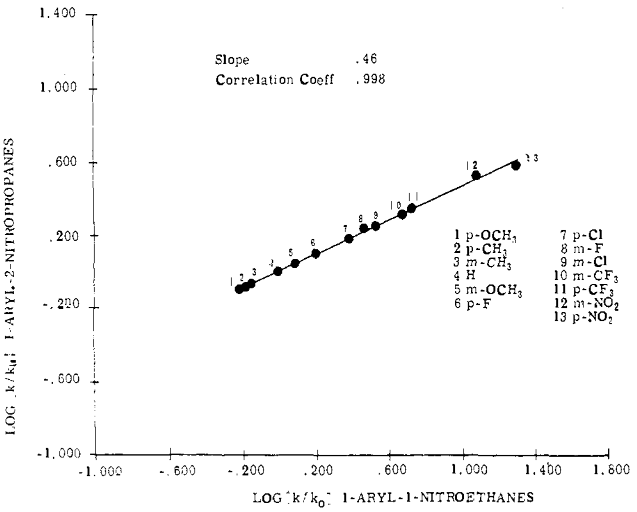

Figure 1. Parallelism in substituent effects for deprotonation in 50% (v/v) H_2O–MeOH at 25°.

The close parallelism between substituent effects in the $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ series is brought out further by comparison of the *para* σ values calculated from the deprotonation rates (Table III). Here, where the measurements can be made with greater precision, a plot of log (k/k_0) for $ArCH_2CHMeNO_2$ *vs.* log (k/k_0) for $ArCHMeNO_2$ gave a remarkably good line (r = 0.998; slope = 0.46). Essentially all of the points for the *para*-, as well as *meta*-substituted compounds fall on the line (Figure 1). The reciprocal of the slope of this line (2.2) represents the transmission coefficient for a methylene group; for equilibrium acidities (see above) the value is 2.6.[23]

Brønsted Relationships and Transition State Structures. The equilibrium acidities of the carbon acids $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ are much less sensitive to substituent effects than are their oxygen or nitrogen analogs: for $ArCO_2H$, ρ = 1.1 in 50% (v/v) H_2O–MeOH as compared to ρ = 0.40 for $ArCH_2CHMeNO_2$ in this solvent; for ArOH, ρ = 3.2 in 30% EtOH–H_2O and for $ArNH_3^+$, ρ = 3.4 in 30% EtOH–H_2O, as compared to 1.1 for $ArCHMeNO_2$ in 50% MeOH–H_2O. The principal reason for this is that for the carbon acids substituents affect the acidity of the acid and the basicity of its conjugate base in the *same* manner. For example, a substituent such as *m*-NO_2 increases the rate of deprotonation of $ArCHMeNO_2$, *but it also increases the rate of protonation of* $ArCMe{=}NO_2^-$.[24] On the other hand, for oxygen and nitrogen acids substituents probably affect the acidity of the acid and the basicity of its conjugate base in an *opposite* manner. Thus it has been shown that a *m*-NO_2 substituent increases the effectiveness of benzoic acid as a catalyst for the dehydration of acetaldehyde hydrate by 2.6-fold,[25] and decreases the catalytic effect of benzoate ion on the base-catalyzed bromination of ethyl acetoacetate by 2.3-fold.[26] The position of the equilibria for reactions of $ArCO_2H$ and ArOH with water are determined primarily by the deprotonation rates, however, since the reverse protonations of $ArCO_2^-$ and ArO^- by H_3O^+ are essentially diffusion controlled.[27]

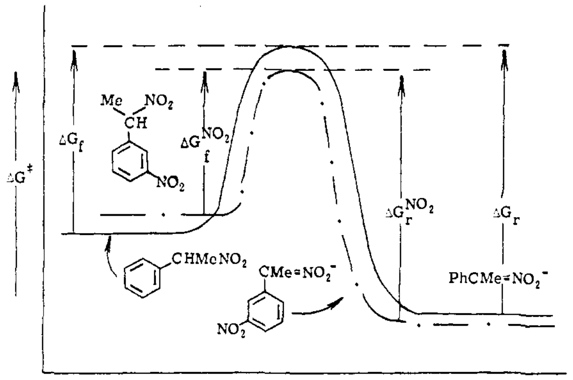

Figure 2. Schematic energy profile for the deprotonation of $PhCHMeNO_2$ (solid line) and *m*-$NO_2C_6H_4CHMeNO_2$ (—●—●) by base, and for the (reverse) protonations of the corresponding anions by solvent.

For the carbon acids $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ the observation that the Brønsted coefficients for the forward (deprotonation) reactions with HO^- (or MeO^-) are greater than one (1.6 and 1.4, respectively) requires that the Brønsted coefficients for the reverse (protonation) reactions of $ArCH_2CMe{=}NO_2^-$ and $ArCMe{=}NO_2^-$ by H_2O (or MeOH) be negative (−0.6 and −0.4), since, by definition the coefficients for the forward and reverse reactions must sum to one.

Using the relationship

$$\rho_{k_{-1}} = \rho_{k_1} - \rho_K$$

gives values of $\rho_{k_{-1}}$ of +0.27 and +0.37, respectively. This requires that an electron-withdrawing group, such as *m*-NO_2, *increase* the rate of the reverse reaction. In other words, the *m*-NO_2 group *increases* the basicity (at carbon) of the $ArCH_2CMeNO_2^-$ and $ArCMeNO_2^-$ ions.[24]

The operation of these substituent effects can be visualized with the aid of the schematic energy profiles shown in Figure 2.

It is assumed in Figure 2 that *m*-$NO_2C_6H_4CHMeNO_2$ has a slightly higher ground-state energy than the parent $C_6H_5CHMeNO_2$. The transition state energy for the *m*-NO_2 derivative is lowered because of the weakening of the H–C bond, due to the inductive effect of the nitro group. The reverse reactions must follow the same profile. The *m*-NO_2 group no doubt

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instances to exert a stronger effect from the *meta* than from the *para* position.[22]

[22] See, *e.g.*, F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, **78**, 87 (1956).

[23] The average transmission coefficient is 2.8. See G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice Hall, Englewood Cliffs, N. J., 1941, p 204; R. W. Taft, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 592.

[24] This remarkable result is not entirely without precedent since R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, **75**, 2439 (1953), have pointed out that, despite the fact that introduction of a second nitro group into nitromethane causes a 6.5-unit decrease in pK_a, the rate of protonation of the $O_2NCH{=}NO_2^-$ by hydronium ion is slightly greater than for $HCH{=}NO_2^-$. Along these same lines, it follows from the relative rates of deprotonation of CH_3NO_2, $MeCH_2NO_2$, and Me_2CHNO_2 by hydroxide ion (113:18:1.0) and the relative pK_a's (10.2:8.6:7.7) that successive substitution of methyl groups causes a *decrease* in protonation rates of the corresponding nitronate ions by the water solvent.[11]

[25] R. P. Bell and W. C. H. Higginson, *Proc. Roy. Soc., Ser. A*, **197**, 141 (1949).

[26] R. P. Bell, E. Gelles, and E. Möller, *ibid.*, **198**, 310 (1949).

[27] M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964).

causes the ground-state energy of the $m\text{-}NO_2C_6H_4CMeNO_2^-$ ion to be lower than that for the parent ion, but this effect is apparently not large enough to compensate for the difference in "hump heights." (The relative ineffectiveness of the $m\text{-}NO_2$ group in stabilizing the nitronate ion is probably a consequence of the extensive delocalization of the negative charge away from the ring to the oxygen atoms of the side-chain nitro group.) As a consequence, protonation of $m\text{-}NO_2C_6H_4CMe{=}NO_2^-$ is faster than protonation of the parent $PhCMe{=}NO_2^-$. The result is that the effect of the $m\text{-}NO_2$ group on the position of the equilibrium is leveled, and the Brønsted coefficient, which compares the relative effectiveness of substituents on the rate of deprotonation and the position of equilibrium, is greater than one.

The correlation of the Brønsted β (or α) to the position of the transition state along the reaction coordinate is based on the assumption that the effect of substituents on the rate will be *intermediate* to the effect of substituents on the equilibrium for the overall reaction.[12] This leads to

$$\delta\Delta G^{\ddagger} = \alpha\delta\Delta G^{\circ}$$

where α is constrained to values between zero and one.[12]

The results with $ArCH_2CHMeNO_2$ and $ArCHMeNO_2$ show that α can be greater than one or less than zero when the substituent changes are in the (acid) substrate rather than in the (base) "catalyst." When $\alpha > 1$, the substituents are affecting the kinetic acidity more than the thermodynamic acidity ($\delta\Delta G^{\ddagger} > \delta\Delta G^{\circ}$). When $\alpha < 0$, the substituents are exerting *opposite* effects in the kinetic reaction (protonation) and in the equilibrium reaction. For example, the *overall* effect of a $m\text{-}NO_2$ substituent on the equilibrium

$$\mathrm{ArCHMeNO_2 + H_2O \rightleftarrows ArCMe{=}NO_2^- + H_3O^+}$$

is acid strengthening, but its accelerating effect on protonation is acid weakening. The result is a Brønsted coefficient larger than one for deprotonation and a negative coefficient for protonation. Similarly, successive methyl substitution into nitromethane (giving $MeCH_2NO_2$ and Me_2CHNO_2) is acid weakening with respect to the rate of deprotonation, but the overall effect is acid strengthening because of the strong stabilizing effect of methyl substitution on the nitronate ion, which strongly retards protonation. The result is a negative Brønsted coefficient for deprotonation, and a coefficient larger than one for protonation. Obviously no conclusions can be drawn from these data concerning the position of the transition state along the reaction coordinate.

When substituents are changed in the basic "catalyst" rather than in the (acid) substrate, as, for example, the deprotonation of nitroethane by various amine bases, substituent effects on the equilibrium reaction ($R_2NH + H_3O^+ = R_2NH_2^+ + H_2O$) are greater than on the rate of deprotonation; this leads to a Brønsted β of 0.5.[11] Whether or not this means that the transition state is midway between reactants and products[11] appears to us now to be open to serious question, despite the wide acceptance of this view.[28]

Transition States for Nitroalkane Deprotonations. In the introduction to this paper we reviewed the conclusions, derived from a variety of studies, with respect to the transition state structure for the reaction of hydroxide (or alkoxide) ion with nitroalkanes, but found little agreement. Additional evidence on this score is provided by the observation that in the series CH_3NO_2, $MeCH_2NO_2$, Me_2CHNO_2 methyl substitution is accompanied by a substantial *increase* in acidity and a substantial *decrease* in rate of deprotonation by hydroxide ion.[1] This shows that the *transition state cannot be product-like* since it fails to reflect the stabilizing effect of methyl substitution on nitronate ion stability. If we accept the Bell and Goodall interpretation of k_H/k_D this gives us a second piece of evidence favoring a nonproduct-like transition state. Even the Hammond postulate argument can be swung over to this side, since examination shows that the reaction is actually exothermic,[29] instead of endothermic as originally assumed.[4] The correspondence of the (negative) activation and equilibrium entropies for deprotonation of nitroethane by hydroxide ion is suggestive of a product-like transition state,[6] but comparison of the entropies of activation with those for other deprotonation reactions does not support this point of view. For example, in the deprotonation of fluorene and fluorene derivatives by methoxide ion the activation entropies are −5 to −8 eu.[30] Here the principal solvation effect on the entropy must be desolvation of the methoxide ion because the negative charge is widely dispersed on the fluorene molecules and there is little opportunity for hydrogen bonding to these molecules. Since the activation entropies for methoxide ion deprotonation of a wide variety of nitroalkanes fall in this same range, a similar interpretation is indicated, and it must be concluded that the strong hydrogen bonding of the solvent to the oxygen atoms present in the nitronate ion has not become important in the transition state. All of the evidence indicates, therefore, that the transition state for the reaction of nitroalkanes with hydroxide or alkoxide ions is *not product-like.*[31]

From the isotope effect studies it is evident that breaking of the H–C bond has progressed to a con-

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[28] (a) T. C. Bruice and S. J. Benkovic, "Bioorganic Mechanisms," Vol. I, W. A. Benjamin, New York, N. Y., 1966, pp 30–37; (b) J. O. Edwards, "Inorganic Reaction Mechanisms," W. A. Benjamin, New York, N. Y., 1964, Chapter 3; (c) E. M. Kosower, "Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 18; (d) R. A. Marcus, *J. Phys. Chem.*, **72**, 891 (1968); (e) R. A. Marcus, *J. Amer. Chem. Soc.*, **91**, 7224 (1969).

[29] For nitromethane $pK_a = 10.2$, and K_{eq} for the reaction $HO^- + CH_3NO_2 = CH_2NO_2^- + H_2O$ is $10^{5.5}$; $\Delta G^{\circ} = -7.5$ kcal/mol. This conclusion also agrees with the Leffler–Grunwald principle,[12] "the transition state will bear the closer resemblance to the less stable species (reactants or products)."

[30] A. Streitwieser, Jr., unpublished data, privately communicated.

[31] The situation is not so clear when weaker bases are used. For bases such as acetate ion, amines, pyridines, and water, the transition state has generally been considered to be product-like.[7,8,11] If we examine the relative rates of reaction of these bases with the series of nitroalkanes CH_3NO_2, $MeCH_2NO_2$, Me_2CHNO_2, we again find that in every instance the order of reactivity is the *inverse* of the order of acidity. For example, with pyridine in water the relative rates in this series are 6.4×10^{-4},[32] 1.5×10^{-4},[33] and 1.8×10^{-5} M^{-1} sec^{-1},[8,34] respectively, whereas the relative pK_a's are 10.2, 8.6, and 7.7, respectively.[35] Even with water acting as a base the rate for nitromethane is slightly faster than for the stronger acid, nitroethane.[36] Judging from this criterion the transition states for these reactions are *not* product-like.

[32] J. A. Feather and V. Gold, *J. Chem. Soc.*, 1752 (1965).

[33] R. G. Pearson and F. V. Williams, *J. Amer. Chem. Soc.*, **75**, 3073 (1953).

[34] E. S. Lewis and J. D. Allen, *ibid.*, **86**, 2022 (1664).

[35] D. Turnbull and S. H. Maron, *ibid.*, **65**, 212 (1943); G. Wheland and J. Farr, *ibid.*, **65**, 1433 (1943).

[36] R. G. Pearson and R. L. Dillon, *ibid.*, **75**, 2439 (1953).

siderable degree in the transition state for deprotonation of nitroalkanes by hydroxide or alkoxide ions. An appreciable negative charge must, therefore, have been developed on carbon, but this charge has not been delocalized to any marked degree to the nitro group (judging from relative reactivity and entropy data). Bonding between the hydroxide (or alkoxide) ion and hydrogen has also progressed to a considerable degree (judging from isotope effects) and this has been accompanied by an appreciable desolvation of the hydroxide (or alkoxide) ion (judging from entropy effects). In succeeding papers in this series we will show that this picture of the transition state can be used to rationalize a variety of reactivity–structure relationships.

Experimental Section

Melting points are uncorrected. The infrared spectra were recorded on a Beckman IR-5 spectrophotometer and the spectra calibrated with polystyrene at 6.238 μ. Proton nuclear magnetic resonance spectra were determined on either Varian Associates Model A-60 or Model T-60 nmr spectrometers. Chemical-shift values are in units of δ (parts per million) relative to internal tetramethylsilane. Ultraviolet spectra were recorded on a Cary recording spectrophotometer, Model 15. The bases used in the kinetic determinations were standardized against hydrochloric acid (Fisher) or potassium hydrogen phthalate. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.

Preparation of 1-Aryl-2-propanones. Arylacetyl chlorides were prepared by the procedure described for the preparation of the acid chloride of 1-keto-2-methyl-1,2,3,4-tetrahydrophenanthrene-2-acetic acid.[37] The aryl-2-propanones were prepared from the corresponding arylacetyl chlorides by reaction with ethyl ethoxymagnesiummalonate and subsequent hydrolysis of the alkoylmalonates.[38] The preparation of 1-*m*-chlorophenyl-2-propanone illustrates a typical procedure for the preparation of the necessary ketones in this series.

Acid Chloride. To a solution of 10 g (0.059 mol) of *m*-chlorophenylacetic acid in 150 ml of benzene containing 10 drops of pyridine, was added 26 ml (43 g, 0.36 mol) of pure thionyl chloride. After 40 min at room temperature, the solution was heated to gentle reflux for 10 min. The excess thionyl chloride and solvent were removed under reduced pressure at room temperature. To the residue 50 ml of benzene was added and the solvent was removed under reduced pressure. This process was repeated until no more thionyl chloride remained in the residue.

Ketone. Into a 250-ml, three-necked round-bottomed flask equipped with stirrer, addition funnel, and reflux condeser (with $CaCl_2$ tube) was placed 1.60 g (0.066 mol) of magnesium, 2 ml of absolute ethanol, and then 0.2 ml of carbon tetrachloride. The reaction which occurred almost immediately was allowed to proceed for several minutes. Then 25 ml of anhydrous ether was added carefully. To this mixture, a solution of 10.6 g (0.066 mol) of diethyl malonate in 8 ml of absolute ethanol and 6 ml of anhydrous ether was added at such a rate that reflux was maintained. After the addition was over, the mixture was refluxed until all magnesium had dissolved (*ca.* 4 hr). The reaction solution was cooled to room temperature. A solution of *m*-chlorophenylacetyl chloride (freshly prepared) in 100 ml of ether was added over a period of 35 min to the well-stirred Grignard reagent at room temperature. After the addition was over, the solution was refluxed for 2 hr, cooled, and acidified with 5% (v/v) of sulfuric acid (*ca.* 60 ml). The organic layer was separated and the aqueous layer was extracted with 30 ml of ether. The organic layers were combined and washed with 50 ml of water, dried ($MgSO_4$), and concentrated. To the crude residue there was added a solution of 15 ml of acetic acid, 2.0 ml of concentrated sulfuric acid, and 10 ml of water. The resulting mixture was refluxed for 5 hr, chilled in an ice bath, made alkaline with 20% potassium hydroxide solution (*ca.* 100 ml), and extracted with two 100-ml portions of ether. The organic extracts were combined and washed with two 100-ml portions of water, dried ($MgSO_4$), and concentrated to give the crude product of ketone which was purified by distillation.

Preparation of 1-Aryl-2-nitropropanes and 1-Aryl-1-nitroethanes. The oximes of the 1-aryl-2-propanones and commercially available substituted acetophenones were prepared by the method of Pearson and Bruton.[39] Oxidation of the oximes with peroxytrifluoroacetic acid according to the procedure of Emmons and Pagano[40] afforded the corresponding nitroalkanes. A typical procedure is illustrated by the preparation of 1-(*m*-chlorophenyl)-2-nitropropane.

Oxime. A cold solution of 4.2 g (0.075 mol) of potassium hydroxide in 9 ml of water was added slowly to a solution of 7.0 g (0.10 mol) of hydroxylamine in 15 ml of water. This solution was added to 7.8 g (0.047 mol) of *m*-chlorophenyl-2-propanone. The mixture was heated while sufficient 95% ethanol (30 ml) was added to produce a homogeneous solution at the boiling point. The reaction solution was refluxed for 1 hr, cooled, and extracted with three 50-ml portions of ether. The organic extracts were combined, dried ($MgSO_4$), and concentrated to give 8.1 g (95%) of *m*-chlorophenyl-2-propanone oxime.

Nitroalkane. A trifluoroperoxyacetic acid solution was prepared from 2.8 ml (0.10 mol) of 90% hydrogen peroxide, 17 ml of trifluoroacetic anhydride, and 25 ml of acetonitrile. This solution was added dropwise over a 60-min period to a well-stirred refluxing mixture of 8.0 g (0.044 mol) of *m*-chlorophenyl-2-propanone oxime, 24 g (0.275 mol) of disodium hydrogen phosphate, and 1 g of urea in 100 ml of acetonitrile. After the addition was over, the reaction mixture was refluxed for an additional 60 min, cooled, and poured into 150 ml of water. The resulting solution was extracted with two 100-ml portions of methylene chloride. The organic extracts were combined and washed with 100 ml of saturated sodium bicarbonate and 100 ml of water. After drying ($MgSO_4$), the solution was concentrated to give 7.0 g of crude product, which was dissolved in a minimum amount of chloroform and added to a column (4 × 60 cm) slurry-packed with silica gel (400 g) and 10% ether–hexane (600 ml). The column was eluted with 5 l. of 10% ether–hexane; 500-ml fractions were collected. Removal of solvent from fractions 4–6 gave 3.85 g of nitro compound, which was purified by evaporative distillation at 105° (0.6 mm): ir $\lambda_{\max}^{\text{film}}$ 3.25, 3.32, 3.40, 6.22, 6.32, 6.43 (NO_2), 6.73, 6.86, 6.95, 7.16, 7.31 (NO_2), 7.56, 7.80, 8.23, 8.51, 8.80, 9.18, 9.61, 9.95, 11.2, 11.48, 11.70, 12.70, 13.68, 14.25, and 14.58 μ; nmr $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.20 (m, Ar-H, 4 H), 4.77 (sextet, $C\mathit{H}NO_2$, $J = 7.0$ Hz, 1 H) 3.12 (complex multiplet, $C\mathit{H}_2Ar$, $J = 7.0$ Hz, 2 H), 1.53 (doublet, methyl H, $J = 7.0$ Hz, 3 H).

The liquid nitroalkanes were purified by evaporative distillation in a Kugelrohr distillation apparatus (Rinco Instrument Co.) and, consequently, boiling points are not available. The analytical data for the arylnitroalkanes are presented in Tables IV and V.

Table IV. Microanalyses of $ArCH_2CHMeNO_2$

	Molecular	Calcd, %		Found, %	
p-MeO	$C_{10}H_{13}NO_3$	61.53	6.71	61.65	6.83
p-Me	$C_{10}H_{13}NO_2$	67.01	7.31	66.89	7.21
m-Me	$C_{10}H_{13}NO_2$	67.01	7.31	67.04	7.26
H[a]	$C_9H_{11}NO_2$				
p-F	$C_9H_{10}FNO_2$	59.01	5.50	58.75	5.60
m-MeO	$C_{10}H_{13}NO_3$	61.53	6.71	61.57	6.78
p-Cl	$C_9H_{10}ClNO_2$	54.15	5.05	54.34	4.90
m-F	$C_9H_{10}FNO_2$	59.01	5.50	58.88	5.70
m-Cl	$C_9H_{10}ClNO_2$	54.15	5.05	54.04	5.19
m-CF$_3$	$C_{10}H_{10}F_3NO_2$	51.50	4.32	51.54	4.34
p-CF$_3$	$C_{10}H_{10}F_3NO_2$	51.50	4.32	51.72	4.52
m-NO$_2$	$C_9H_{10}N_2O_4$	51.43	4.80	51.50	4.79
p-NO$_2$	$C_9H_{10}N_2O_4$	51.43	4.80	51.62	4.74

[a] H. Shechter, D. E. Ley, and E. B. Roberson, *J. Amer. Chem. Soc.*, **78,** 4984 (1956).

In addition to analytical data, the identity of the compounds was established from the infrared and nmr spectra. The infrared spectra of the arylnitropropanes are similar to that reported above for 1-(*m*-chlorophenyl)-2-nitropropane. Likewise, the nmr spectra are similar to that described for the *m*-chloro isomer. The resonance of the methine proton occurs in each case as a sextet at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 4.74–4.95.

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(37) A. L. Wilds and L. W. Beck, *J. Amer. Chem. Soc.*, 66, 1688 (1944).

(38) (a) C. G. Overberger and H. Biletch, *ibid.*, 73, 4881 (1951); (b) H. G. Walker and C. R. Hauser, *ibid.*, **68,** 1386 (1946).

(39) D. E. Pearson and J. D. Bruton, *J. Org. Chem.*, **19,** 957 (1954).

(40) W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, 77, 6341 (1955).

Table V. Microanalyses of 1-Aryl-1-nitroethanes

Substituent	Molecular formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-CH$_3$O	$C_9H_{11}NO_3$	59.66	6.12	59.77	6.10
m-CH$_3$O	$C_9H_{11}NO_3$	59.66	6.12	59.66	6.01
p-CH$_3$[a]	$C_9H_{11}NO_2$	*a*			
m-CH$_3$	$C_9H_{11}NO_2$	65.43	6.71	65.34	6.48
H[b]	$C_8H_9NO_2$	*b*			
m-F	$C_8H_8FNO_2$	56.80	4.77	56.83	4.89
p-F	$C_8H_8FNO_2$	56.80	4.77	56.33	4.77
m-Cl	$C_8H_8ClNO_2$	51.76	4.34	51.94	4.17
p-Cl	$C_8H_8ClNO_2$	51.76	4.34	51.97	4.56
m-CF$_3$	$C_9H_8F_3NO_2$	49.32	3.68	49.29	3.81
p-CF$_3$	$C_9H_8F_3NO_2$	49.32	3.68	49.31	3.37
m-NO$_2$[c]	$C_8H_8N_2O_4$	*c*			
p-NO$_2$[d]	$C_8H_8N_2O_4$	*d*			

[a] n^{20}D 1.5270. P. W. K. Flanagan, Ph.D. Dissertation, Ohio State University, 1957, reports bp 81°, n^{20}D 1.5288. [b] n^{20}D 1.5211, P. W. K. Flanagan[a] reports bp 68°, n^{20}D 1.5218. [c] Mp 79–80°, P. W. K. Flanagan[a] reports mp 80–80.5°. [d] Mp 67–68°, P. W. K. Flanagan[a] reports mp 66–67°.

The 1-aryl-2-nitropropanes also exhibit very similar infrared and nmr spectra. A typical spectrum is that of 1-(m-chlorophenyl)-1-nitroethane: ir $\lambda_{\max}^{\text{film}}$ 6.44 (NO$_2$), 7.21, and 7.35 μ (NO$_2$); nmr $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.3–7.5 (m, Ar-H, 4 H), 5.58 (quartet, C*H*NO$_2$, J = 7 Hz, 1 H), 1.83 (doublet, CH_3, J = 7 Hz, 3 H). The methine proton of the 1-aryl-1-nitroethanes appears always as a doublet at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.55–5.75, J = 7 Hz.

Determination of the pK_a's of 1-Aryl-2-nitropropanes and 1-Aryl-1-nitroethanes. Solutions (1.0×10^{-2} M) of the nitroalkanes were prepared by dissolving a weighed portion in 50% by volume methanol–water in a 100-ml, volumetric flask. Aliquots of solution (25, 25, 25, and 20 ml) were pipetted into four weighing bottles (Kimble Products, Art. No. 15145, size 40 × 80 mm). These solutions were partially neutralized with 3, 4, 5, and 5 ml of freshly prepared carbonate-free sodium hydroxide solution (2.00×10^{-2} M) in 50% (v/v) methanol–water to give solutions 24, 32, 40, and 50% neutralized, respectively. The bottles were flushed with nitrogen, stoppered, and allowed to reach thermal equilibrium at room temperature (23 ± 1°). After periods of 6, 18, 24, and 28 hr for 1-aryl-2-nitropropanes and 4–10 hr with 1-aryl-1-nitroethanes, the pH 's of the solutions were measured by means of a glass electrode on a Sargent recording titrator, Model D. The glass electrode was a Corning triple-purpose electrode (catalog number 476022) and was used with a saturated calomel reference electrode. Solutions were stirred magnetically during the pH measurements and the instrument was standardized (chart width 9.5 in. = 5 pH units) before each determination with standard buffer solutions of pH 7.00 and 9.00 (Fisher Scientific Co.). The pK_a values were determined from the equation

$$pK_a = pH + \log [AH]/[A^-]$$

and the average of the determinations at 24, 32, 40, and 50% was taken from the later readings. Changes in readings taken at earlier times indicate that *ca.* 15–20 hr is necessary for establishment of the desired equilibrium for the 1-aryl-2-nitropropanes while ≥2 hr is sufficient for the 1-aryl-1-nitroethanes. This is due to the very slow rate of reaction of the nitroalkanes with water.[8] The values of the pK_a's are not corrected for hydrolysis nor for the salt effect (although these corrections are probably minor) and should therefore be considered as relative values rather than absolute ones. Furthermore, extensive studies have shown[41] that when the glass electrode is standardized in water buffers and then used in water–methanol solutions a constant correction should be applied to each reading to obtain the true activity of the hydrogen ion in solution. For 50% (v/v) methanol–water this correction is about 0.10 pH unit. This correction factor should be subtracted from the reported pK_a's to obtain a more accurate value of the thermodynamic equilibrium constant; the relative values are, of course, unaffected.

Kinetic Procedure. The rates of reaction of the nitroalkanes with base (hydroxide or methoxide ion) in methanol (1-aryl-2-nitropropanes) and 50% (v/v) methanol–water (arylnitropropanes and arylnitroethanes) were determined spectrophotometrically on a Cary Model 15 recording spectrophotometer. The nitronate ions derived from the nitroalkanes all have characteristic ultraviolet spectra with $\lambda_{\max}$ *ca.* 230 nm (1-aryl-2-propanenitronates) and $\lambda_{\max}$ *ca.* 280–305 nm [1-aryl-1-ethanenitronates, except p-NO$_2$ ($\lambda_{\max}$ *ca.* 383)] and $\epsilon_{\max}$ *ca.* 10^4. The rates were measured by following the increase in absorbance at the $\lambda_{\max}$ of the nitronate ion as a function of time.

The Cary 15 was equipped with a brass cuvette holder through which water was circulated at 25 or 15°. The temperature within the cell block was constant within ±0.1° for long periods of time. Samples of base (3 ml) were pipetted into 1-cm quartz cells and allowed to equilibrate at the temperature of the cell block for 1 hr or more. The nitroalkane was introduced by adding 10–30 μl of a solution (*ca.* 5×10^{-3} M) in methanol *via* a Hamilton microliter syringe to the cell and stirring briefly. The resulting substrate concentrations were *ca.* 5×10^{-5} M. The base concentration was 5×10^{-3} to 2×10^{-2} M except for the highly reactive m-nitro and p-nitro derivatives of the 1-aryl-1-nitroethane series. With these the base concentration was $1\text{–}2 \times 10^{-3}$ M and extra precaution was necessary to avoid exposure to atmospheric carbon dioxide. The reactions were allowed to continue for *ca.* 10 half-lives after which time the absorbance value did not change measurably. The maximum absorbance was taken as A_∞. The pseudo-first-order rate constants were evaluated by computer using a single regression least-squares analysis of a plot of ln ($A_\infty - A$) *vs.* t. Data through 4 half-lives (94% reaction) were used in evaluation of the rate constants and correlation coefficients (r) were typically 0.999 or greater; runs with $r < 0.999$ were rejected

Hammett and Brønsted Plots. The Hammett and Brønsted relationships were evaluated by least-squares computer analysis and were presented on plots drawn on a California Computer Products plotter.

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(41) (a) C. L. de Ligny, P. F. M. Luykx, M. Rehbach, and A. A. Nieneke, *Recl. Trav. Chim. Pays-Bas*, **79**, 699, 713 (1960); (b) R. G. Bates, M. Paabo, and R. A. Robinson, *J. Phys. Chem.*, **67**, 1833 (1963).