

Kinetics of Hydroxide and Nitromethide Ion Addition to Substituted β -Nitrostyrenes in Me₂SO-Water Mixtures. Solvent Dependence of π -Donor Substituent Effects and of Intrinsic Rate Constants

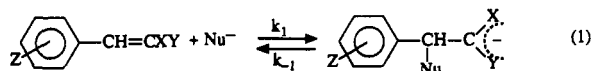
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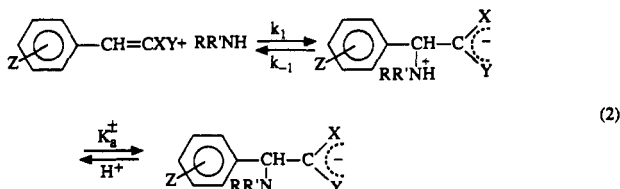
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The kinetics of nucleophilic addition of hydroxide (k_1^{OH}) ion and nitromethide (k_1^{NM}) ion to phenyl-substituted β -nitrostyrenes ($Z = 4\text{-Me}_2\text{N}$, 4-MeO , H , 3-Cl , 4-Br , 4-CN , and 4-NO_2) have been measured in water, 50% Me₂SO-50% water, 70% Me₂SO-30% water (OH⁻ reaction only), and 90% Me₂SO-10% water. Equilibrium constants, K_{eq} , for the addition of piperidine to the same β -nitrostyrenes, to form $\text{ArCH}(\text{NC}_5\text{H}_{10})\text{CH}=\text{NO}_2^- + \text{H}^+$, have also been determined. The latter were measured in lieu of the equilibrium constants of hydroxide ion addition (K_1^{OH}) which are experimentally difficult to come by; they are used to model the substituent dependence of K_1^{OH} . Hammett plots of $\log k_1^{\text{OH}}$ and $\log k_1^{\text{NM}}$ show positive deviations for $Z = 4\text{-Me}_2\text{N}$ in water, but increasingly strong negative deviations as the Me₂SO content of the solvent increases. A similar trend is observed for $Z = 4\text{-MeO}$ although the magnitude of the deviations, positive and negative, is much smaller. The $4\text{-Me}_2\text{N}$ - and 4-MeO -derivatives also show positive deviations from a Brønsted-type plot of $\log k_1^{\text{OH}}$ vs $\log K_{\text{eq}}$ in water, while a similar plot in 90% Me₂SO-10% water may or may not show small negative deviations. The negative deviations from the Hammett plot are caused by the strong resonance stabilization of the π -donor-substituted β -nitrostyrenes which also depresses the equilibrium constants for these substrates. The positive deviations from the Hammett and Brønsted-type plots are attributed to a preorganization of the electronic structure towards that of the product, induced by the through resonance that occurs with π -donor substituents. This preorganization facilitates the delocalization of the negative charge into the nitro group at the transition state and enhances the intrinsic rate constant ($k_0 = k$ when $K = 1$) of the reaction.

Olefins activated by strong electron-withdrawing groups (X, Y) undergo facile nucleophilic addition, as shown in eq 1 for an anionic nucleophile.¹ With amine nucleophiles,



the reaction is typically followed by a rapid acid-base equilibrium¹ (eq 2), although in some cases deprotonation of the zwitterion is slower than the k_{-1} step and can become (partially) rate limiting.²

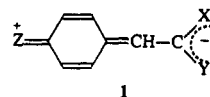


Electron-withdrawing phenyl substituents (Z) typically enhance k_1 and $K_1 (= k_1/k_{-1})$ and decrease k_{-1} , but with amine nucleophiles these substituent effects are usually not very large because of partial compensation by the effect of creating a positive charge on the amine nitrogen. In most cases, π -donor substituents in the para position show deviations from Hammett ($\log k_1$ vs σ or σ^+) or Brønsted ($\log k_1$ vs $\log K_1$) plots that are defined by non- π -donor substituents. Both negative and positive deviations have been reported.

Examples that show negative deviations are the reactions of substituted benzyldene Meldrum's acids with piperidine and morpholine in water and in 50% Me₂SO-50% water³ and of substituted benzyldene malonitriles

with piperidine in 50% Me₂SO-50% water.⁴ Positive deviations have been observed for the reactions of substituted β -nitrostyrenes with piperidine⁵ and thiolate ions such as $\text{HOCH}_2\text{CH}_2\text{S}^-$ and $\text{MeOOCCH}_2\text{S}^-$ ⁶ in water and also for the reaction of 1,1-diaryl-2-nitroethylenes with CN^- in water.⁷

The interpretation of the negative deviations is simple and noncontroversial: the π -donor substituents provide extra resonance stabilization to the olefin 1. This reduces



both K_1 and k_1 and explains why both k_1 and K_1 deviate negatively from the Hammett plots;^{3,4} even though smaller, these negative deviations persist when σ^+ substituent constants are used which implies that the resonance effect is very strong.

The interpretation of the positive deviations has been the subject of some controversy. The explanation we have favored^{1,5,6} is that the resonance form 1 leads to a preorganization of the electronic structure towards that of the product and facilitates the delocalization of the negative charge into XY at the transition state. In the reactions of nitro-activated olefins the resulting transition-state stabilization is apparently stronger than the resonance stabilization of the olefin and hence leads to a net rate enhancement; in the reactions of the benzyldene malonitriles and benzyldene Meldrum's acids the stabilization of the reactant outweighs the beneficial effect on the transition state and leads to a net decrease in k_1 . What appears to determine whether transition-state or reactant-state stabilization is dominant is the strength of X and/or Y as π -acceptor(s). In the absence of the preor-

(1) For a recent review, see: Bernasconi, C. F. *Tetrahedron* 1989, 45, 4017.

(2) Bernasconi, C. F.; Carré, D. J. *J. Am. Chem. Soc.* 1979, 101, 2698. (b) Bernasconi, C. F.; Fox, J. P.; Fornarini, S. *Ibid.* 1980, 102, 2810. (c) Bernasconi, C. F.; Murray, C. J.; Fox, J. P.; Carré, D. J. *Ibid.* 1983, 105, 4349.

(3) Bernasconi, C. F.; Panda, M. J. *Org. Chem.* 1987, 52, 3042.

(4) Bernasconi, C. F.; Killion, R. B., Jr. *J. Org. Chem.* 1989, 54, 2878.

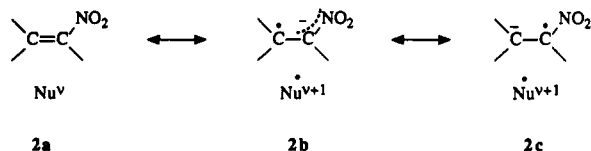
(5) Bernasconi, C. F.; Renfrow, R. A.; Tia, P. R. *J. Am. Chem. Soc.* 1986, 108, 4541.

(6) Bernasconi, C. F.; Schuck, D. F. *J. Org. Chem.*, in press.

(7) Gross, Z.; Hoz, S. *J. Am. Chem. Soc.* 1988, 110, 7489.

ganization provided by 1, delocalization of the negative charge and hence resonance stabilization of the transition state is modest, irrespective of the identity of XY.^{1,8} On the other hand, with preorganization, the transition state will benefit from resonance stabilization to the extent allowed by the inherent capability of X and Y to delocalize the charge, i.e., more strongly in the reactions of nitro-activated olefins than with the other substrates.

An alternative explanation for the positive deviations was offered by Gross and Hoz.⁷ These authors assumed that the reactions with nitro-activated olefins have some of the characteristics of an electron transfer; i.e., the transition state has radicaloid character that can be understood as a resonance hybrid of 2a-2c. In water 2b is



the major resonance form and rate enhancements arise from mesomeric stabilization of the lone electron on the benzylic carbon by *p*-MeO and *p*-Me₂N substituents. The results of our recent study of the reaction of substituted β -nitrostyrenes with thiolate ions⁶ do not, however, support the notion of a radicaloid transition state, and hence this interpretation will not be further discussed in this paper.

The objectives of the present investigation were 2-fold. The first was to test whether the rate enhancements by π -donors in the nucleophilic addition to substituted β -nitrostyrenes is a general phenomenon that occurs irrespective of the type of nucleophile used. To this end we studied the reactions with hydroxide ion and nitromethide ion (NM⁻) in aqueous solution, two nucleophiles that represent opposite extremes in Pearson's⁹ hard/soft classification.

The second objective was to examine how a change in solvent would affect the behavior of the π -donor substituents. We therefore extended our investigation to various Me₂SO-water mixtures of up to 90% Me₂SO content by volume.

One problem in dealing with the hydroxide and nitromethide ions as nucleophiles is that the equilibrium constants (K_1) are either difficult to obtain experimentally (OH⁻) or cannot be measured at all (NM⁻) (see Discussion). However, since we are mainly interested in the substituent dependence of K_1 rather than their absolute values, the much more easily accessible equilibrium constants for piperidine addition were determined and used to model the substituent dependence on K_1 for hydroxide ion addition.

Results

General Features. All kinetic experiments were performed at 20 °C, either in a stopped-flow or a conventional UV/vis spectrophotometer, and monitored at or near the λ_{max} of the respective β -nitrostyrene. The reactions with OH⁻ as nucleophile were conducted in water, 50% Me₂SO-50% water (v/v), 70% Me₂SO-30% water (v/v), and 90% Me₂SO-10% water (v/v), those with CH₂=NO₂⁻ as nucleophile in water, 50% and 90% Me₂SO only. In water and 50% Me₂SO the ionic strength was maintained at 0.5 M with KCl, in 70% Me₂SO at 0.25 M, and in 90%

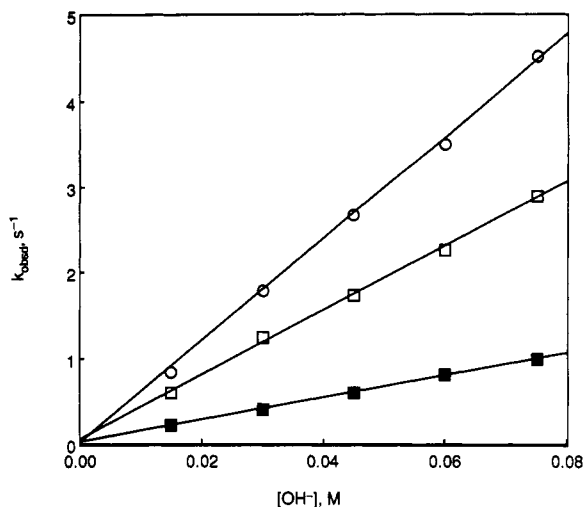


Figure 1. Representative plots of k_{obsd} vs $[\text{OH}^-]$ for the reaction of OH^- with substituted β -nitrostyrenes in 70% Me₂SO-30% water: ■, Z = 4-Br; □, Z = 4-CN; ○, Z = 4-NO₂.

Table I. Rate Constants, k_1^{OH} , for Nucleophilic Addition of Hydroxide Ion to Substituted β -Nitrostyrenes at 20 °C^a

Z	water ^b	50% Me ₂ SO ^b	70% Me ₂ SO ^c	90% Me ₂ SO ^d
4-Me ₂ N	0.194	0.301	0.691	7.13
4-MeO	0.263	0.821	2.99	55.3
H	0.306	1.37	5.91	192
4-Br	0.364	2.19	13.3	375
3-Cl	0.461	2.25		486
4-CN	0.708	5.09	37.5	1040
4-NO ₂	0.875	6.86	60.5	1630

^a In units of M⁻¹ s⁻¹; estimated error limits $\pm 3\%$ or better. ^b $\mu = 0.5$ M. ^c $\mu = 0.25$ M. ^d $\mu = 0.06$ M.

Me₂SO at 0.06 M. Pseudo-first-order conditions were used throughout with the nucleophile as the excess component.

Reactions with Hydroxide Ion. First-order rate constants, k_{obsd} , were typically determined at five to six different OH⁻ concentrations. The raw data are summarized in Tables S1-S4 of the supplementary material.¹⁰ In all cases, plots of k_{obsd} vs $[\text{OH}^-]$ were strictly linear, as shown in Figure 1 for some representative reactions in 70% Me₂SO. The intercepts of these plots were indistinguishable from zero. This indicates that, for all practical purposes, the reaction is irreversible, and k_{obsd} is given by

$$k_{\text{obsd}} = k_1^{\text{OH}}[\text{OH}^-] \quad (3)$$

with k_1^{OH} being the bimolecular rate constant for nucleophilic attack by hydroxide ion on the β -nitrostyrene (see Discussion). All k_1^{OH} values are reported in Table I.

Reactions with Nitromethide Ion. At the concentrations used for kinetic experiments ($\sim 10^{-3}$ -0.05 M), solutions of the nitromethide ion (NM⁻) are not very stable, especially in the presence of Me₂SO. In order to minimize the decomposition, NM⁻ was generated by adding KOH to a nitromethane solution in a double-mixing-stopped-flow apparatus. Deprotonation of the nitromethane was complete within a few seconds whereupon its solution could be immediately mixed with the β -nitrostyrene substrate. With this methodology clean first-order kinetics were observed. Representative plots of k_{obsd} vs $[\text{NM}^-]$ are shown in Figure 2. They are consistent with eq 4, i.e., the ob-

$$k_{\text{obsd}} = k_1^{\text{NM}}[\text{NM}^-] \quad (4)$$

(8) Bernasconi, C. F. *Acc. Chem. Res.* 1987, 20, 301. (b) Bernasconi, C. F. *Adv. Phys. Org. Chem.* 1992, 27, 119.

(9) Pearson, R. G. *Surv. Prog. Chem.* 1969, 5, 1. (b) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* 1967, 89, 1827.

(10) See paragraph concerning supplementary materials at the end of this paper.

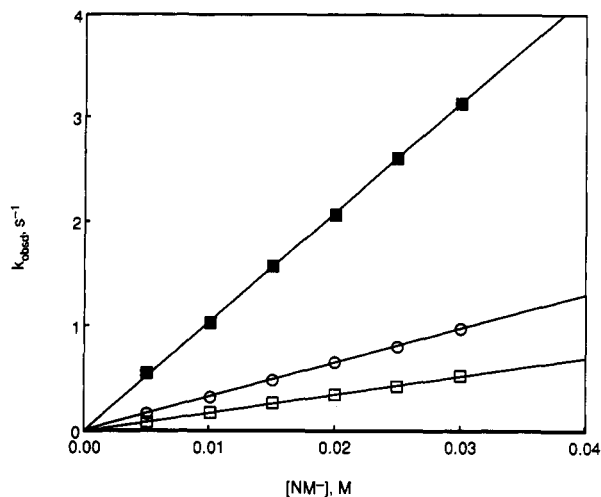


Figure 2. Representative plots of k_{obsd} vs $[\text{NM}^-]$ for the reaction of NM^- with substituted β -nitrostyrenes in 50% Me_2SO -50% water; \square , $Z = \text{H}$; \circ , $Z = 4\text{-Br}$; \blacksquare , $Z = 4\text{-NO}_2$.

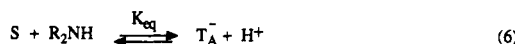
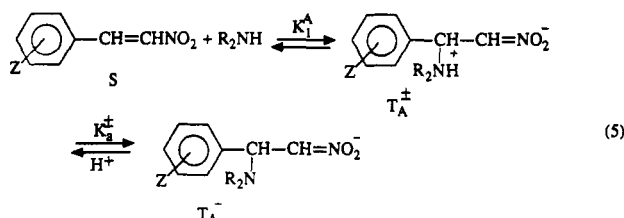
Table II. Rate Constants, k_1^{NM} , for Nucleophilic Addition of Nitromethide Ion to Substituted β -Nitrostyrenes at 20 °C^a

Z	water ^a	50% Me_2SO ^b	90% Me_2SO ^c
4- Me_2N	2.60	4.35	53.2
4-MeO	2.29	10.4	306
H	2.91	17.6	777
4-Br	3.70	32.6	2610
3-Cl	4.68	39.9	3150
4-CN	7.36	83.6	8060
4- NO_2	8.30	103	14400

^a In units of $\text{M}^{-1} \text{s}^{-1}$; estimated error limits $\pm 5\%$ or better. ^b $\mu = 0.5 \text{ M}$. ^c $\mu = 0.06 \text{ M}$.

served kinetic process refers to nucleophilic attack by NM^- . The raw data are summarized in Tables S5-S7 of the supplementary material¹⁰ while Table II reports the k_1^{NM} values.

Equilibrium Addition of Piperidine. Piperidine adds to β -nitrostyrenes as described by eq 5. We were par-



ticularly interested in the overall equilibrium constant for the process of eq 6 in 90% Me_2SO with $K_{\text{eq}} = K_1^\ddagger K_a^\ddagger$. All equilibrium determinations were made spectrophotometrically by measuring the absorbance at or near λ_{max} of the respective β -nitrostyrene. At these wavelengths neither T_A^\ddagger and T_A^- nor the buffers (see below) have significant absorptions and the relation of eq 7 holds where OD_0 is the absorbance in the absence, OD the absorbance in the presence of piperidine.

$$\frac{\text{OD}_0}{\text{OD}} = 1 + \left(K_1^\ddagger + \frac{K_1^\ddagger K_a^\ddagger}{a_{\text{H}^+}} \right) [\text{R}_2\text{NH}] \quad (7)$$

With all but the two least reactive substrates ($Z = 4\text{-MeO}$ and $4\text{-Me}_2\text{N}$), competing irreversible hydrolysis of the olefin led to time-dependent absorbance readings. Since the establishment of the equilibrium of eq 5 is quite fast, the absorbance measurements were performed in a

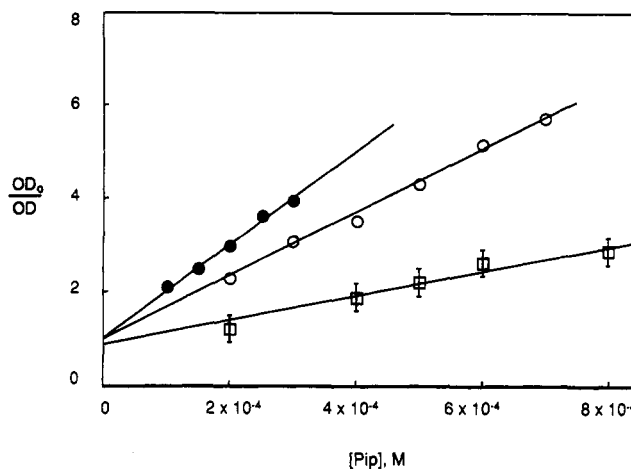


Figure 3. Representative plots of OD_0/OD vs piperidine concentration (eq 8) for piperidine addition to substituted β -nitrostyrenes in 90% Me_2SO -10% water at pH 13.67; \square , $Z = \text{H}$; \circ , $Z = 4\text{-Br}$; \bullet , $Z = 3\text{-Cl}$.

Table III. Equilibrium Constants, $K_{\text{eq}} = K_1^\ddagger K_a^\ddagger$, for Piperidine Addition to Substituted β -Nitrostyrenes According to eq 6 at 20 °C

Z	water ^a	90% Me_2SO ^b
4- Me_2N	9.8×10^{-8}	2.27×10^{-13}
4-MeO	5.9×10^{-7}	6.03×10^{-12}
H	2.9×10^{-6}	3.80×10^{-11}
4-Br	4.6×10^{-6}	1.48×10^{-10}
3-Cl	8.7×10^{-6}	2.06×10^{-10}
4-CN	1.6×10^{-5}	7.50×10^{-10}
4- NO_2	2.25×10^{-5}	1.63×10^{-9}

^a $\mu = 0.5 \text{ M}$, ref 5. ^b $\mu = 0.06 \text{ M}$, this work; estimated error limits $\pm 10\%$ or better.

stopped-flow apparatus. This allowed the determination of the equilibrium absorbance (OD) with relatively little interference by the slower hydrolysis, although in many cases it still required an extrapolation to "zero" time.

Based on a previous study of piperidine addition to β -nitrostyrene in water, 50% Me_2SO , and 70% Me_2SO ⁵ we anticipated that the $\text{p}K_a^\ddagger$ values would be $\ll 10$. Thus, by conducting our measurements at $\text{pH} \gg 10$, eq 7 should simplify to

$$\frac{\text{OD}_0}{\text{OD}} = 1 + \frac{K_1^\ddagger K_a^\ddagger}{a_{\text{H}^+}} [\text{R}_2\text{NH}] \quad (8)$$

This necessitated the use of external buffers such as 4-chloro or 4-cyanophenol to assure good pH control. Measurements were typically performed at two different pH values and five to six piperidine concentrations for each substrate. Figure 3 shows representative plots according to eq 8 while the raw data are summarized in Table S8 of the supplementary material.¹⁰ The K_{eq} values are reported in Table III along with data in water published previously.⁵

Discussion

General Considerations. When dealing with substituent effects on reactions, it is desirable to determine both rate and equilibrium constants whenever this is experimentally feasible. This allows one to evaluate or estimate *intrinsic* rate constants and treat the data not only in terms of the Hammett (or similar) relationship ($\log k$ vs σ) but also in terms of the Brønsted relationship ($\log k$ vs $\log K$). The former is useful in providing a measure of the absolute magnitude of the substituent dependence of rate and, in conjunction with a plot of $\log K$ vs σ , of equilibrium constants and also in identifying the presence of strong

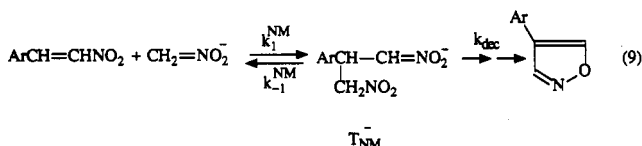
Table IV. Equilibrium Constants for Nucleophilic Addition of Various Bases to β -Nitrostyrene at 20 °C

Nuc	H ₂ O			50% Me ₂ SO		
	log K_1^{Nuc}	p K_a^{NucH}	(log K_1^{Nuc} - p K_a^{NucH})	log K_1^{Nuc}	p K_a^{NucH}	(log K_1^{Nuc} - p K_a^{NucH})
HO ⁻	≈4.90 ^a	15.64	≈-10.74	5.53 ^b	17.34	-11.81
piperidine	2.90 ^c	11.55	-8.65	1.50 ^c	11.02	-9.52
HOCH ₂ CH ₂ S ⁻	6.52 ^d	9.65	-3.13	≈6.47 ^e	10.56	≈-4.09
CH ₂ =NO ₂ ⁻	≈6-8 ^f	10.28	≈-2.28 to -4.28	≈6-8 ^f	11.32	≈-3.32 to -5.32

^a Estimated on the basis of log K_1^{Nuc} in 50% Me₂SO, see text. ^b Reference 13. ^c Reference 5. ^d Reference 6. ^e Estimated on the basis of log K_1^{Nuc} in water, see text. ^f Estimated based on models from ref 15, see text.

resonance effects on either rate or equilibrium constants. The Brønsted plot, on the other hand, gives a better measure as to what extent the substituent effect has developed in the transition state and, in the case of resonance effects, whether these develop synchronously or asynchronously with the inductive effects. It also avoids the problems associated with uncertain σ -values, e.g., for the 4-Me₂N substituent.¹¹

In the reactions of substituted benzylidenemalononitriles,⁴ benzylidene Meldrum's acids,³ and β -nitrostyrenes with piperidine⁵ and the reactions of β -nitrostyrenes with thiolate ions,⁶ both rate and equilibrium constants were experimentally accessible; for the reactions of 1,1-diaryl-2-nitroethylenes with cyanide ion only rate constants were reported.⁷ In the present work no equilibrium constants for OH⁻ or NM⁻ addition to the β -nitrostyrenes were experimentally determined either. In the case of NM⁻ addition, the equilibrium constant, K_1^{NM} , cannot be measured because irreversible decomposition of the adduct T_{NM}⁻ to what is most likely an isoxazole¹² is faster than the k_{-1}^{NM} step in eq 9.



In the reactions with OH⁻, the equilibrium constant is, in principle, accessible by means of kinetic measurements. However, the procedure is complex and laborious, as has been demonstrated for the reactions of β -nitrostyrene and the 4-chloro- and 3-nitro derivatives in 50% Me₂SO,¹³ and leads to equilibrium constants, K_1^{OH} , that are associated with substantial experimental error.

In view of these problems, we have chosen the experimentally much simpler approach of determining K_{eq} for piperidine addition and to construct Brønsted-type plots of log k_1^{OH} vs log K_{eq} in lieu of plots of log k_1^{OH} vs log K_1^{OH} . This approach also allows us to use data on K_{eq} for piperidine addition to β -nitrostyrenes in water published previously.⁵ The justification for the substitution of K_{eq} for K_1^{OH} is our expectation that K_{eq} and K_1^{OH} should respond in a similar way to the phenyl substituents.¹⁴ This expectation is based on the fact that both OH⁻ and piperidine are hard bases,⁹ which, after suitable correction for the difference in their p K_a values, have comparable affinities for the olefin (see below).

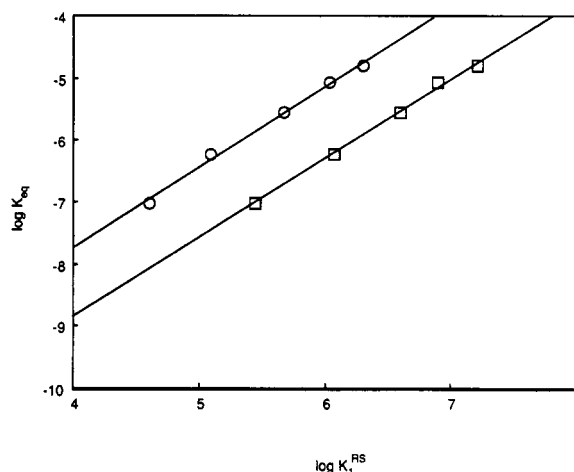


Figure 4. Correlation of log K_{eq} for piperidine addition to substituted β -nitrostyrenes with log K_1^{RS} for HOCH₂CH₂S⁻ (□) and MeO₂CCH₂S⁻ (○) (Z = 4-Me₂N, 4-MeO, H, 3-Cl, 4-CN).

Support for our approach comes from the observation that a reasonably linear correlation even exists between log K_{eq} and log K_1^{RS} ⁶ (RS⁻ = HOCH₂CH₂S⁻ and MeO₂CCH₂S⁻), as shown in Figure 4, despite the fact that thiolate ions are soft⁹ and hence constitute a more questionable model for OH⁻ or amine addition. The slopes of the correlations in Figure 4 are 1.30 and 1.29, respectively, indicating an attenuation of the substituent effect on the thiolate ion reactions which may be related to the higher stability of the thiolate ion adducts (see below). It is likely that the correlations of log K_{eq} vs log K_1^{OH} would have slopes closer to unity.

Equilibrium Affinities of OH⁻, RS⁻, CH₂=NO₂⁻, and Piperidine for β -Nitrostyrene. Table IV reports equilibrium constants for nucleophilic addition of four nucleophiles to β -nitrostyrenes in water and 50% Me₂SO. Note that in the case of piperidine, K_1 for the formation of T_A⁻ rather than $K_{\text{eq}} = K_1K_a^{\pm}$ for the formation of T_A⁻ + H⁺ is given. Some of the values listed in the table are estimates: K_1^{OH} in water, $K_1^{\text{HOCH}_2\text{CH}_2\text{S}^-}$ in 50% Me₂SO and K_1^{NM} in both solvents. log K_1^{OH} in water was estimated as log K_1^{OH} (50% Me₂SO) - p $K_a^{\text{H}_2\text{O}}$ (50% Me₂SO) + p $K_a^{\text{H}_2\text{O}}$ (H₂O) + p K_a^{NM} (50% Me₂SO) - p K_a^{NM} (H₂O) while log $K_1^{\text{HOCH}_2\text{CH}_2\text{S}^-}$ in 50% Me₂SO was obtained as log $K_1^{\text{HOCH}_2\text{CH}_2\text{S}^-}$ (H₂O) + p $K_a^{\text{HOCH}_2\text{CH}_2\text{SH}}$ (50% Me₂SO) - p $K_a^{\text{HOCH}_2\text{CH}_2\text{SH}}$ (H₂O) + p K_a^{NM} (H₂O) - p K_a^{NM} (50% Me₂SO). The estimates of K_1^{NM} are very uncertain and based on a comparison with 1,3-indandione anion addition to benzylidene-1,3-indandione and malononitrile anion addition to benzylidenemalononitrile.¹⁵

It is clear from the data in Table IV that the two soft bases HOCH₂CH₂S⁻ and NM⁻ have a much higher inherent affinity for the soft β -nitrostyrene than the hard bases OH⁻ and piperidine. This becomes even more evident when the

(11) Exner, O. E. In *Correlation Analysis in Chemistry*; Chapman, N. B., Shorter, J., Eds.; Plenum: New York, 1978; p 439.

(12) Heim, F. *Chem. Ber.* 1911, 44, 2016. (b) Meisenheimer, J.; Weizebahn, K. *Chem. Ber.* 1921, 54, 3200. (c) Worrall, D. E. *J. Am. Chem. Soc.* 1935, 57, 2299. (d) Pagano, A. H.; Schechter, H. *J. Org. Chem.* 1970, 35, 295. (e) Buchan, G. M.; Turner, A. B. *J. Chem. Soc., Perkin Trans. 1* 1975, 2115.

(13) Bernasconi, C. F.; Paschalis, P. *J. Am. Chem. Soc.* 1989, 111, 5893.

(14) Note that K_1 for the formation of the zwitterionic T_A⁻ would provide a less suitable model for K_1^{OH} than $K_{\text{eq}} = K_1K_a^{\pm}$ because the positive charge on T_A⁻ affects the substituent effects significantly.⁵

(15) Bernasconi, C. F.; Laibelman, A.; Zitomer, J. L. *J. Am. Chem. Soc.* 1985, 107, 6570.

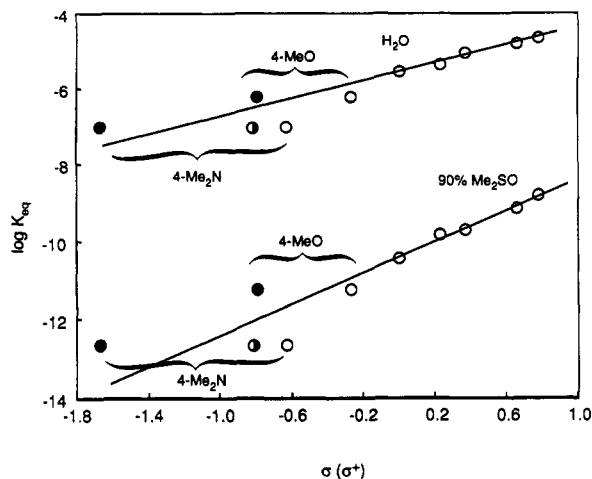


Figure 5. Correlation of $\log K_{eq}$ for piperidine addition to substituted β -nitrostyrenes with Hammett σ -values in water (top) and 90% Me₂SO–10% water (bottom). Half-filled circles refer to $\sigma = -0.83$ for 4-Me₂N and filled circles refer to σ^+ for Z = 4-MeO and 4-Me₂N, see text.

Table V. Structure–Reactivity Parameters for the Reactions of Nucleophiles with β -Nitrostyrene^a

	H ₂ O	50% Me ₂ SO	70% Me ₂ SO	90% Me ₂ SO
$\rho(k_1^{OH})^b$	0.60 ± 0.04	0.90 ± 0.09	1.24 ± 0.07	1.16 ± 0.05
$\rho(K_{eq})^b$	1.16 ± 0.08			1.98 ± 0.12
$\rho(k_1^{OH})/\rho(K_{eq})$	0.52 ± 0.07			0.59 ± 0.06
$\alpha_{nuc}^{b,c}$	0.52 ± 0.04			0.58 ± 0.02 ^d
$\rho(k_1^{NM})^b$	0.61 ± 0.03	0.98 ● 0.04		1.52 ± 0.13

^a Error limits are standard deviations from least squares analysis. ^b Calculated excluding Z = 4-Me₂N and 4-MeO. ^c Slope of Brønsted plots. ^d If 4-Me₂N and 4-MeO are included in the correlation (dashed line in Figure 8), $\alpha_{nuc}^d = 0.61 \bullet 0.01$.

differences in the pK_a^{NucH} values are factored in by comparing the quantity $\log K_1^{Nuc} - pK_a^{NucH}$ rather than $\log K_1^{Nuc}$ for the different bases. A less negative number means a higher inherent affinity. Our results are consistent with similar findings in other systems.^{9,16,17} The more than 2 log units higher $\log K_1^{Nuc} - pK_a^{NucH}$ value for piperidine compared to OH⁻ probably exaggerates the inherent affinity of the slightly softer amine for the olefin and may be partly explained by electrostatic and perhaps intramolecular hydrogen bonding stabilization of the zwitterionic T_A[±].

Substituent and Solvent Effects on K_{eq} . Figure 5 shows correlations of $\log K_{eq}$ with standard Hammett σ -values¹⁸ (open circles) in water and 90% Me₂SO; ρ -values, calculated by omitting the points for Z = 4-Me₂N and 4-MeO, are reported in Table V. The larger ρ -value in 90% Me₂SO (1.98) compared to water (1.16) reflects the greater demand for internal stabilization due to the reduced solvation of negative charge. This reduced solvation also manifests itself in much lower K_{eq} values in 90% Me₂SO, e.g., for Z = H, $K_{eq} = 2.90 \times 10^{-6}$ in water and 3.82×10^{-11} in 90% Me₂SO, and is reminiscent of the solvent effect on the acidity constant of nitromethane.²⁰ In fact,

(16) (a) Sander, E. G.; Jencks, W. P. *J. Am. Chem. Soc.* 1968, 90, 6154. (b) Hine, J.; Weimar, R. D., Jr. *J. Am. Chem. Soc.* 1965, 87, 3387. (c) Hine, J. *Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; p 225.

(17) Bernasconi, C. F.; Killion, R. B., Jr. *J. Am. Chem. Soc.* 1988, 110, 7506.

(18) The following σ -values have been used: 4-Me₂N, -0.63¹¹; 4-MeO, -0.28¹¹; 4-Br, 0.23¹⁹; 3-Cl, 0.37¹⁹; 4-CN, 0.66¹⁹; 4-NO₂, 0.78¹⁹.

(19) Reference 16c, p 66.

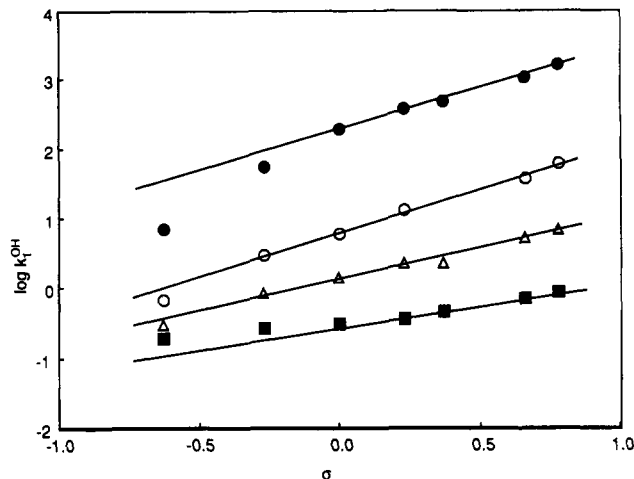


Figure 6. Hammett plots for k_1^{OH} in water (■), 50% Me₂SO (△), 70% Me₂SO (○), and 90% Me₂SO (●).

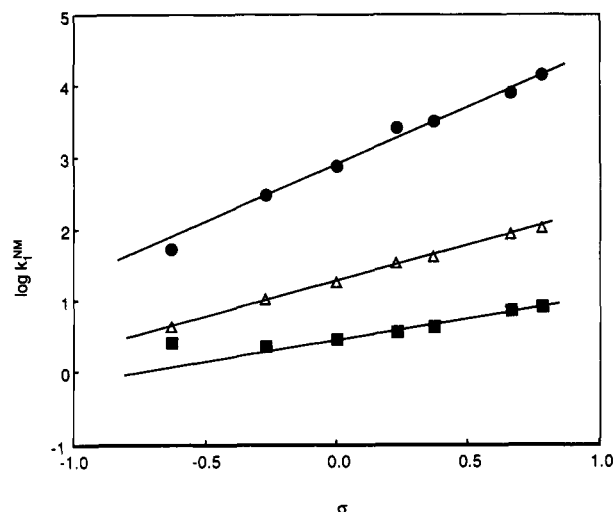
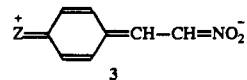


Figure 7. Hammett plots for k_1^{NM} in water (■), 50% Me₂SO (△), and 90% Me₂SO (●).

the ratio $K_{eq}(H_2O)/K_{eq}(90\% Me_2SO) = 7.59 \times 10^4$ is quite similar to the ratio $[K_a^{NM}(H_2O)/K_a^{NM}(90\% Me_2SO)]/[K_a^{PipH^+}(H_2O)/K_a^{PipH^+}(90\% Me_2SO)] = 2.14 \times 10^5$,²⁰ with K_a^{NM} and $K_a^{PipH^+}$ being the acid dissociation constants of nitromethane and piperidinium ion, respectively.

The points for Z = 4-MeO and 4-Me₂N deviate negatively from the Hammett plots. For 4-MeO these deviations amount to ≈ 0.3 log units in water and ≈ 0.4 log units in 90% Me₂SO, for 4-Me₂N to ≈ 0.8 log units in water, ≈ 1.0 log units in 90% Me₂SO. If Hine's¹⁹ σ -value for 4-Me₂N (-0.83) is used instead (half-filled circles in Figure 5), the negative deviations reduce to ≈ 0.55 log units in water and 0.6 log units in 90% Me₂SO. These deviations indicate that through-resonance (3) makes a significant contribution



to the stabilization of the olefin in both solvents. However, this resonance effect is not as strong as in carbocationic systems,²¹ as seen by the positive deviations in the correlation with σ^+ (filled circles in Figure 5).

(20) Bernasconi, C. F.; Kliner, D. A. V.; Mullin, A. S.; Ni, J. X. *J. Org. Chem.* 1988, 53, 3342.

(21) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* 1958, 80, 4979. (b) Hoefnagel, A. J.; Wepster, B. M. *Ibid.* 1973, 95, 5357.

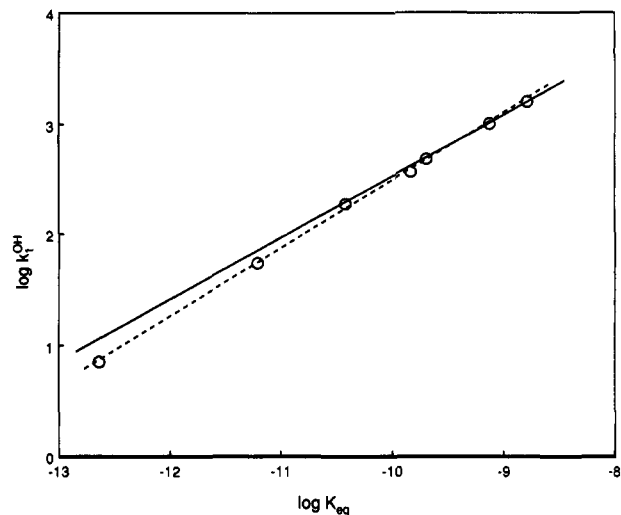


Figure 8. Brønsted-type plot of $\log k_1^{\text{OH}}$ vs $\log K_{\text{eq}}$ in 90% Me_2SO .

Substituent and Solvent Effects on k_1^{OH} and k_1^{NM} . Figure 6 shows Hammett plots¹⁸ for the rate constants of hydroxide ion addition to substituted β -nitrostyrenes in water, 50% Me_2SO , 70% Me_2SO , and 90% Me_2SO , while Figure 7 shows similar plots for nitromethide ion addition in water, 50% Me_2SO , and 90% Me_2SO . Standard σ -values¹⁸ have again been used throughout. ρ -values are summarized in Table V. It is noteworthy that $\rho(K_1^{\text{OH}}) = 0.60$ in water is very close to the ρ -value for piperidine addition (0.56) which is obtained after correction for the effect of the developing positive charge on the amine nitrogen.⁵

$\rho(k_1^{\text{OH}})$ and $\rho(k_1^{\text{NM}})$, just as $\rho(K_{\text{eq}})$, tend to increase with increasing Me_2SO content of the solvent, reflecting a decrease in solvational stabilization of the transition state in the less aqueous solvent. The finding that $\rho(k_1^{\text{OH}})$ in 90% Me_2SO is slightly lower than in 70% Me_2SO is somewhat surprising, though, and suggests a smaller degree of charge transfer from OH^- to the olefin at the transition state in 90% Me_2SO .

The most interesting feature of the plots in Figures 6 and 7 are the results for the π -donors 4-MeO and 4-Me₂N. Since the effects are much more clear cut with 4-Me₂N we shall focus the discussion on this substituent. In the hydroxide ion reaction the 4-Me₂N point shows a negative deviation of ≈ 0.7 log units in 90% Me_2SO . This negative deviation decreases to ≈ 0.2 log units in 70% Me_2SO and ≈ 0.1 in 50% Me_2SO , while in water there is a positive deviation of ≈ 0.25 log units. With $\sigma = -0.83$ ¹⁹ for 4-Me₂N, the deviations are ≈ -0.47 , ≈ 0 , $\approx +0.1$, and $\approx +0.3$, respectively (points not shown in Figure 6). In the nitromethide ion reaction there is a similar trend with a negative deviation of ≈ 0.2 log units in 90% Me_2SO , no deviation in 50% Me_2SO , and a positive deviation of ≈ 0.4 in water; here the corresponding numbers with $\sigma = -0.83$ are $\approx +0.1$, $\approx +0.2$, and $\approx +0.5$, respectively.

The negative deviations are reminiscent of similar observations in the reactions of benzylidene Meldrum's acids³ and benzylidenemalononitriles⁴ with piperidine and can be interpreted in the same way, i.e., k_1^{OH} and k_1^{NM} are depressed because of the stabilization of the olefin by through-resonance (3), the same effect that depresses K_{eq} . In 90% Me_2SO the negative deviation of k_1^{OH} for the 4-Me₂N derivative is about 70% of that of the corresponding K_{eq} ($\approx 78\%$ if $\sigma = -0.83$ is used), suggesting that approximately 70% (78%) of the resonance effect has been lost at the transition state. This compares with $\rho(k_1^{\text{OH}})/\rho(K_{\text{eq}}) = 1.16/1.98 = 0.59$ (Table V) which may be interpreted

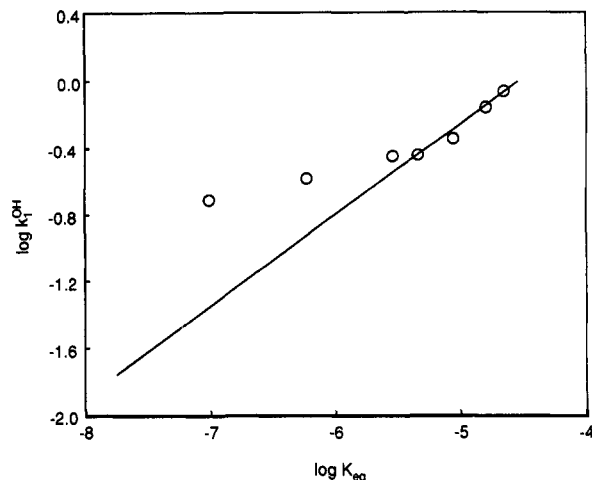


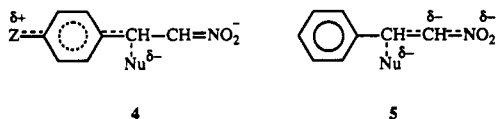
Figure 9. Brønsted-type plot of $\log k_1^{\text{OH}}$ vs $\log K_{\text{eq}}$ in water.

as indicating approximately 59% C-O bond formation at the transition state. These numbers suggest that loss of resonance may be ahead of C-O bond formation but in view of the relatively small difference between these numbers and the considerable experimental uncertainty in their values, this conclusion cannot be firm.

The same ambiguity remains when the data are represented by a Brønsted-type plot of $\log k_1^{\text{OH}}$ vs $\log K_{\text{eq}}$ (Figure 8). One may either draw a straight line through the points for $Z = \text{H}$, 4-Br, 3-Cl, 4-CN, and 4-NO₂ (solid line) which shows a small negative deviation for $Z = 4\text{-Me}_2\text{N}$ and 4-MeO or a line through all the points (dashed line). The slope of the former is $\alpha_{\text{nuc}}^{\text{H}} = 0.58 \pm 0.02$, the slope of the latter $\alpha_{\text{nuc}}^{\text{H}} = 0.61 \pm 0.01$. Since both slopes are consistent with $\rho(k_1^{\text{OH}})/\rho(K_{\text{eq}}) = 0.59 \pm 0.06$ and the standard deviations of the slopes are comparable, it cannot be decided which interpretation is more appropriate; i.e., it is not clear whether the loss of resonance at the transition state is slightly ahead of C-O bond formation (negative deviation from Brønsted-type plot) or synchronous with it (points on the line), a question to which we shall return below.

In the more aqueous solvents the negative deviation for k_1^{OH} with the π -donor substituents is much smaller and turns into a positive deviation in the purely aqueous solvent (Figure 6). This decrease and reversal has no counterpart in $\log K_{\text{eq}}$ for which the negative deviation in water is only slightly smaller than in 90% Me_2SO (Figure 5). Hence, these observations indicate that in the more aqueous solvents a factor comes into play which opposes the reduction in the rate constant caused by the resonance stabilization of the olefin. This factor becomes increasingly important with a decrease in Me_2SO content and in water overcompensates the rate-retarding resonance effect, as was already observed in the reactions of piperidine⁵ and thiolate ions⁶ with substituted β -nitrostyrenes in aqueous solution. This rate enhancement is the consequence of an increase in the intrinsic rate constant, as is most clearly manifested by the positive deviations from the Brønsted-type plot of Figure 9.

As mentioned in the introduction, the most plausible explanation for these rate enhancements is the preorganization of the electronic structure toward that of the product which is induced by π -donor substituents (1) and facilitates delocalization of the negative charge into the nitro group at the transition state. This is shown, in exaggerated form, by 4 while 5 represents the "normal" transition state, which prevails in the absence of a π -donor substituent.²²



In conjunction with previous results, the present study now allows a fairly definite assessment of what determines the balance between the rate-retarding resonance stabilization of the olefin and the rate-enhancing preorganization. For the latter influence to prevail, X or Y must not only be a very strong π -acceptor, but the solvent must enhance the resonance effect of X and/or Y in the adduct by strong hydrogen bonding solvation. The only X, Y/solvent combination investigated thus far which has the requisite properties is X, Y = NO₂, H in aqueous solution. This combination leads to rate enhancements with π -donor substituents in the phenyl group in all systems studied thus far, i.e., the reactions of β -nitrostyrenes with piperidine, thiolate ions, hydroxide ion, and nitromethide ion, as well as the reaction of 1,1-diaryl-2-nitroethylenes with cyanide ion in water.

Other X, Y groups, such as cyano, or the cyclic diester moiety in benzylidene Meldrum's acid are not strong enough π -acceptors, and even the nitro group loses most of its preorganization effect when the solvent is not purely aqueous. This latter conclusion not only derives from the present study but fits with results obtained for the reaction of 1,1-diaryl-2-nitroethylenes with cyanide ion in dimethyl sulfoxide.⁷

Why do only the reactions of nitro-activated olefins in aqueous solution benefit sufficiently from the preorganization as to lead to a net increase in the intrinsic rate constant? The intrinsic rate constants (k_0) of carbanion-forming reactions are inversely related to the degree of resonance stabilization of the carbanion;⁸ i.e., k_0 is high when there is little resonance, but low when the resonance effect is large. This is because the development of the resonance effect lags behind bond changes in the transition state, a phenomenon that, according to the Principle of Non-perfect Synchronization (PNS),⁸ depresses k_0 in proportion to the resonance stabilization of the carbanion. This explains why nitronate ion forming reactions have particularly low intrinsic rate constants. For example, the log k_0 values for the addition of piperidine/morpholine to benzylidenemalononitrile, benzylidene Meldrum's acid, and β -nitrostyrene in 50% Me₂SO are 4.94,⁴ 4.10,³ and 2.55,⁵ respectively, and the log k_0 values for the deprotonation of malononitrile, Meldrum's acid, and nitromethane by piperidine/morpholine in the same solvent are ≈ 7.0 ,²³ 3.90,^{8b} and 0.73,²⁰ respectively.

However, because the k_0 -lowering PNS effect of the delayed resonance is especially strong in these reactions, any (partial) circumvention of the PNS effect should also have a particularly large impact on k_0 . The facilitation of the delocalization of the negative charge into the nitro group at the transition state (4) can be viewed as such partial circumvention of the strong PNS effect that has its roots in the weak delocalization of the charge in the "normal" transition state (5).²⁴ In reactions of substrates

activated with XY groups other than nitro, and of nitro-activated olefins in solvents other than water, the k_0 -lowering PNS effects are much smaller, but so are the benefits of avoiding them. However, it is unlikely that the effect of preorganization is completely absent in these cases. If this were the case one should expect stronger negative deviations for Z = 4-Me₂N and 4-MeO from the Brønsted-type plot in Figure 8. This is because loss of resonance from a reactant is always found to be significantly ahead of (or development of resonance in a product always lags significantly behind) bond changes which,^{8b} according to the PNS always leads to a lowering of the intrinsic rate constant. In other words, the k_0 -enhancing preorganization compensates for the k_0 -lowering resonance effect.

Experimental Section

Materials. β -Nitrostyrene was obtained from Aldrich Chemical Co. and recrystallized from ethanol, mp 56–57 °C (lit.²⁵ mp 58 °C). The remaining β -nitrostyrenes, except for the 4-Me₂N-derivative that was synthesized according to Bennington et al.,²⁶ were prepared by the method of Worrall²⁷ and recrystallized from ethanol or ethanol/acetic acid: 4-(*N,N*-dimethylamino)- β -nitrostyrene, mp 181 °C (lit.²⁸ mp 182–183.5 °C); 4-methoxy- β -nitrostyrene, mp 84–87 °C (lit.²⁸ 86 °C); 4-bromo- β -nitrostyrene, mp 168–172 °C (lit.²⁹ mp 173 °C); 3-chloro- β -nitrostyrene, mp 47–49 °C (lit.²⁹ mp 47 °C); 4-cyano- β -nitrostyrene, mp 185.5–187.5 °C (lit.³⁰ mp 186–188 °C), 4-nitro- β -nitrostyrene, mp 168–172 °C (lit.²⁹ mp 173 °C). Nitromethane (Aldrich) was distilled from CaSO₄ and its purity checked by ¹H-NMR. Piperidine (Aldrich) was refluxed over CaH₂ and distilled prior to use. Dimethyl sulfoxide was dried over CaH₂ and distilled at reduced pressure before use. 4-Cyanophenol and 4-chlorophenol (Aldrich) were recrystallized from toluene, and 2-chlorophenol (Aldrich) was used without further purification. Glacial acetic acid (Mallinckrodt) and KCl (Fisher Scientific) were used without further purification. KOH and HCl solutions were "Dilute-it" (Baker) diluted to appropriate volumes with deionized water.

Reaction Solutions and pH Measurements. The solutions were prepared essentially as described before.³¹ For the 50% Me₂SO solutions, appropriate amounts of aqueous stock solutions were added to the Me₂SO, and the volumetric flasks were topped off with water at 20 °C. For the 70% and 90% Me₂SO solutions, Me₂SO was added to the aqueous phase and the flasks were topped off with Me₂SO. The pH-measurements for the equilibrium determinations in 90% Me₂SO were performed in a water-jacketed cup at 20 °C with an Orion 611 digital pH meter with a Corning No. 476022 glass electrode and a Ross "Sure-Flow" reference electrode. The pH meter was calibrated with Hallé³² buffers. At pH > 14 the pH meter showed a slightly nonlinear response. The problem could be alleviated by using calibration buffers whose pH values were close to the pH being measured. The pH determinations were carried out in mock mixing experiments that simulated the corresponding stopped-flow experiment.

Kinetic Experiments. The slow reactions were measured in a Perkin-Elmer 559 spectrophotometer, the fast ones in a Durum-Gibson stopped-flow spectrophotometer. The slow reactions were initiated by injecting a few μ L of a concentrated substrate stock solution in Me₂SO into the cuvette of the spectrophotometer which contained all the other ingredients and was temperature equilibrated. For the stopped-flow experiments the substrate was injected into the substrate syringe containing solvent and KCl.

(25) *Handbook of Chemistry and Physics*, 56th ed.; CRC Press: Cleveland, OH, 1975.

(26) Bennington, F.; Morin, R. D.; Clark, L. C. *J. Org. Chem.* 1956, 21, 1470.

(27) Worrall, D. E. In *Organic Syntheses*; Gilman, H., Blatt, A., Eds.; Wiley: New York, 1941; Collect. Vol. 1, p 143.

(28) Kamlet, M. J. *J. Am. Chem. Soc.* 1955, 77, 4896.

(29) *Beilstein Handbuch der Organischen Chemie*; Springer Verlag: New York, 1979; 4th Suppl., Vol. 5, p 1354.

(30) Vecchi, A.; Melone, G. *J. Org. Chem.* 1957, 22, 1636.

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

(32) Hallé, J.-C.; Gaboriaud, R.; Schaal, R. *Bull. Soc. Chim. Fr.* 1970, 2047.

(22) A reviewer inquired whether preorganization is an enthalpy or entropy effect, or both. Since all our data refer to rate constants at one temperature a breakdown in terms of ΔH^\ddagger and ΔS^\ddagger effects cannot be given.

(23) In water: Hibbert, F. *Compr. Chem. Kinet.* 1977, 8, 97.

(24) Instead of viewing the enhanced negative charge delocalization in **3** as leading to a partial circumvention of the k_0 -lowering PNS effect of the normally delayed delocalization (4), it may also be regarded as representing an earlier development of the product stabilizing resonance effect. According to the PNS,⁸ such advanced development of a product stabilizing factor always leads to an increase in k_0 .

The reactions with the nitromethide ion were conducted in a Durrum-Gibson stopped-flow apparatus with double mixing capability. In the first mixing process nitromethane was reacted with 0.5 equiv of KOH to produce a 1:1 NM/NM⁻ buffer. After a few seconds, this latter solution was reacted with the substrate in the second mixing process.

Equilibrium Measurements. The equilibrium constants for piperidine addition (K_{eq}) were measured spectrophotometrically at the wavelengths reported in Table S8.¹⁰ These wavelengths were chosen such that the respective β -nitrostyrene was the only contributor to the absorbance. Due to competing hydrolysis¹³ OD readings decreased with time and, in most cases, had to be determined in the stopped-flow apparatus by extrapolation to "zero time" with respect to the hydrolysis reaction. To minimize

errors, OD₀ readings were taken from the same substrate solution that was used for the OD measurements in the presence of piperidine.

Acknowledgment. This research was supported by Grant CHE-8921739 from the National Science Foundation.

Supplementary Material Available: Kinetic and equilibrium measurements, Tables S1–S8 (10 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

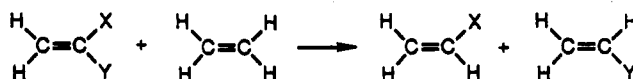
A Theoretical Analysis of the Relative Reactivity in Radical Addition Reactions: Acceptor–Donor, Acceptor–Acceptor, and Donor–Donor 1,1-Disubstituted Ethenes. The Effect of Ground-State Destabilization on Reactivity

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Ab initio theoretical calculations have been carried out on a number of acceptor–donor, acceptor–acceptor, and donor–donor 1,1-disubstituted ethenes and on related monosubstituted ethenes and 2-substituted propenes. Ground-state effects in the 1,1-disubstituted ethenes have been evaluated using the isodesmic reaction



Acceptor–donor and acceptor–acceptor 1,1-disubstituted ethenes suffer considerable ground-state destabilization, while the donor–donor disubstituted ethenes vary considerably from enjoying a high degree of ground-state stabilization to a high degree of destabilization. The 1,1-disubstituted systems possessing significant ground-state destabilization also possess relatively low-lying LUMOs. The relative reactivity data [$\ln k_{rel}$] for the addition of alkyl free radicals to monosubstituted ethenes and 2-substituted propenes produces a linear correlation with the energy of the LUMO. The limited relative reactivity data for the free-radical addition to the 1,1-disubstituted ethenes also gives a very reasonable linear correlation with the energy of the π LUMOs. The regioselectivity of the alkyl free-radical addition processes is also consistent with a FMO-controlled process, the attack occurring at the 2p AO of the LUMO possessing the largest coefficient which is at C₂ of the acceptor–donor and acceptor–acceptor 1,1-disubstituted ethenes.

Introduction

The effect of substituents on the relative reactivity and regioselectivity in radical addition reactions with substituted alkenes has been an area of intense interest. In general, it has been observed that the presence of an electron-withdrawing group on the alkene increases the reactivity of the substituted alkene toward alkyl radical addition.^{1–6} What appears to be the first rationalization

of the relative reactivity of substituted alkenes in radical addition reactions was by Fukui and co-workers, who suggested that reactivity is controlled by a dominant radical SOMO–alkene LUMO interaction.⁷ This suggestion was later criticized on the basis that the energy gap between the SOMO of the free radical and the HOMO of the alkene must be smaller than that between the SOMO of the free radical and the LUMO of the alkene, leading to the conclusion that the reactivity and regioselectivity of the radical addition reactions must be SOMO–HOMO-controlled.⁸ SOMO–HOMO control was claimed to be supported by the results of calculations.⁹ In an early review of the kinetics and orientation of free-radical addition to olefins, Tedder and Walton concluded that the rate and orientation of free-radical addition reactions

(1) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* 1944, 66, 1594. Lewis, F. M.; Mayo, F. R.; Hulse, W. F. *J. Am. Chem. Soc.* 1945, 67, 1701. Mayo, F. R.; Lewis, F. M.; Walling, C. *J. Am. Chem. Soc.* 1948, 70, 1529.

(2) Mayo, F. R.; Lewis, F. M.; Walling, C. *Discuss. Faraday Soc.* 1947, 2, 285.

(3) Szwarc, M. *J. Polym. Sci.* 1955, 16, 367. Leavitt, F.; Levy, M.; Szwarc, M.; Stannett, V. *J. Am. Chem. Soc.* 1955, 77, 5493.

(4) James, D. G. L.; Agawa, T. *Can. J. Chem.* 1965, 43, 640.

(5) Minisci, F.; Zammori, P.; Bernadi, R.; Cecere, M.; Galli, R. *Tetrahedron* 1970, 4153. Citterio, A.; Minisci, F.; Arnoldi, A.; Pagano, R. *J. Chem. Soc., Perkin Trans 2* 1978, 519. Citterio, A.; Arnoldi, A.; Minisci, F. *J. Org. Chem.* 1979, 44, 2674.

(6) Giese, B.; Meister, J. *Chem. Ber.* 1977, 110, 2558. Giese, B.; Meister, J. *Angew. Chem., Int. Ed. Engl.* 1997, 10, 178.

(7) Fujimoto, H.; Yamabe, S.; Minato, T.; Fukui, K. *J. Am. Chem. Soc.* 1972, 94, 9205.

(8) Poblet, J. M.; Canadell, E.; Sordo, T. *Can. J. Chem.* 1983, 61, 2068.

(9) Canadell, E.; Poblet, J. M.; Olivella, S. *J. Phys. Chem.* 1983, 87, 424.