J. Am. Chem. Soc. **1988**, *110*, 7489–7493

the rate of σ-complex formation.

The good correlation between the data obtained for TPB and the data obtained in superacidic media proves that the study of the protonation of TPB may provide a detailed insight into the mechanism of σ-complex formation. Since for TPB the measurements are performed in dilute solutions, the influence of the solvent and the influence of substituents can be studied separately. To this purpose, further measurements are in progress.

Acknowledgment. We thank Prof. F. Effenberger, Universität Stuttgart, for providing the substituted benzenes and Prof. A. J. Kresge, University of Toronto, for valuable discussion.

Appendix

Relaxation Times. The rate law for reaction 5 is given in eq A1. From this equation the relaxation time is calculated in the

$$d[\mathrm{TPBH_C}^+]/dt = k_{1,\mathrm{OH}}[\mathrm{TPB}] - k_{-1,\mathrm{OH}}f_\pm^2[\mathrm{TPBH_C}^+][\mathrm{OH}^-] + k_1[\mathrm{TPB}][\mathrm{H}^+] - k_{-1}[\mathrm{TPB_C}^+] \quad \text{(A1)}$$

usual way;[16] i.e. the actual concentration [A] is replaced by the time-independent equilibrium concentration $[\bar{\mathrm{A}}]$ and the "deviation" x_A, where $x_\mathrm{A} \ll [\bar{\mathrm{A}}]$.

For reaction 5 we have due to the conservation of mass

$$x_\mathrm{TPB} = -x_\mathrm{TPBH,C} \quad \text{(A2)}$$

The law of electroneutrality requires

$$x_\mathrm{H} + x_\mathrm{TPBH,C} = x_\mathrm{OH} \quad \text{(A3)}$$

Equation A3 is valid for unbuffered solutions, where only H_2O and no other base or acid reacts with TPB. Finally, the neutralization reaction $H^+ + OH^- \rightleftarrows H_2O$ is fast compared to the protonation of TPB, and therefore this dissociation equilibrium is always established, which means that eq A4 applies. Combining eq A1–A4 leads to eq A5 with $1/\tau$ given by eq 6a.

$$\overline{[\mathrm{OH}^-]}x_\mathrm{H} = -\overline{[\mathrm{H}^+]}x_\mathrm{OH} \quad \text{(A4)}$$

$$dx_\mathrm{TPBH,C}/dt = -(1/\tau)x_\mathrm{TPBH,C} \quad \text{(A5)}$$

In buffered solution eq A3 is not appropriate, since the buffer ions contribute to the electroneutrality. However, since the solutions are buffered, we may apply eq A6. Combining eq A1, A2, and A6 leads to eq A5 with $1/\tau$ given by eq 6b.

$$x_\mathrm{H} = x_\mathrm{OH} = 0 \quad \text{(A6)}$$

In order to derive eq 11 we start with eq 8 and insert the deviation x_i. Equation 8 is applied only in the range pH <3.5, and therefore the proton concentration is large compared to that of TPB. That means the solutions are buffered and the reaction proceeds under pseudo-first-order conditions; i.e., we may assume eq A7 applies. This leads to eq A8. The reactions leading to

$$x_\mathrm{H} = 0 \quad \text{(A7)}$$

the equilibria 9 and 10 are fast compared to reaction 8; i.e., with eq A7 we have eq A9 and A10. Inserting eq A9 and A10 into eq A8 leads to eq A11 with $1/\tau$ given by eq 11.

$$-d(x_\mathrm{TPB} + x_\mathrm{TPBH,N} + x_\mathrm{TPBHH,NN})/dt = k_{1,\mathrm{OH}}x_\mathrm{TPB} + k_{1,\mathrm{H}}\overline{[\mathrm{H}^+]}x_\mathrm{TPB} + k_\mathrm{CN}x_\mathrm{TPBH,N} + k_5 f_1^2 f_{11}^{-1}\overline{[\mathrm{H}^+]}x_\mathrm{TPB,N} + k_6 x_\mathrm{TPBHH,NN} \quad \text{(A8)}$$

$$x_\mathrm{TPB} = (\overline{[\mathrm{TPB}]}/\overline{[\mathrm{TPBH_N}^+]})x_\mathrm{TPBH,N} \quad \text{(A9)}$$

$$x_\mathrm{TPBHH,NN} = (\overline{[\mathrm{TPBH_N H_N}^{2+}]}/\overline{[\mathrm{TPBH_N}^+]})x_\mathrm{TPBH,N} \quad \text{(A10)}$$

$$-dx_\mathrm{TPBH,N}/dt = (1/\tau)x_\mathrm{TPBH,N} \quad \text{(A11)}$$

Registry No. MeTPB, 20758-47-8; EtTPB, 20758-48-9; TMB, 16857-97-9; TPiB, 16857-95-7; TPB, 16857-93-5; TPB$^+$, 103979-21-1; TPB^{2+}, 116054-41-2.

Supplementary Material Available: Tables of relaxation times measured for solutions of TPB, MeTPB, and EtTPB and equilibrium constants (6 pages). Ordering information is given on any current masthead page.

Radical-Anionic Nature of the Transition State in the Michael Addition Reaction[1]

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Abstract: The kinetics of the addition of CN$^-$ to a series of para mono- and disubstituted 1,1-diaryl-2-nitroethylene was studied in water and DMSO. log k correlates with σ^0 better than with σ with a ρ value of 0.24 in water and 1.16 in DMSO. The points for the mono- and dimethoxy derivatives (**1** and **3**) in water deviate positively from the Hammett type line. When a Yukawa–Tsuno type equation is used, a linear plot that includes the p-MeO derivatives is obtained with $R = -0.5$. Contrary to expectations, the ρ value in DMSO is ca. 5-fold larger than that in water and the data points for the p-MeO substituents do not deviate from the Hammett type correlation. In the reaction of the p-dinitro derivative **9** in DMSO, 10% of a product rising from nucleophilic attack at the other terminus of the double bond (α to the nitro group) was observed. These unusual results are rationalized by using current theories, which assign the transition state a significant contribution of charge-transfer configurations (configurations B and C). The relative and absolute contribution of each of the configurations to the transition state is responsible for the observed phenomena.

Nucleophilic additions to highly activated systems are of prime importance from both synthetic and mechanistic points of view. The common feature of these activated compounds, which include aromatics substituted by electron-withdrawing groups,[2] carbonium ions,[3] carbonyl derivatives,[4] and activated olefins,[5] is that they all posses low LUMOs (LL). Several years ago we suggested that, at the transition state of their reaction with nucleophiles, these

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(1) Nucleophilic Attacks on Low LUMO Compound. 5. Part 4: Reference 8.

(2) Miller, J. *Aromatic Nucelophilic Substitution*; Elsevier: Amsterdam, The Netherlands, 1968. Bernasconi, C. F. *MTP Int. Rev. Sci.:Org. Chem., Ser. One* **1973**, *3*, 33. Barlin, G. B. *Aromt. Heteraromat. Chem.* **1974**, *2*, 271.

(3) Ritchie, C. D. *Pure Appl. Chem.* **1978**, *50*, 1281.

(4) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1969. Bender, M. L. *Mechanism of Homogeneous Catalysis from Proton to Proteins*, Wiley: New York, 1971. Patai, S., Ed. *The Chemistry of the Carbonyl Group*; Wiley: London, 1972; Vol. 1. Zabicky, J., Ed. *The Chemistry of the Carbonyl Group*; Wiley: London, 1972; Vol. 2. Cordes, E. H. Bull, H. G. *Chem. Rev.* **1974**, *74*, 581. Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1.

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Table I. λ_{max} (nm) of $XC_6H_4(YC_6H_4)C{=}CHNO_2$ in Water and DMSO and Second-Order Rate Constants[a] for the Reactions with CN^- at 25 °C

	1	**2**	**3**	**3′**	**4**	**5**	**5′**	**6**	**7**	**8**	**9**
p-X	OMe	Me	H	OMe	H	H	Cl	F	H	H	NO_2
p-Y	OMe	Me	OMe	H	H	Cl	H	F	CN	NO_2	NO_2
(H_2O), 10^3k M^{-1} s^{-1}	5.3	4.0	5.1^b		4.5	5.2^b		5.8	7.1	7.3	11.0
$\lambda_{max}(H_2O)$	366	330	365	327	322	320	321	321	311	282	283
(DMSO), k M^{-1} s^{-1}	0.15	0.25	0.22	0.28	0.46	0.98	1.13	1.26	3.30	4.05	27.1
λ_{max} (DMSO)	354	327	358	304^c	320	313	313	316	313	274	285

[a] Experimental error is ±3%. [b] Equilibration of the two isomers is faster than the nucleophilic addition. [c] Shoulder.

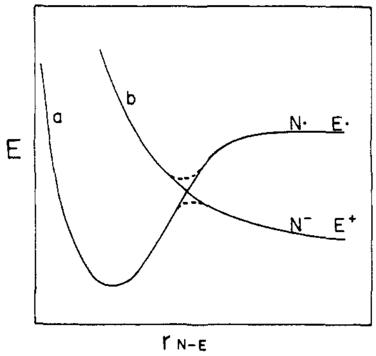


Figure 1. Construction of the reaction profile for anion–cation combination reaction from cross sections of the radical-covalent (a) and ionic (b) potential surfaces.

substrates acquire a partial radical character along with partial charge.[6,7] Thus, when conventional notation is used, a neutral substrate (E) should be denoted at the transition state as $E^{\delta\cdot\delta-}$. Similarly, a neutral nucleophile should bear the notation $\delta\cdot\delta+$ while a negatively charged one has the notation $\delta\cdot\delta-$. Using this model, we were able to explain the α effect, the nucleophilicity parameter N^+,[7] and the positional selectivity in a given nucleophilic reaction.[8]

More recently, Kochi has shown[9] that, in electrophilic aromatic substitution (which can be viewed as a nucleophilic attack of the aromatics on the electrophilic agent), the transition state resembles an excited charge-transfer complex. Namely, in a nucleophile–electrophile (N–E) encounter, the transition state is a resonance hybrid of the structures N, E and $N^{\cdot+}$, $E^{\cdot-}$, with the latter configuration being dominant. Moreover, Kochi has convincingly argued[9] that the positional selectivity on the aromatic nucleus is governed by the spin density on the various carbons of the aromatic radical cation. In spite of the different approaches, these two models clearly convey essentially the same message, which for LL substrates also coincides with that of the Shaik–Pross model.[10]

It is important to note that an electron-transfer component in the transition state does not necessarily imply the formation of a radical-pair intermediate. This is most easily evidenced from an examination of the reaction profile for the anion–cation combination reaction shown in Figure 1 (which can be extended to nucleophilic reactions with other LL substrates[6]). When we go from the ionic state to the covalent product (motion from right to left in Figure 1), the transition state is achieved at the avoided crossing zone of the curves for the radical-covalent (a) and ionic (b) states. Since at this point the electronic structure of the transition state must have an equal contribution from the two states, it is clear that electron transfer must take place at the transition state. The latter will decay directly to the covalent product. The formation of a radical pair, which may either collapse to the covalent product or diffuse apart, will occur only when the two curves cross at the plateau region of curve a.

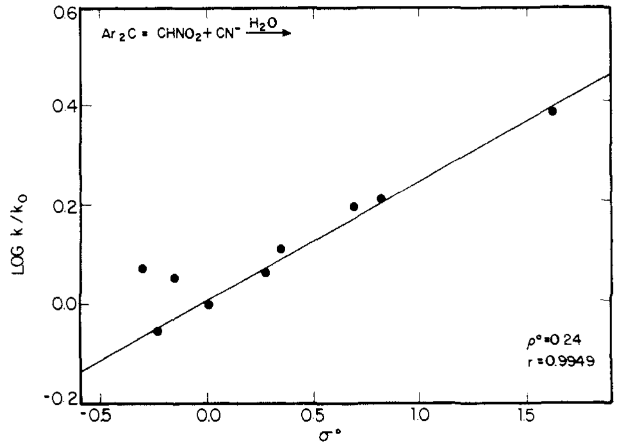
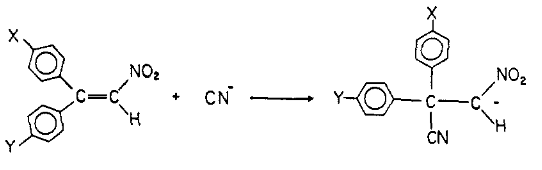


Figure 2. Hammett type plot for the reaction of CN^- with a series of 1,1-diaryl-2-nitroethylenes in water.

It is somewhat surprising that this basic idea did not surface much earlier, especially since nucleophilic reactions in general have been studied in detail for several decades. The reason lies apparently in the absence of a suitable probe for detection of radicaloid centers. The common probes, e.g. solvent and substituent effects, are by far more sensitive to polar effects[11] and therefore mask the presence of radical features. Although it is difficult to detect the presence of a radical constituent in the transition state of a nucleophilic reaction, the importance of the aforementioned models, besides providing a better understanding, is manifested in those rare cases where the usually latent radical effect is disclosed at the transition state.

In the present paper we will focus on the Michael addition reaction and present some evidence indicating that, contrary to the traditional understanding, its transition state is not an intermediate structure between that of the reactant and the product.[12] Instead, and in accordance with the aforementioned models, it will be shown that the experimental results can be best accommodated by assuming that at the transition state the substrate acquires a partial radical-anionic character. The reactions examined are the addition of CN^- to a series of substituted 1,1-diaryl-2-nitroethylenes (eq 1).



(1)

Results and Discussion

The kinetics of the addition reaction (eq 1)[13] were studied in water at 25 °C by monitoring the disappearance of the UV ab-

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(5) Patai, S.; Rappoprt, Z. In *The Chemistry of Alkenes*; Patai, S., Ed.; Wiley: New York, 1964. Rappoprt, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. Bernasconi, C. F. *Pure Appl. Chem.* **1982**, *54*, 2335.

(6) Hoz, S. *J. Org Chem.* **1982**, *47*, 3545.

(7) Hoz, S.; Speizman, D. *J. Org. Chem.* **1983**, *48*, 2904.

(8) Hoz, S. In *Nucleophilicity*; Harris, J. M., McManus, S., Eds.; Advances Chemistry Series 215; American Chemical Society: Washington, DC, 1987; Chapter 12.

(9) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 7240.

(10) Shaik, S. S. *Prog. Phys. Org. Chem.* **1985**, *15*, 197. Pross, A. *Adv. Phys. Org. Chem.* **1985**, *15*, 99.

(11) *Advancecs in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972.

(12) Leffler, J. E.; Grunwald, E. *Rates and Equilibria of Organic Reactions*, Wiley: New York, 1963.

(13) The pK_a of the analogous product, 9-cyano-9-(nitromethyl)fluorene, in which the two aryl groups are replaced by a fluorenyl moiety is 9.6 in 25% v/v aqueous sulfolane: Hoz, S.; Gross, Z.; Cohen, D. *J. Org. Chem.* **1985**, *50*, 832. It therefore can be assumed that the product in eq 1 remains ionized under the reaction conditions.

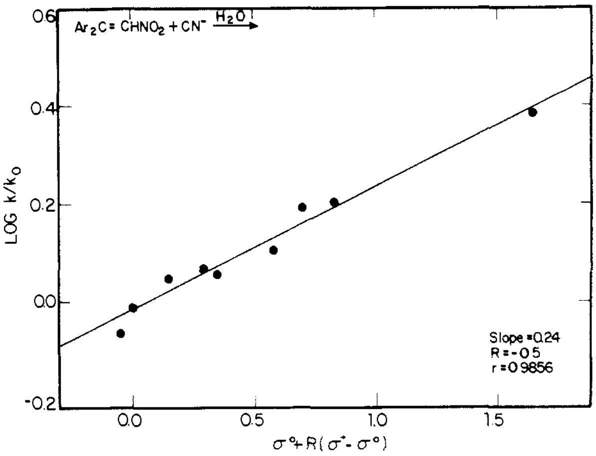
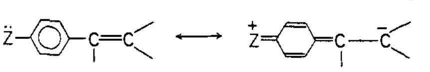


Figure 3. Yukawa–Tsuno type plot for the reaction of CN^- with a series of 1,1-diaryl-2-nitroethylenes in water.

sorption of the substrates under pseudo-first-order conditions (excess CN^-). Second-order rate constants are given in Table I.[14]

Attempts to correlate the kinetic data with σ as well as with σ^0 gave a much better correlation with σ^0 ($\rho^0 = 0.24$, $r = 0.9949$; Figure 2) than with σ ($\rho = 0.23$, $r = 0.9836$). In both cases however, the points for the *p*-MeO-substituted substrates (**1** and **3**) deviate positively from the Hammett type plot.[15] This is a somewhat surprising phenomenon since substituents that are mesomerically good donors usually deviate negatively from the correlation line.[16] The common explanation for this negative deviation is that in these cases the ground state of the substrate is highly stabilized due to resonance interaction between the substituent and the electrophilic double bond[17] (eq 2).

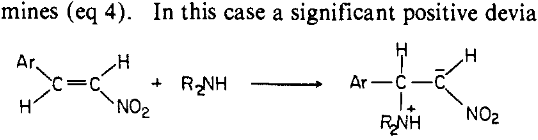

(2)

Correlating our data with a combination of σ^0 and σ^+, according to the Yukawa–Tsuno equation[18] (eq 3), brought the two deviating

$$\log k/k_0 = \rho[\sigma^0 + R(\sigma^+ - \sigma^0)] \qquad (3)$$

points to the line (Figure 3). The *R* value was found to be negative (−0.5), reflecting the fact that substituents with a negative σ^+ value enhance the reaction rate.

A positive deviation similar to this one was previously reported by Bernasconi and co-workers[17] for the reaction of β-nitrostyrenes with amines (eq 4). In this case a significant positive deviation


(4)

was observed for the *p*-NMe_2-substituted olefin from a Hammett plot ($\rho = 0.27$). More recently, these researchers obtained similar results for the reactions of OH^- and $CH_2{=}NO_2^-$ with β-nitrostyrenes in various DMSO–water mixtures.[19] In water-rich

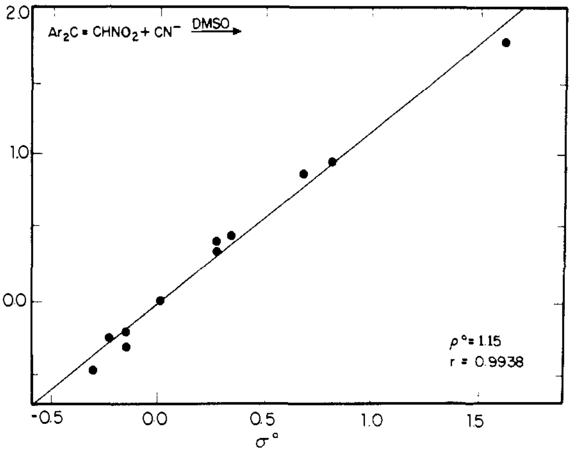
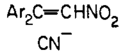
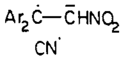


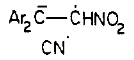
Figure 4. Hammett type plot for the reaction of CN^- with a series of 1,1-diaryl-2-nitroethylenes in DMSO.

solvents positive deviation for *p*-OMe and *p*-NMe_2 derivatives was always observed.

On the basis of the models mentioned in the introduction, transfer of spin density from the nucleophile to the substrate should take place at the transition state of these reactions. Thus, in the present case the transition state will be a resonance hybrid of three major structures (A–C), with structures B and C dominating.


$$\begin{array}{c} Ar_2C{=}CHNO_2 \\ CN^- \end{array}$$
A


$$\begin{array}{c} Ar_2\dot{C}{-}\bar{C}HNO_2 \\ CN^{\cdot} \end{array}$$
B


$$\begin{array}{c} Ar_2\bar{C}{-}\dot{C}HNO_2 \\ CN^{\cdot} \end{array}$$
C

The relative contribution of structures B and C is governed by intrinsic parameters such as the activating group and the solvent. However, it is clear that substituents with a positive mesomeric effect will be very effective in stabilizing structure B where the radical center resides on the benzylic carbon.[20-22]

It is therefore highly likely that the reason for the excessive reactivity of substrates substituted with groups such as *p*-MeO (**1** and **3** in the present case) as well as *p*-NMe_2 (in the Bernasconi studies[17,19]) is the ability of these groups to stabilize effectively a radicaloid center on a benzylic carbon (configuration B).

Apart from the fact that substituents respond to the negative charge transferred to the substrate at the transition state by giving rise to a positive ρ value,[23] the overall ρ value is governed by two other effects that need to be considered. These are the resonance interaction with the double bond (eq 2) and the resonance interaction with the radicaloid center. Obviously, the strongest effect due to the two latter interactions will be exhibited by substituents with a large positive mesomeric effect. Such a substituent will,

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(14) A reviewer has suggested that the isomerization of the pairs **3**, **3′** and **5**, **5′** occurs by a reversible nucleophilic addition of CN^- to the substrate. On the contrary we have found that the reactions are irreversible and the isomerization mechanism involves removal of the vinylic proton. NMR studies of **3** in 25% D_2O–75% acetone-d_6 in the presence of 0.1 mol equiv of KCN show that the isomerization is accompanied by H/D exchange of the proton α to the nitro group.

(15) Statistical treatment by the T-test analysis shows that the deviating points (substrates **1** and **3**) are outside the correlation range in 99.8 and 99% confidence level, respectively: Draper, N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; Wiley: New York, 1981.

(16) Schreiber, B.; Martinek, H.; Wilschann, P.; Schuster, P. *J. Am. Chem. Soc.* **1979**, *101*, 4708. Bernasconi, C. F.; Fornarini, S. *J. Am. Chem. Soc.* **1980**, *102*, 5329. Bernasconi, C. F.; Leonarduzzi, G. D. *J. Am. Chem. Soc.* **1982**, *104*, 5133. Bernasconi, C. F.; Fox, J. P.; Kanavarioti, A.; Panda, M. *J. Am. Chem. Soc.* **1986**, *108*, 2372.

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

(18) Yukawa, Y.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 971.

(19) Bernasconi, C. F., personal communication.

(20) Yamamoto, T.; Otsu, T. *Chem. Ind.* (*London*) **1967**, 787. Walling, C.; Mintz, M. J. *J. Am. Chem. Soc.* **1967**, *89*, 1515. Sakurai, H.; Hayaski, S.; Hosomi, A. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1945. Dincturk, S.; Jackson, R. A.; Townson, M. *J. Chem. Soc., Chem. Commun.* **1979**, 172. Bordwell, F. G.; Bausch, M. J. *J. Am. Chem. Soc.* **1986**, *108*, 1979.

(21) The extent of deviation as a function of substituent can be inferred from a Yukawa–Tsuno type equation: $\log (k/k_0) = \rho^0\sigma^0 + \rho(\sigma^+ - \sigma^0)$. According to this equation, the term $\sigma^+ - \sigma^0$ governs the deviation from the Hammett type plot (first term on the right-hand side of the equation). For a substituent such as *p*-MeO, this deviation is expected to be large since σ^+ and σ^0 reflect opposing mechanisms by which this substituent interacts with positive (radical) and negative centers ($\sigma^+ - \sigma^0 = 0.6$). In some cases it was found that *p*-CN for example can also stabilize radical centers.[20] Yet, even if we use σ^- instead of σ^+ in this case (assuming the mechanism for stabilization in the case of CN is similar for radicals and anions), the difference $\sigma^- - \sigma^0$ is likely to be smaller since both σ^- and σ^0 describe interaction with a negative charge (actual value ~0.2).

(22) Creary, X. *J. Org. Chem.* **1980**, *45*, 280.

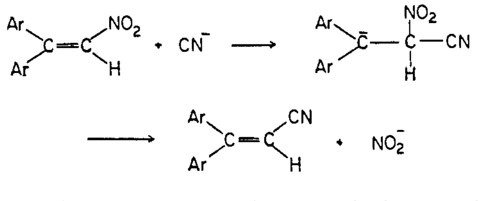
(23) This should not necessarily result in a correlation with σ^- as is evident from literature studies of the ionization of 1-arylnitroethanes; Bordwell, F. G.; Boyle, W. J., Jr.; Yee, K. C. *J. Am. Chem. Soc.* **1970**, *92*, 5926. Bordwell, F. G.; Boyle, W. J. Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3907. Fukuyama, M.; Flanager, P. W. K.; Williams, F. T., Jr.; Frainier, L.; Miller, S. A.; Shechter, J. H. *J. Am. Chem. Soc.* **1970**, *92*, 4689.

as mentioned previously, stablize the ground state of the reactants and thus lower the reaction rate constants. Its interaction with the radicaloid center on the other hand will enhance the reaction rates. The final outcome will probably depend largely on the relative contribution of structure B to the transition state. This in turn will depend on the activating group, the substituents, the solvent, and the coplanarity of the substrate in a manner that is difficult to predict. Nevertheless, general trends can be outlined, and in the sequel we will discuss first the solvent effect and afterward that of the substituents.

According to the classical type of argument, the special effect of the *p*-MeO substituent in stabilizing the ground state depends on the ability of the activating group(s) to accommodate the delocalized negative charge and polarize the double bond. Water, being a highly polar solvent with a large capability for hydrogen bonding, will tend to increase the amount of the negative charge delocalized onto the nitro oxygen atoms in the ground state. This will lead to a stabilization of the ground state and a significant rate retardation by the *p*-MeO substituent. On the other hand, in DMSO, which assists the polarization of the double bond to a lesser extent, this effect will be much reduced, and the rate constant for the *p*-MeO derivative will *relatively* increase. In other words, the data point for *p*-MeO in DMSO will be located higher than that for the reaction in water *with respect to the Hammett line*. Yet, contrary to this expectation, the data show that in water this point deviates positively from the Hammett plot and in DMSO it falls on the Hammett line (Table I and Figure 4, similar observations were made by Bernasconi's group for the reactions in the DMSO-rich region[19]). This contradiction between prediction based on classical model and the experimental observation is absent in the present model. This model predicts that since changing the solvent from water to DMSO will diminish the contribution of structure B by polarizing the double bond to a lesser extent, the stabilizing interaction of the *p*-MeO substituent with the radicaloid center at the transition state in DMSO will be *diminished* relative to water. As a result the positive deviation observed in water will be reduced.

Another point of importance is the absolute magnitude of the ρ value. Since CN^- is solvated only poorly in DMSO as compared to water, its reactivity in DMSO is expected to be larger (as was indeed found) and the transition state, according to the Hammond postulate,[24] should be achieved earlier. Consequently, a smaller amount of the negative charge will be transferred to the substrate at the transition state, and the ρ value should be smaller than in water.[25] However, the experimental data reveal the opposite effect. While the ρ value in water is 0.24, its value in DMSO is ca. 5-fold larger (1.16). This observation agrees very well with the proposed model. According to this model, structure C, which places negative charge on the benzylic carbon, contributes relatively more than structure B in DMSO than in water. Thus, while it is possible that the total amount of charge transferred to the substrate at the transition state is smaller in DMSO than in water, the larger contribution of structure C may compensate for this and lead to a higher ρ value, as was indeed observed.

Finally, we address the issue of the substituent effect. The relative contribution of structures B and C is extremely important in determining the regiochemistry of the reaction. As was pointed out by Kochi,[9] the selectivity among the various positions in an electrophilic reaction correlates well with the spin density on the various carbons of the derived radical cation of the aromatic substrate. A similar argument was used in the case of nucleophilic attack on 9-(nitromethylene)fluorene.[8] This argument implies that in the present case the CN group will bond to the benzylic carbon when structure B is dominant and to the carbon α to the nitro group when structure C is dominant (obviously, account must taken of other important factors such as steric effect etc.). In the case where the system is nearly balanced, varying the substituents along the σ scale will alter the relative importance of these two structures. Such a situation is probably encountered in the reactions in DMSO. In a reaction on a preparative scale with a substrate at the right-hand side of the σ scale (**9**), 90% of the "normal" product and 10% of 1-cyano-2,2-bis(4-nitrophenyl)ethylene were obtained. The latter product is apparently obtained via the nucleophilic vinylic substitution mechanism (eq 5).



(5)

In the reactions of the other derivatives only the normal addition product was obtained.

Summary and Conclusions

Several unusual observations were made in this study: (a) In the reaction of $Ar_2C{=}CHNO_2$ with CN^- in water, the points for the *p*-MeO derivatives (**1** and **3**) deviate positively from the Hammett plot. (b) No such deviation was observed when the reactions were conducted in DMSO. (c) Contrary to expectations, the ρ value in DMSO is 5 times larger than in water. (d) In a preparative reaction (of **9**) performed in DMSO, 10% of a product arising from a nucleophilic attack at the other terminus of the double bond (eq 5) was obtained, whereas, the reactions of **8**, **5**, **3**, and **2** gave only the normal products. Most of these observations cannot be accommodated by the "traditional" model, which assigns to the transition state a structure intermediate between that of reactants and products. The current model proposed for nucleophilic attacks on low-lying LUMO substrates requires that structure B and C, which are characteristic features of neither the reactants nor the products, are essential features of the transition state. When this model is used, points a–d are satisfactorily rationalized. The rationale is based on the assumption that substituents such as *p*-MeO give rise to a stabilizing interaction with structure B and a destabilizing one with C. The overall effect is governed therefore by the absolute and relative contributions of each of these structures to the transition state. In a case of a balanced situation, a substituent may tilt the balance, turning one of the structures into the dominant one.

It should be pointed out that this model like the classical one is only qualtative. Nevertheless, and in spite of this limitation, this model seems to be able to accommodate more facts than the classical one.

Experimental Section

Instrumentation. Kinetic measurements were performed on a Uvikon 810-820 spectrophotometer equipped with an Apple II microcomputer for data acquisition. pH measurements were taken with a Radiometer PHM-52 digital pH meter. ^1H NMR spectra were recorded on a Bruker AM 300 spectrometer. Mass spectra were taken with a Finnigan 4021 mass spectrometer.

Preparation of 1,1-Diaryl-2-nitroethylene. Substrates **1**, **4**, and **2** are known compounds and were prepared according to literature procedures.[26,27] Substrates **3**, **5**, **5′**, and **6** were prepared in the following way: to a well-stirred solution of 1 mmol of 1,1-diarylethylene in 50 mL of glacial acetic acid was added 0.5 mL of red fuming HNO_3. After 4 h at room temperature, ice water was added, and the reaction mixture was washed with three portions of $CHCl_3$. The combined organic fractions were washed twice with 5% $NaHCO_3$ solution and dried over $MgSO_4$, and the solvent was evaporated. The residue was chromatographed on

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(24) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

(25) In general, the ρ value increases upon moving from polar solvents to nonpolar ones. Thus, one could have expected that the reactions in DMSO will indeed exhibit ρ values higher than in water. However, this increase in ρ is usually much smaller than the factor of 5 observed in the present case. Examples taken from the analysis made by Ritchie and co-workers (Ritchie, C. D.; VanVerth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491) are the following: for thiols, thiophenols, benzoic acids, and phenols, the factors are 1.4, 2.8, 2.6, and 2.2, respectively. It should be emphasized that in both solvents the charge differences between the reactants and products is constant (unity), whereas in the present case it is expected to be much smaller in DMSO.

(26) Tadros, W.; Awad, S. B.; Sakla, A. B.; Abdul-Malik, N. F.; Armanious, E. R. *Indian J. Chem., Sect. B* **1980**, *19B*, 119.

(27) Charles, G. *Bull. Soc. Chim. Fr.* **1963**, 1573.

a silica column (CH_2Cl_2–hexanes 2:1 (v/v)). In cases where two isomers were obtained, column chromatography was repeated with ether–hexanes (3:1 (v/v)). The products crystallize spontaneously from the eluent. Recrystallization from hexane gave the pure product; **3** (only one isomer; 35%, mp 98 °C). Two isomers of the *p*-Cl derivative were obtained in ca. 20% yield each. One (**5**) was in a pure form, mp 105 °C, and the other isomer (**5′**) was contaminated with ca. 10% of the first one (mp of the mixture 56 °C); **6** (33%, mp 82 °C). Literature procedure[26] (followed by column chromatography with ether–hexane 3:1) was employed for the preparation of additional derivatives; **3** (10%, mp 89 °C), **3′** (14%, mp 74 °C); **7** (20%, 134 °C). The *p*-nitro derivatives (**8** and **9**) were prepared according to the following procedure. To a stirred ice-cold solution of 0.45 g (2 mmol) of **4** and 0.4 g of concentrated H_2SO_4 in 20 mL of CF_3COOH was added 0.15 g of red fuming nitric acid in 10 mL of CF_3COOH over 3 min. After 30 min at 0–5 °C, crushed ice was added, and the aqueous solution was extracted twice with $CHCl_3$. The combined organic fractions were washed with saturated NaCl solution and dried over $MgSO_4$, and the $CHCl_3$ was evaporated. The oily residue was separated by column chromatography (CH_2Cl_2–hexane 2:1). The first fraction contained only one isomer of **8**: 20.4%; mp 125 °C. The dinitro derivative **9** was obtained in a much lower yield; 0.02 g (3.4%); mp 129 °C. ^1H NMR spectra of all substrates will be reported along with that of another series of olefins in a separate paper. The mass spectra (EI) of all compounds showed a molecular peak along with fragmentations typical of nitroolefins. Satisfactory C, H, N (and for **5** and **6** also Cl and F, respectively) elemental analysis were obtained.

Preparation of 2-Cyano-2,2-diarylnitroethanes. Some of the cyano adducts of 1,1-diaryl-2-nitroethylenes were prepared by a general procedure as follows: A mixture of 0.38 mmol of 1,1-diaryl-2-nitroethylene in 5 mL of dry DMSO was added at once to a well-stirred solution of 24.7 mg (0.38 mmol) of KCN in 10 mL of dry DMSO. After the substrate was consumed (TLC, 1–20 min), the reaction mixture was poured into 50 mL of well-stirred and ice-cooled 5% HCl solution. The white to yellowish precipicate was collected and analyzed by ^1H NMR. In all cases (except for **9**) only a single product, with the typical absorptions of $-CH_2NO_2$ and substituted aromatic protons, was obtained. In all cases yields (in mean values of dry but not recrystallized product) were quantitative. Recrystallizations were carried out from hexanes.

In the case of **9**, the presence of an additional product was indicated by NMR analysis. This product was separated (12 mg, 10%) by column chromatography (silica, ether–hexanes, 3:1), recrystallized from 95% EtOH, and identified as 1-cyano-2,2-bis(4-nitrophenyl)ethylene: mp 134 °C; MS (EI) *m/e* 295 (100%, M^+), 265 (7.5%, –NO), 249 (5%, $-NO_2$); ^1H NMR ($CDCl_3$) δ 6.01 (s, 1 H), 7.46, 7.62, 8.28, 8.32 (2 H each, two sets of AA′XX′ multiplets); ^{13}C NMR ($CDCl_3$) δ 100.36 (d, olefinic CH), 115.93 (s, CN), 124.23 (d), 129.17 (d), 130.45 (d), 141.90 (s), 143.33 (s), 148.93 (s), 149.11 (s), 158.24 (s, olefinic C). C, H, N elemental analysis obtained was satisfactory. The second compound eluted from the column (32 mg, 24%, recrystallized from 95% EtOH–5% HCl(aq) solution) was the normal addition product, 2-cyano-2,2-bis(4-nitrophenyl)nitroethane: mp 157 °C; MS (CI) *m/e* 343 ($M^+ + 1$); ^1H NMR ($CDCl_3$) δ 5.33 (s, 2 H), 7.62, 8.34 (4 H each, AA′XX′ multiplets); ^{13}C NMR ($CDCl_3$) δ 49.82 (s), 78.33 (t), 117.67 (s, CN), 125.02 (d), 127.96 (d), 140.73 (s), 148.53 (s). C, H, N elemental analysis obtained was satisfactory.

Properties of the other 2-cyano-2,2-diarylnitroethanes (adducts) prepared by this general procedure are as follows.

Adduct of 8: did not crystallize; 5.24 (s, 2 H), 7.35 (m, 5 H), 7.55, 8.18 (AA′XX′, 2 H each).

Adduct of 5: mp 101 °C; ^1H NMR ($CDCl_3$) δ 5.19, 5.23 (AB q, 2 H), 7.31–7.46 (m, 9 H).

Adduct of 2: mp 76 °C; ^1H NMR ($CDCl_3$) δ 2.34 (s, 6 H), 5.17 (s, 2 H), 7.18, 7.21, 7.23, 7.26 (AA′XX′, 2 H each).

Adduct of 3: mp 133 °C; ^1H NMR ($CDCl_3$) δ 3.81 (s, 3 H), 5.18, 5.20 (AB q, 2 H), 6.92, 7.28 (AA′XX′, 2 H each) 7.34–4.45 (m, 5 H).

Satisfactory C, H, N (and Cl for the adduct of **5**) and molecular peaks in their mass spectra (CI) have been obtained for all the adducts described.

Olefin **9** has been reacted also with KCN in water. A total of 100 mg (0.3 mmol) of **9**, dissolved in 1 mL of acetone, was added in 20-μL protions over 1 h to a well-stirred soltuion of 65 mg (1 mmol) of KCN in 100 mL of H_2O. The heterogeneous reaction mixture was stirred overnight. Even so, much of the starting material that precipitated in the course of the addition remained undissolved. The unreacted olefin (NMR analysis) was completely removed from the reaction mixture by extracting with three portions of 25 mL of CH_2Cl_2. The reaction mixture was neutralized with 10 mL of 5% HCl solution and washed with three portions of 25 mL of CH_2Cl_2. TLC and NMR analyses were identical with those of the major product obtained in the reaction in DMSO (2-cyano-2,2-bis(4-nitrophenyl)nitroethane). No indication was obtained for the presence of 1-cyano-2,2-bis(4-nitrophenyl)ethylene.

Kinetic Measurements. KCN was dissolved in double-distilled preheated water (to expel CO_2). The concentration of the free CN^- was calculated from its pK_a value (9.2) and K_w. The pH measurements were in excellent agreement with the calculated hydroxide concentration. After incubation of the KCN solutions in the thermostated spectrophotometer until the temperature of 25 ± 0.2 °C was reached, the substrate was injected into the cells in an ethanolic solution (ca. 2.5 μL into 2.5 mL). The concentration of the substrate was in the range of 10^{-5}–10^{-6} M. Higher concentrations were not employed due to zero-order complications.[28] The concentration of KCN was always at least 100 larger than that of the substrate. In each case first-order rate constants were determined for five different concentrations of KCN. The reactions were usually followed by monitoring the disappearance of substrate absorption at its λ_{max}. In cases where λ_{max} was below 300 nm the reactions were followed at 320 nm. In DMSO (distilled over BaO; shown by NMR to contain ca. 0.04% H_2O), the same procedure was followed, with the substrates' concentrations being in the range of 10^{-5}–10^{-4} M. First-order rate constants were determined for three to four different concentrations of KCN. Each experiment was repeated three times. In both solvents the reactions were cleanly first order with respect to each of the reactants.

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Registry No. **1**, 36697-31-1; **1** (cyano adduct), 116437-76-4; **2**, 97498-75-4; **2** (cyano adduct), 116437-77-5; (*E*)-**3**, 116437-69-5; (*Z*)-**3**, 116437-68-4; **3** (cyano adduct), 116437-78-4; **4**, 5670-69-9; **4** (cyano adduct), 116437-79-7; (*E*)-**5**, 116437-70-8; (*Z*)-**5**, 116437-71-9; **5** (cyano adduct), 116437-80-0; **6**, 116437-72-0; **6** (cyano adduct), 116437-81-1; **7**, 116437-73-1; **7** (cyano adduct), 116437-82-2; **8**, 116437-74-2; **8** (cyano adduct), 116437-83-3; **9**, 116437-75-3; **9** (cyano adduct), 116437-84-4; CN^-, 57-12-5; $(O_2NC_6H_4\text{-}p\text{-})_2C{=}CHCN$, 116437-85-5.

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(28) Hoz, S.; Gross, Z.; Speizman, D. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1143.