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Kinetics of Bromination of Highly Reactive α-Methoxystyrenes. The Balance between Thermodynamic and Intrinsic Kinetic Contributions to the Selectivity in Bromination and Protonation of Styrenes

Marie-Françoise Ruasse* and Jacques-Emile Dubois*

Contribution from the Institut de Topologie et de Dynamique des Systèmes, Université Paris VII, associé au C.N.R.S., 1, rue Guy de la Brosse, 75005 Paris, France. *Received July 13, 1983. Revised Manuscript Received December 16, 1983*

Abstract: Ring substituent effects in bromination of highly reactive α-methoxystyrenes, X—C_6H_4—C(OMe)=CH_2 (for X = H, $k = 2.1 \times 10^9$ M^{-1} s^{-1}), are measured to evaluate the change in selectivity with the reactivity in electrophilic additions on styrenes. In methanol, the ρ^n value is very small, −1.85, and ρ^r is near zero. These unusually low values for a reaction leading to a benzylic carbocation are accompanied by small solvent effects, $m = 0.45$ for X = H. The attenuation of both selectivity coefficients, m and ρ, is attributed to charge delocalization in the methoxy group, to a very early transition state, and to thermodynamic effects including resonance saturation in the intermediate. Inclusion of these ρ values in rate–selectivity relationships for the bromination of Y-substituted styrenes, X—C_6H_4—C(Y)=CH_2 (Y = H, Me, MeO, and HO), indicates that the selectivity decreases markedly with increasing olefin reactivity. Dependence of the charge–substituent distance on Y makes the ρ^n/log k plot curved, but the ρ^r variation is linearly related to the reactivity and is attributed to a shift in the transition-state position and to changes in thermodynamic factors. Since ρ variation in protonation of the same olefins is mainly determined by thermodynamic factors similar to those affecting bromination, the former is used to estimate the thermodynamic contribution in the latter. Linear relationships between the ρ values of these two additions, with slopes of about 2, show that a variation in the transition-state position contributes to the ρ variation in bromination by doubling the influence of the thermodynamic factors.

Data at the boundaries of the chemical reactivity ranges would greatly help to clarify the current debate about the meaning of the selectivity coefficients in free energy relationships as regards the transition-state position.[1] The most important questions at present are the following: Do reactivity variations induced by changes in structure or medium shift the transition state and, if so, how large is this effect?[2] Can this question be handled in terms of LFER parameters, i.e., do the α, β, ρ, or m variations observed from kinetic data result solely from acidity, basicity, substituent, or solvent effects on the reaction free energy (thermodynamic effect) or do they reflect also a kinetic effect related to a shift in the transition-state position?[3] To answer these fundamental questions, the attention is mainly focused on curvatures in rate–equilibrium relationships and on intrinsic kinetic barriers deduced from them since these supply quantitative data on the transition state and its dependence on the reactivity.[4] When equilibrium data are not available, thermodynamic and kinetic contributions to the selectivity coefficients could perhaps be separated out from rate–selectivity relationships. However, this possibility has until now received little attention because ρ–log k or m–log k relationships are scarce and/or cover narrow reactivity ranges.

In this respect, the idea of using deactivating groups[5] such as trifluoromethyl to extend the range of S_N1 solvolysis could be a step in the right direction since the very negative ρ^+ value, −7.46, obtained for ethanolysis of the 1-aryl-1-(trifluoromethyl)ethyl tosylates,[6] increases the range of the rate–selectivity relationship,[7] $\rho = f(\log k)$, by 2.2 units of ρ. Unfortunately, solvolysis data have been obtained in such a variety of experimental conditions, involving different leaving groups, temperature, or solvent, that it is impossible to attain the precision necessary for quantitative interpretations.

In this paper, we report results on the bromination of α-methoxystyrenes in which the methoxy group strongly enhances the electrophilic reactivity of the double bond. Bromination is a well-documented reaction for which kinetic data have been obtained under rigorously standardized conditions;[8] it should be possible to include the results for α-methoxystyrenes in a wide-ranging rate–selectivity relationship.[9] Moreover, available data on the hydrolysis of these enol ethers[10] make it possible to compare directly bromination and hydration, two closely related electrophilic additions leading to benzylic carbocations. Since the rates of these additions, but probably not their equilibria, respond differently to substituent effects, this comparison could give useful information about the selectivity-determining factors. Thus, although rate–equilibrium relationships are available for neither addition, some knowledge of the balance between the thermodynamic and intrinsic kinetic contributions to the reactivity of these systems would be acquired.

Results

Bromination rate constants of α-methoxystyrenes **1a–h** are measured by couloamperometry[11] at 25 °C in methanol containing 0.2 M NaBr.

In this medium, the experimental rate constants are composite[12] since the analytical bromine concentration is the sum of two electrophilic species: free bromine and tribromide ion, related

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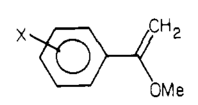

1a, X = 4-OMe **1e**, X = 3-Cl
b, X = 4-Me **f**, X = 3-CF$_3$
c, X = H **g**, X = 3-NO$_2$
d, X = 4-F **h**, X = 4-NO$_2$

to each other by the equilibrium

$$Br_2 + Br^- \overset{K}{\rightleftharpoons} Br_3^- \qquad (1)$$

The rate constant, k, for free bromine addition is obtained by extrapolating the experimental bromide ion effect to [Br$^-$] = 0, according to the classical equation[12]

$$k_{\text{exptl}}(1 + K[\text{Br}^-]) = k + \beta[\text{Br}^-] \qquad (2)$$

Rate constants k for **1a**, **1c**, and **1h** are measured by this method (Table IV). It has been shown[12] that structural effects on k and k_{exptl} are parallel if the ratios, $Q = k_{\text{Br}_2}/k_{\text{Br}_3^-}$, are higher than 16 in methanol. For compounds **1a**, **1c**, and **1h**, Q is 1530, 160, and 40, respectively. It is, therefore, possible to use[12] the empirical linear relationship (eq 3) established from these three compounds in order to obtain log k for the other α-methoxystyrenes **1b**, **1d**, **1e**, **1f**, and **1g**. The results are given in Table I.

$$\log k = 1.15 \log k_{\text{exptl}} + 0.32 \qquad (R = 0.999) \qquad (3)$$

For bromination, the diffusion-controlled rate is considered[13] to be near (5 × 10^9)–10^{10} M^{-1} s^{-1}. Therefore, bromination rates for α-methoxystyrenes, although very high, cannot be considered to be diffusion controlled. Only for **1a** does the measured rate constant very closely approach this limit; however, since this compound does not deviate significantly from the general $\sigma\rho$ relationship, it can be assumed that **1a** is not diffusion controlled.

Substituent effects on α-methoxystyrene bromination are fairly correlated by σ^n substituent constants[14] (Figure 1). The correlation

$$\log k = -1.85\sigma^n + 9.22 \qquad R = 0.998 \qquad s_\rho = 0.05 \qquad (4)$$

using σ^0 constants is almost as satisfactory ($\rho^0 = -1.83$, $R = 0.997$), but we prefer relationship 4 since it facilitates comparison with hydration reactions for which σ^n constants have been used. σ^+ constants are inappropriate, the log k–σ^+ plot showing pronounced curvature. The fact that **1d** is less reactive than **1c** confirms the fitness of σ^n constants ($\sigma^n_{4\text{-F}} > 0$ but $\sigma^+_{4\text{-F}} < 0$).

Table I. Experimental Substituent and Solvent Effects in α-Methoxystyrene Bromination

X	k_{exptl}[a]	log k[b]	$m_{\text{W-G}}$[c]
4-NO$_2$	2.95 × 10^6	7.79	
3-NO$_2$	4.10 × 10^6	7.92	0.48
3-CF$_3$	9.20 × 10^6	8.32	0.47
3-Cl	1.47 × 10^7	8.55	0.46
4-F	2.88 × 10^7	8.90	
H	6.90 × 10^7	9.32	0.44
4-Me	7.95 × 10^7	9.40	
4-OMe	1.00 × 10^8	9.54	

[a] k in M^{-1} s^{-1} in methanol, 0.2 M NaBr at 25 °C. [b] Rate constant for free bromine addition, obtained either by extrapolation of kinetic bromide ion effect or from eq 3. [c] Winstein–Grunwald coefficient for solvent effects; ref 23.

Table II. Coefficients of Free Energy Relationships for Ring Substituent and Solvent Effects on Bromination of Styrenes, X–C$_6$H$_4$–C(Y)=CH$_2$

Y	ρ^n_{MeOH}	ρ^r_{MeOH}	log k_{MeOH}	$\rho^n_{\text{H}_2\text{O}}$[a]	$m_{\text{W-G}}$
H[b]	−4.80	−4.80	2.77		0.96[c]
Me[b]	−4.26	−2.8	5.14	−3.2	0.86[a]
OMe[d]	−1.85	0	9.32	−1.5	0.45[a]
OH[e]	0	0	*e*	0	

[a] Reference 23. [b] Reference 24. [c] Reference 22. [d] This work. [e] Enol bromination is diffusion controlled; ref 25.

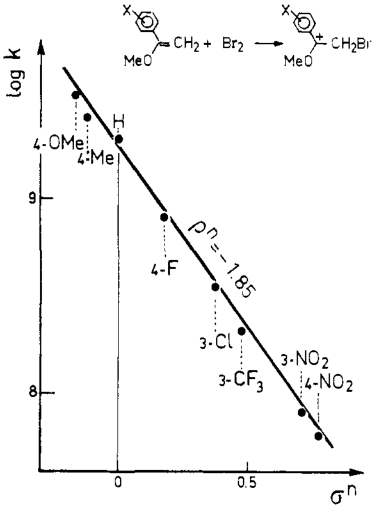

Figure 1. The $\rho\sigma$ relationship for α-methoxystyrene bromination.

Discussion

Early Transition States in α-Methoxystyrene Bromination. Substituent effects on α-methoxystyrene bromination are particularly small: ρ^n is only −1.85. The second striking point is the absence of conjugation between the ring substituent and the cationic center, as revealed by the fact that σ^n, and not σ^+, is appropriate. Such small |ρ| values for reactions via cationic intermediates have already been observed in S$_N$1 solvolysis of aryldi-*tert*-butylcarbinyl *p*-nitrobenzoates.[15] In this case low substituent effects are associated with small solvent effects, and the decrease of both substituent (ρ) and solvent[16] ($m_{\text{W-G}}$) coefficients has been attributed to an early transition state due to F-strain effects. In the bromination of α-methoxystyrenes the attenuation of substituent effects cannot result from steric effects since the hybridization does not change on going from ground to transition state. However, several other factors can lead to very low |ρ| values. Some of them are readily excluded for methoxystyrene bromination, i.e., solvent nucleophilic assistance is not expected for a very fast reaction leading to a stable cation.[17] Analogously, intervention of a bromonium ion pathway is highly improbable[18] due to the presence of the strongly electron-donating methoxy group on the double bond.[19] On the other hand, the very small |ρ| value and the absence of conjugation between X and the cationic center could be attributed to an early transition state, as required by the highly resonantly stabilized intermediate,[20] and/or to an increase of the substituent–charge distance due to

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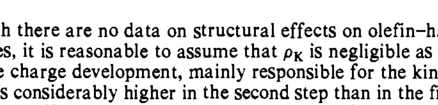

Although there are no data on structural effects on olefin–halogen complex stabilities, it is reasonable to assume that ρ_K is negligible as compared to ρ_d since the charge development, mainly responsible for the kinetic substituent effects, is considerably higher in the second step than in the first. Moreover, substituent effects on ketone–halogen complex formation (Laurence, C.; Guiheneuf, G.; Wojtkowiak, B. *J. Am. Chem. Soc.* **1979**, *101*, 4793–4801) overestimate the same effects on the halogen–olefin complexes. Comparison of the data for ketone CTC's with bromination rate constants of isologous olefins confirms that ρ_K is small as compared to ρ_d ($\rho_K \leq 0.07\rho_d$).

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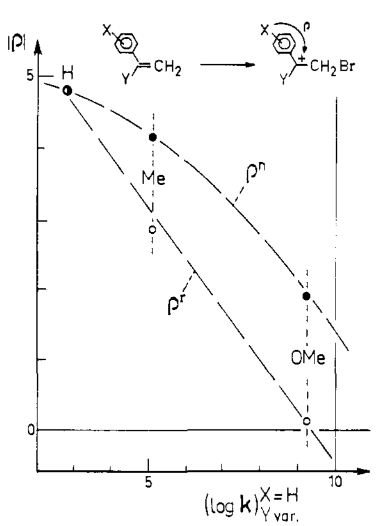
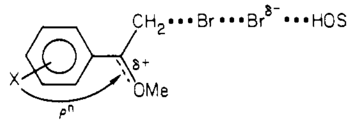


Figure 2. Selectivity relationships in bromination of X—C_6H—C(Y)=CH_2 styrenes with variable Y. Only ρ^r, the sensitivity to resonance effects of X, is linearly related to the reactivity.

charge delocalization[21] in the methoxy group. To distinguish between the effects of these two factors, it would be useful to evaluate the total charge developed at the transition state. To this end, we measured kinetic solvent effects which in bromination are known to be related principally to the charge on the leaving bromide ion.[22]



The measured solvent effect (Table I) corresponds to a very small *m* value. Consequently, the low values of both ρ and *m* are in agreement with an early transition state. Changes in charge distribution, superimposed on this Hammond effect, may reinforce the attenuation of the ring substituent effects. In addition to its kinetic effect (transition-state shift), the enhancement of the intermediate stability by resonance saturation has a thermodynamic effect on the ρ and *m* parameters since resonance saturation diminishes the influence of the solvent and the substituents on the formation of the α-methoxy carbocation.[21] Conclusively, attenuation of ρ and *m* values for α-methoxystyrene bromination results from a shift in the transition-state position, from a lengthening in the charge–substituent distance and from resonance saturation. The purpose of the following discussion is to separate the relative contributions of these three factors.

Rate–Selectivity Relationships in the Bromination of Styrenes. An early transition state for the highly reactive methoxystyrenes suggests the existence of a rate–selectivity relationship in bromination. To check this proposal, we compare in Table II the ring substituent effects in the methanolic bromination of several styrenes,[24,25] X—C_6H_4—C(Y)=CH_2, of differing reactivities. As expected, the reactivity increase corresponds roughly to an attenuation of both polar and resonance effects, expressed by ρ^n and ρ^r, respectively.[26] The rate–selectivity relationships based on the data of Table II are approximately linear for ρ^r but not for ρ^n (Figure 2). The curvature of the ρ^n–log *k* plot can be attributed to the change in the charge distribution due to charge delocalization in Y. This assumption is confirmed by the linearity of the ρ^r–log *k* plot: since there is through conjugation between the charge and the substituent, ρ^r has nothing to do with the charge distribution, neither in bromination nor in protonation (vide infra). Therefore, the problem of the balance between the transition-state position and the thermodynamic contribution should be approached via ρ^r and not ρ^n. It is not possible to estimate quantitatively the relative magnitude of these contributions from the data of Table II only. However, the large *m* variations (Table II) imply a considerable shift in the transition-state position in bromination.

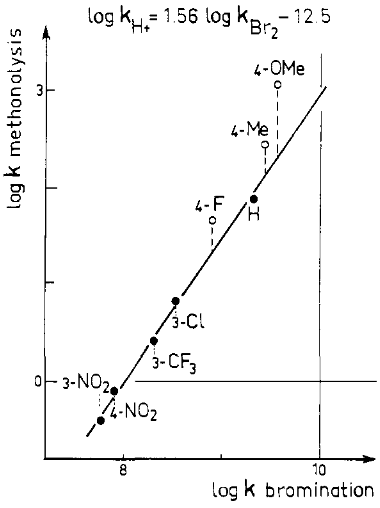
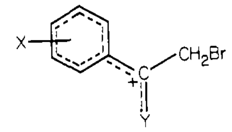


Figure 3. Ring substituent effects on methanolic bromination and methanolysis of α-methoxystyrenes.

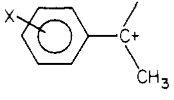
Table III. ρ Values for Ring Substituent Effects in Protonation of Styrenes, X–C_6H_4–C(Y)=CH_2

Y	$\rho^n_{H_2O}$	$\rho^r_{H_2O}$	$\log k_{H_2O}{}^a$	ρ^n_{MeOH}	α^b
H^c	−3.6	−3.4	−6.96	-4.3^d	
Me^c	−3.4	−2.4	−4.02	-4.05^d	0.6^c
OMe	-2.33^e	-0.97^e	1.74^e	-2.89^f	0.6^f
OH^g	−1.57	−0.75	3.24	−1.9	0.6

[a] *k* in $M^{-1}\,s^{-1}$ at 25 °C, extrapolated to $[H^+] = 0$. [b] Brønsted exponent. [c] Reference 30. [d] Estimated from the solvent effect on methoxystyrene protonation, see text. [e] Reference 10. [f] Reference 29. [g] Reference 25.



Comparison of Protonation and Bromination. The rate-determining step in olefin hydration is the proton transfer from an acid to the double bond.[27] This reaction is, therefore, an electrophilic addition which leads to carbocations analogous to those formed in bromination. Although the substituent effects on the stabilities of benzylic cations in hydroxylic media are unknown, it is reasonable to assume that the effect of Y on the ρ values for the thermodynamic data (ρ^t) on ions **2** and **3** is rather similar.[28] Consequently, comparison of the kinetic data on these two additions should reflect the differences in their transition states.



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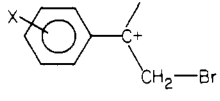

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Table IV. Experimental Rate Constants of α-Methoxystyrene Bromination at Various Bromide Ion Concentrations in Methanol at 25 °C

X	k_{exptl}[a]				k[d]	Q[e]
	0.1 M	0.2 M	0.3 M	0.4 M		
4-NO_2[b]	4.85×10^6	2.95×10^6	2.38×10^6		6.20×10^7	40
H[c]	1.25×10^8	6.90×10^7	5.05×10^7		2.10×10^9	160
4-OMe[c]		1.00×10^8	6.80×10^7	5.20×10^7	3.45×10^9	1530

[a] In $M^{-1}\ s^{-1}$. [b] k_{exptl} at ±2%. [c] k_{exptl} at ±4%. [d] k for free bromine addition at ±5%, extrapolated by eq 2 to $[Br^-] = 0$. [e] $Q = k_{Br_2}/k_{Br_3^-}$; ref 12.

An important study on α-methoxystyrene methanolysis has recently been reported,[29] and a direct comparison with bromination is possible. From the log k–log k plot of Figure 3, it appears that methanolysis is more sensitive to substituent polar effects than bromination and, since conjugated substituents deviate from the line defined by nonconjugated substituents, that the relative contributions of polar and resonance effects are not the same in these reactions. The differences are expressed by different ρ^n and ρ^r values, −2.89 and −1.00, respectively, for methanolysis whereas for bromination ρ^r is nil and ρ^n is −1.85. The greater sensitivity of α-methoxystyrene methanolysis is rather unexpected since generally ρ values are smaller for olefin hydration than for bromination.[8] In fact, the inversion of reaction constants for the bromination and protonation of methoxystyrene is due only to the greater Y dependence of bromination, as shown below in a more extensive comparison. As a preliminary to this comparison, since their rates have not been measured in the same solvent, it is necessary to estimate the effect on these reactions of changing the solvent from water to methanol.

In Table III are listed the available data on hydration of various substituted styrenes.[25,29,30] Part of the difference between protonation and bromination must be due to a solvent effect since the change of the medium dielectric constant changes[31] ρ^n from −2.89 in methanol to −2.33 in water and does not significantly alter ρ^r, when Y is OMe. The ρ^n values for styrene protonation in methanol have been estimated from these data on the assumption that the local dielectric constant is not seriously affected by the substituent Y and that the differences between lyonium and hydronium ions are not very large.[29] These estimates are reliable only if the extent of proton transfer does not change significantly with Y; the almost constant α-Brønsted exponent suggests that this assumption is reasonable. On the other hand, going from water to methanol does not change ρ^r for α-methoxystyrenes. This result can be extended to the other styrenes since resonance, an intrinsic property of reactants and transition states, should not be solvent dependent.[32] Protonation data in methanol, estimated along these lines, are gathered in Table III.

In Figure 4, the dependence of ρ on Y is compared for bromination and protonation, both in methanol. The two reactions can also be compared in water, since some data on bromination in this medium are available (Table II). The resulting linear correlations are as follows:

$$\rho^n_{Br_2,MeOH} = 2.06\rho^n_{H^+,MeOH} + 3.86 \quad (R = 0.999,\ s = 0.08) \tag{5}$$

$$\rho^r_{Br_2,MeOH} = 2.00\rho^r_{H^+,MeOH} + 2.0 \quad (R = 0.999,\ s = 0.01) \tag{6}$$

$$\rho^n_{Br_2,H_2O} = 1.74\rho^n_{H^+,H_2O} + 2.67 \qquad (R = 0.998,\ s = 0.14) \tag{7}$$

It appears from these equations that ρ^n and ρ^r are much more sensitive to Y in bromination than in protonation and that polar and resonance effects run parallel in methanol.

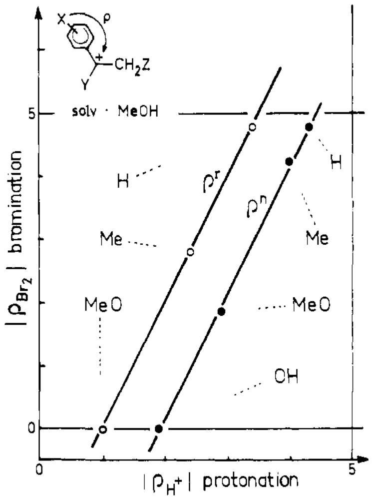

Figure 4. Comparison of ρ values *for bromination and protonation of styrenes*, $X—C_6H_4—C(Y)=CH_2$, with variable Y. Selectivity coefficients depend on Y more in bromination than in protonation.

The Balance between Thermodynamic and Intrinsic Kinetic Contributions to the ρ Variations. Since the substituent effects on the stabilities of cations **2** and **3** (thermodynamic effect on ρ) are probably similar, the slopes of eq 5–7 reflect differences in the sensitivity to Y of the transition-state position of these two additions. In protonation, the experimentally measured Brønsted exponent does not depend significantly on Y, i.e., the transition-state position is not greatly affected when Y goes from H to OH; therefore, ρ variation in protonation is mainly due to thermodynamic factors[28] and may be used to estimate the thermodynamic contribution in bromination. From eq 5 or 6, it appears that the superimposed intervention of an intrinsic kinetic contribution enhances the ρ dependence on Y in bromination by a factor of about 2.

It is surprising that eq 5 and 6 are linear although the balance between the thermodynamic and kinetic contributions differs in protonation and bromination. A variation in the transition-state position would not basically modify but only enhances the influence of the thermodynamic factors. This result may be rationalized by considering the classical relationships between kinetics and thermodynamics.[4,33] The second term of eq 9 is negligible in

$$\rho^k = \partial\Delta G^{\ddagger} = \alpha\partial\Delta G^{\circ} = \alpha\rho^t \tag{8}$$

$$\frac{\partial\rho^k}{\partial Y} = \alpha\frac{\partial\rho^t}{\partial Y} + \rho^t\frac{\partial\alpha}{\partial Y} \tag{9}$$

protonation but not in bromination. A linear relationship between ρ values for these two additions could imply in particular that $\partial\alpha/\partial Y$ is related to $\partial\rho^t/\partial Y$. If the Marcus equation is chosen to describe α,[34] this relationship would suggest that the ρ^t de-

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[31] This assumption is supported by recent work by Ehrenson: Ehrenson, S. *J. Am. Chem. Soc.* **1982**, *104*, 4793–4798.

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[34] It is obvious that the Marcus equation cannot be applied in bromination, but it is chosen here to emphasize that $\delta\alpha$ should be proportional to $\delta\Delta G_0$ and inversely proportional to c. The same trend is expected in any more sophisticated equation relating the transition-state position to the free energy changes.

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pendence on Y is proportional to the effect of Y on bromination free energy. Whatever the restrictions imposed by eq 5 and 6

$$\alpha = \tfrac{1}{2} + \Delta G^\circ/8c \tag{10}$$

$$\frac{\partial \alpha}{\partial Y} = \frac{1}{8c}\,\frac{\partial \Delta G^\circ}{\partial Y} \tag{11}$$

on the relative variations of ρ^t and α, our experimental results support a much higher intrinsic barrier for protonation than for bromination.

It is also noteworthy that eq 5 for ρ^n is linear and exhibits the same slope as eq 6 for ρ^r, although ρ^n and not ρ^r depends on the charge-substituent distance (vide supra). The similarity in the behavior of these coefficients suggests that changes in charge distribution due to charge delocalization are similar in both reactions and proportional to the resonance effect on the thermodynamic contribution. This result is in agreement with recent findings of Jencks[35] concerning the absence of a specific role of resonance delocalization on the transition-state position for proton-transfer reactions.

Concluding Remarks. Change in charge distribution due to delocalization in Y makes the rate–selectivity relationship curved for protonation and bromination of Y-substituted styrenes, when the selectivity coefficient is ρ^n. When ρ^r, a coefficient insensitive to charge distribution, is chosen the same relationship is a straight line and the ρ^r variation is due only to thermodynamic and intrinsic kinetic factors. In protonation there is no substantial dependence of the transition-state position on the reactivity so that the variation of the selectivity coefficient, ρ^r, for this reaction is mainly due to thermodynamic factors. Therefore, this addition is used as a reference for separating out the role of the change in transition-state position in bromination: the intervention of this latter term approximately doubles the sensitivity of bromination to the other selectivity-determining factors. It is noteworthy that the variation of the transition-state charge with the reactivity does not modify but only enhances the effect of the thermodynamic contribution.

To go deeper in the meaning of the selectivity coefficients, it would be instructive to understand why such closely related electrophilic additions behave so differently as regards the dependence of the transition-state charge on the reactivity; further data on these reactions must be available before the various possible interpretations can be discussed.

Experimental Section

Synthesis of α-methoxystyrenes and the kinetic procedure[11] have been published already.

Determination of k, the Rate Constant for the Free Bromine Addition. Experimental rate constants, k_{exptl}, are measured at three bromide ion concentrations. As previously shown, the bromide ion effect follows eq 2 where K is the equilibrium constant of the Br_2/Br_3^- equilibrium; β is usually identified with $Kk_{Br_3^-}$ where $k_{Br_3^-}$ is the rate constant for tribromide ion addition.[12] Thus the plot of $k_{\mathrm{exptl}}(1 + K[Br^-])$ against $[Br^-]$ gives k at $[Br^-] = 0$ and $k_{Br_3^-}$ from the slope (Table IV).

Registry No. 1a, 51440-56-3; **1b**, 51440-57-4; **1c**, 4747-13-1; **1d**, 67471-38-9; **1e**, 89726-07-8; **1f**, 89726-06-7; **1g**, 89726-05-6; **1h**, 3440-23-1.

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S_N2 Reactions of Nitranions with Benzyl Chlorides

Frederick G. Bordwell* and David L. Hughes

Contribution from the Department of Chemistry, Northwestern University,
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Abstract: The rates of S_N2 reactions of 19 nitranions with $PhCH_2Cl$ and 9 nitranions with m-$CF_3C_6H_4CH_2Cl$ were measured in Me_2SO at 25 °C. Brønsted plots of log k vs. pK_{HA} for reactions of anion families derived from carbazoles, phenothiazines, and diphenylamines with $PhCH_2Cl$ are linear with slopes of 0.32–0.33. Extension of the carbazole and phenothiazine family lines, which are collinear, provided a reference line by which nucleophilicities of other nitranions could be assessed at constant basicity. Nitranions of varied structural types were found to have remarkably similar nucleophilicities when compared at the same basicities. Steric effects caused rates of reactions of $ArAr'N^-$ ions and acetanilide ion to be retarded slightly and that of benzanilide ion to be retarded appreciably. Evidence is presented to show that nitranions, like carbanions, utilize the electron pair in a p orbital for bonding to an electrophile whereas pyridines utilize a nonbonded electron pair. Comparisons with literature data for neutral nitrogen nucleophiles, such as n-$BuNH_2$ and $PhNH_2$, indicate that they are 10–100 times more reactive than nitranion nucleophiles of comparable basicity. The order of nucleophilicities toward $PhCH_2Cl$ of anion families with different donor atoms when compared at the same basicity was found to be the following: 9-methylfluorenide ion family (25) > 2-naphthoxide ion family (3) > carbazole ion family (1.0). The results show that basicity is the primary factor in controlling nucleophilicities of nitranions, carbanions, and oxanions of diverse structural types in S_N2 reactions. Donor atom, solvation, and steric effects generally play a secondary role.

The alkylation of nitrogen anions (nitranions) has played an important role in synthetic organic chemistry since Gabriel showed nearly a century ago that reactions of phthalimide ion with alkyl halides, followed by hydrolysis, could provide a preparative route to primary amines.[1] Alkylations of these and other common nitranions, including those derived from sulfonamides,[2,3] cyanamides,[4] carboxamides,[5] pyrroles,[6] indoles,[7] carbazoles,[8] phenothiazines,[9] and diphenylamines,[10] have since been widely used in

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