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Selectivity Relationships and Substituent–Substituent Interactions in Carbocation-Forming Bromination. The Transition-State Contribution to the ρ Variation[†]

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Abstract: For arylolefin bromination through benzylic carbocations, $X\text{–}C_6H_4\text{–}C^+(R)\text{–}CHBr\text{–}R'$, there are 18 reaction constants, ρ^R, describing ring-substituent effect X, which vary from −1.6 to −5.9 depending on R and R′ (H, Me, OMe, or Ar′). This reaction has, therefore, been chosen as a model for determining the factors which affect ρ in carbocation-forming reactions. The ρ^R values are found to be dependent on the reactivity, log $k_H{}^R$, of the parent olefin. Two precise relationships, $\rho^R = a \log k_H{}^R + b$, are obtained, one where R is H or Me (set A) with $a = 0.26$ and the other with $a = 0.46$ where R is a conjugatively electron-donating group such as Ar′ or OMe (set B). In bromination, the expected inverse relationship between selectivity and reactivity is observed only if olefins included in the same set are compared. A resonant substituent R (set B) not only decreases the ρ^R value but also increases its sensitivity to the reactivity. The a value for rates, a^k, arises from the superposition of a thermodynamic contribution and of an intrinsic kinetic contribution related to the transition-state position. In both sets, the variation of the transition-state position contributes to the a value. In set A, the thermodynamic term can be neglected with respect to the kinetic one, whereas in set B, the higher a^k value results from the additional intervention of a significant thermodynamic term. This interpretation is supported experimentally by solvent effects and by comparison with available data on S_N1 solvolysis leading to carbocations analogous to bromination intermediates.

Most of the information concerning the mechanism of a reaction obtained from LFER's comes[1] from the interpretation of the reaction constant ρ. However, though ρ is a quantitative value its interpretation is based mainly on qualitative analogical comparison between closely related reactions and is still the object of controversy.[1c] Depending on the author's viewpoint, quite different mechanistic interpretations of ρ are given. The most general states that ρ is a measure of the charge seen by the substituent,[2] but this encompasses others such as the measure of the electronic demand,[3] of the charge delocalization,[4] of the transition-state position,[5] and/or of the transmission of substituent effects.[6,7] This list is in fact a short inventory of the factors commonly supposed to have an effect on ρ. Since these factors are not independent, it has been most often impossible to distinguish their effects. This explains why ρ has not yet been given a definite mechanistic interpretation.

Several attempts have been made to ascribe a quantum mechanical meaning to ρ^+ when the intermediate is a carbocation.[8-10] However, these methods deal only with carbocation energies and cannot constitute a general approach to the identification of the factors which affect ρ.

IFER for MSE (Interactive Free Energy Relationships for Multiple Substituent Effects) opens the way to a quantitative evaluation of the ρ variation.[11] In this formalism the ρ value for one substituent, X, depends on the other, Y, according to relationship 1 where the structural changes are described by a substituent constant. The requirement that σ_Y be known limits the

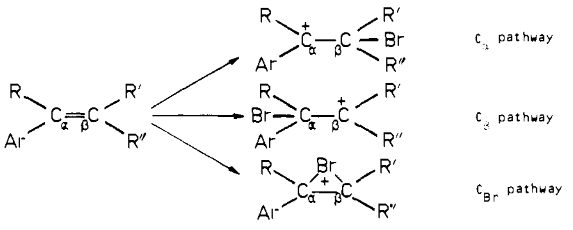
$$\rho^Y = \rho^H + q\sigma_Y \tag{1}$$

$$\rho^R = a \log k_H{}^R + b \tag{2}$$

application of eq 1 to systems where the reactivity and the ρ variation are affected only by the physicochemical factors involved in the substituent constant σ_Y. In order to overcome this limitation, one can describe the ρ variation by a classical selectivity relationship 2 where the substituent effect on ρ is expressed by its effect on the reactivity.[4b,12] No assumptions about the origin of the substituent effect is needed, relationship 2 assuming only that the effects on ρ and on reactivity are of similar nature. Although the formalism of eq 2 is well established, it has been only seldom and partially justified experimentally.

Scheme I

Scheme II



The main objective of this paper is to determine the factors which cause ρ to vary and particularly to distinguish between the influence of the transition-state position and that of the thermodynamic contribution to the reactivity. To this end, reliable quantitative information must be obtained: ρ values must be measured under standardized conditions over a large range of structural changes, for a reactivity-independent mechanism. All

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Table I. Reaction Constants ρ for the Bromination of Arylolefin $X—C_6H_4—C(R)=CHR'$ in Methanol at 25 °C.

no.	R	R′	$-\rho$	log k_H[a]
1	H	H	4.80	2.77
2	Me	H	4.26	5.14
3	H	Me	4.72	2.87
4	H	C_6H_5	5.52	-0.02
5	H	4-Cl-C_6H_4	5.63	-0.41
6	H	3-Cl-C_6H_4	5.70	-0.66
7	H	4-NO_2-C_6H_4	5.91	-1.36
8	Me	C_6H_5	4.87	2.65
9	Me	4-MeC_6H_4	4.69	2.90
10	Me	3-CF_3-C_6H_4	5.17	1.72
11	OMe	H	1.58	9.00
12	3-NO_2-C_6H_4	H	4.65	2.27
13	3-Cl-C_6H_4	H	4.08	3.27
14	4-Br-C_6H_4	H	3.67	3.96
15	C_6H_5	H	3.57	4.62
16	3-Me-C_6H_4	H	3.42	4.91
17	4-Me-C_6H_4	H	3.03	5.58
18	4-MeO-C_6H_4	H	2.27	6.95

[a] Rate constants of free bromine addition to $H—C_6H_4—C(R)=CHR'$, in $M^{-1}\ s^{-1}$.

these requirements are met in arylolefin bromination which is a convenient model for reactions with carbocationic intermediates. We therefore investigate ρ^R variation in carbocation-forming bromination of arylolefins $X—C_6H_4—C(R)=CH—R'$ (Scheme I) where R and R′ are chosen specially to discriminate between polar and resonance effects on ρ^R for the ring substituent X. The balance between thermodynamic and intrinsic kinetic contribution can, then, be assessed by comparing selectivity results on conjugated and unconjugated olefin reaction.

The Acquisition of Standardized Data in Bromination via Carbocationic Intermediates

The general mechanism for the electrophilic bromination of olefin (Scheme II) can be described by a three-pathway scheme.[13] Two of them lead to carbenium ions, C_α^+ and C_β^+, and the third to the bromonium ion, C_{Br}^+. Only the parameters of the C_α pathway are of interest for our study of the variation of ρ.

When the aromatic ring and the substituent R are sufficiently electron releasing to stabilize the charge on the C_α carbon in the transition state, only the C_α pathway is followed. This has been shown in α-methylstyrene[14] (R = Me; R′ = H), α-methylstilbene[15] (R = Me; R′ = C_6H_5), 1,1-diarylethylene[16] (R = C_6H_4-Y; R′ = H), and α-methoxystyrene[17] (R = OMe; R′ = H) bromination. For these compounds the ρ value of the C_α path is readily determined from the kinetic effect of ring substituents. For α-methylstilbenes[18] (R = Me; R′ = C_6H_4-Y) when Y is a strongly electron-donating group, the C_β pathway competes with C_α. However, the values of ρ and the rate constant of each pathway can be obtained from a Hammett-type analysis of the experimental data. In the bromination of styrenes,[14] the bromonium ion intermediate is formed competitively with the benzylic cation when the ring substituent is electron attracting. Rate constants and reaction constants have been obtained by an iteration procedure which selects the ρ values of the dual pathway scheme most closely corresponding to the experimental results. The same treatment has been used for stilbene bromination (R = H; R′ = C_6H_4-Y) where the competition between the three pathways depends on the substituents.[19]

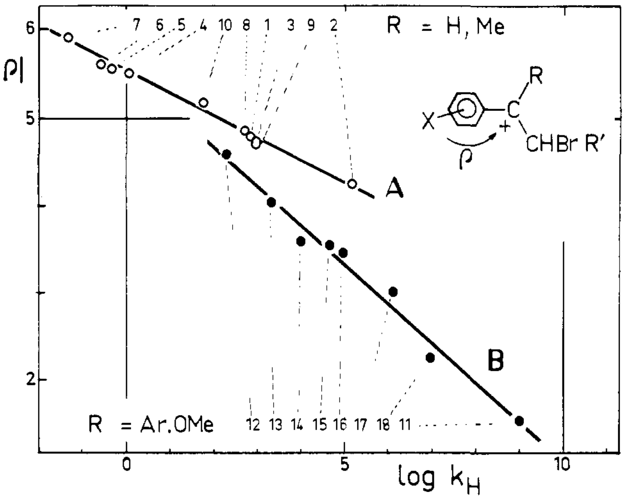

Figure 1. Selectivity relationships in arylolefin bromination.

Since the substituents R and R′ are not bulky, there is no primary steric effect. However, when R is not a hydrogen the aromatic ring bearing the substituent X is more or less rotated out of the plane of the double bond or of the carbocationic intermediate due to the crowding around C_α. The resonance interaction between the substituent X and the carbon that bears the charge is modified. The ρ values have therefore been calculated by the Yukawa–Tsuno procedure,[20] i.e., from the meta-substituted compounds only, to avoid the inclusion of this secondary steric effect on ρ.

The ρ values obtained in this way are listed in Table I, with the rate constants of the corresponding unsubstituted compound (X = H). All the ρ values correspond to a rigorously constant mechanism and to standardized experimental conditions. They are obtained from the second-order rate constants of the non-nucleophilically assisted free bromine addition.[21] According to the Ad_EC1 mechanism the rate-determining step is the breaking of the Br–Br bond and the formation of the C–Br bond. The rate constants have been measured in the same solvent, methanol, at the same temperature, 25 °C, using reactant concentrations below 10^{-3} M. These conditions have been chosen to exclude the occurrence of other mechanisms[22,23] (termolecular addition, assistance by bromide ion or solvent...).

Selectivity Relationships

When our data on $|\rho|$ are plotted against log k_H (Figure 1), two straight lines are obtained which separately correlate 1,1-diarylethylenes (**12–18**) and α-methoxystyrene (**11**) for line B and styrenes (**1–3**) and stilbenes (**4–10**) for line A. The following correlations are obtained for A and B: The arylolefins of set

$$\text{Set A}\quad \rho = 0.26 \log k_H - 5.53;\ R = 0.995,\ s = 0.009 \qquad (3)$$

$$\text{Set B}\quad \rho = 0.46 \log k_H - 5.61;\ R = 0.995,\ s = 0.019 \qquad (4)$$

B are about twice as sensitive to reactivity effects as those of set A.

The results of the selectivity relationships can be shown to be consistent with those obtained from the IFER for MSE. The coefficients of these expressions, $a(=\partial\rho/\partial \log k)$ and $q\ (=\partial\rho/\partial\sigma)$, are related by eq 5.

$$a = \frac{\partial\rho}{\partial\sigma}\,\frac{\partial\sigma}{\partial \log k} = \frac{q}{\rho} \qquad (5)$$

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Table II. Variation of the Transition-State Position in the Bromination of Styrenes and Stilbenes; Parallelism between Structure and Solvent effects

	$\log k_{M70}/k_{MeOH}$[a]	ρ	$\log k_H$
stilbene	2.33	−5.52	−0.02
α-methylstilbene	2.01	−4.87	2.65
styrene	2.10	−4.80	2.77
α-methylstyrene	1.76	−4.26	5.14

[a] M70: methanol–30% v/v water.

Equation 5 is readily tested on 1,1-diarylethylenes ($R = C_6H_4$–Y and R′ = H, compounds **12–18** in Table I) where q, −1.55, and ρ^H, −3.57, lead to a calculated a value, 0.44, similar to that in relationship 4. Similarly, for the stilbenes (R = H and $R' = C_6H_4$–Y, compounds **4–7** in Table I) included in selectivity relationship 3, the q value obtained is −0.5; associated with $\rho^H = -1.7$, this leads to an a value of 0.29 very close to the experimental value of 0.26. The agreement is poorer for α-methylstilbenes (0.42 instead of 0.26). However, considering the differences between the methods of calculating the parameters a and q it is sufficient to justify relationship 5.

A selectivity relationship, eq 6, has been found in solvolysis but it is rather approximate because the data are extrapolated from widely differing experimental conditions.[24] Equation 6, analogous to eq 4, can only be used to detect large mechanistic changes such as anchimeric assistance as long as changes in reactivity are not less than several logarithmic units.

$$\rho = 0.57 \log k - 0.19 \qquad R = 0.912 \qquad (6)$$

A similar situation can be considered for hydration of olefins where a single $\rho\sigma$ relationship has been proposed to account for the acid-catalyzed hydration of all olefins.[4a] This interpretation assumes that the ρ value is the same for all the arylolefins and that variations in transition-state position do not exist in hydration. However, the constancy of ρ is only approximative since when homogeneous populations are singled out, significant variations of ρ appear.[25,26] For instance, for styrenes X–C_6H_4–C(R)=CH_2, ρ decreases from −2.2 to −2.9 and even −4.0 when R is OMe, H, and CF_3, respectively. In view of our results in bromination, it is not possible to maintain that these variations of ρ are negligible. In hydration as in bromination, ρ varies with the reactivity even if the amplitude of the variation is less than in bromination.

How the Selectivity Coefficients *a* Reflect a Variation in the Transition-State Position

Any discussion of the selectivity coefficients for bromination in terms of the thermodynamic and intrinsic kinetic components[27] of the reactivity must account for the following results: (i) the dependence of the kinetic selectivity, expressed by ρ, on the reactivity is in agreement with RSP[4,12,28] only if two olefins included in the same selectivity relationship are compared; (ii) the resonant character of R modifies the selectivity coefficient, a, and for a substituent R capable of charge delocalization, ρ is smaller and more sensitive to the reactivity than when R is not conjugated. Smaller ρ in set B are readily interpreted by a decrease in the net charge on the benzylic carbon atom, due to charge delocalization by R. But the interpretation of the differences in the selectivity coefficients needs closer examination of the a-determining factors.

The intrinsic kinetic contribution and the thermodynamic contribution[29] to the a value can be separated via relationship 7 obtained by differentiating the usual expression,[1b,30] $\rho^k = \alpha\rho^t$, where ρ^k expresses the substituent effects on rates, ρ^t that on the corresponding equilibria, and α the transition-state position.

$$a^k = \frac{q^k}{\rho^k} = \frac{q^t}{\rho^t} + \frac{1}{\alpha}\frac{\partial\alpha}{\partial\sigma} = a^t + \frac{1}{\alpha}\frac{\partial\alpha}{\partial\sigma} \qquad (7)$$

The thermodynamic contribution in set A can be neglected since R is an unconjugated substituent;[31] then the major part of the a value should arise from the kinetic contribution related to a variation in the transition-state position. The influence of this latter factor is experimentally evidenced by the parallel trends of solvent effects and ρ values (Table II). Solvent effects in bromination result principally from electrophilic assistance to the departure of the bromide ion and express the charge separation at the transition state.[32] Variation of ρ associated with variation of the solvent effects shows, therefore, that ρ reflects at least in part a variation in the transition state and that the second term of eq 7 contributes significantly to the a value in set A (eq 3).

In set B, the thermodynamic term, which is no longer negligible, should add to the kinetic term, leading to a higher a value in the selectivity relationship. This assumption could be tested if it were possible to compare substituent effects on rates and on the corresponding equilibria. Thermodynamic data are not available at present for bromination but they are for methanolysis of benzhydryl chlorides, a reaction analogous to methanolic bromination of 1,1-diphenylethylenes. From the solvolysis rates,[34] selectivity relationship 8 is obtained. Equation 8 is to be compared with

$$\rho^k = 0.52 \log k - 210 \qquad (8)$$

$$\rho^t = 0.34 \log k - 0.44 \qquad (9)$$

eq 9 obtained from the equilibrium data for the formation of benzylhydryl cations.[35] The differences between the coefficients, 0.52 for a^k and 0.34 for a^t, make it evident that there is an intrinsic kinetic contribution in methanolysis as expressed in eq 7. The transposition of this conclusion to bromination is justified by the similarity of both these carbocationic reactions.

The high selectivity coefficient in set B for conjugated R substituent arises from the cumulative contribution of thermodynamic and kinetic factors. In set A, where a is smaller, the thermodynamic term can be assumed to be negligible with respect to the kinetic term.

In both sets the variation in transition-state position contributes significantly to the a value.

Concluding Remarks

Until now, the use of ρ has been limited to the attribution of an overall mechanism, i.e., to estimate the sign, the order of magnitude, and the localization of the charge at the transition

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(29) A classical tool for interpreting the ρ variation for reaction rates leading to carbocations is based on the "electronic demand" of the cationic center. This concept is not strictly appropriate for analyzing kinetic data because it takes into account only the influence of the thermodynamic factors on the reactivity. This approach gives a rough but correct estimation of the trend in ρ variation if the thermodynamic and kinetic contributions vary in parallel. If this assumption is not valid the tool of electronic demand fails. In the case of bromination, the inductive effects of R and R′ substituents on carbocations predict the following order for ρ values: $\rho_{\alpha\text{-methylstyrene}} > \rho_{\alpha\text{-methylstilbene}} > \rho_{\text{styrene}} > \rho_{\text{stilbene}}$. This is not the order experimentally observed in Table I since resonance stabilization of the ground state of stilbenes causes a discontinuity in the parallelism between the transition-state position and the stability of the cations.

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state.[36] In view of the selectivity relationships in bromination which make it possible to interpret small ρ variations, one can obtain precise information about the shifts of the transition-state position induced by structural changes. The utility of the FER coefficients for describing the energy profile of a reaction has been severely criticized in the last few years.[4,36,37] By using selectivity relationships or IFER for MSE, the factors affecting the reactivity can be more accurately quantified by the constants a and q. In particular, our results provide a new criteria for the application of the RSP, the limits of which have been discussed at great length: for the same log k, two different selectivities are observed depending on whether resonance effects occur or not, since there are two selectivity relationships for the same reaction (Figure 1). It was already known that the RSP cannot be applied to reactions where several bonds are modified;[12,37] it appears now that the reactivity-determining factors must be of the same type.

The present methods for interpreting reactivity are based on mathematical formulations of earlier qualitative concepts such as BEP modelisations of potential energy surfaces,[38] the Hammond postulate,[39] Thornton's rules,[37] etc.... Several authors[4a,40] currently question the validity of these concepts because there are few extensive data bases for testing them and their theoretical applications. There are several reasons for thinking that bromination may be helpful in this respect: (i) abundant kinetic data under standardized conditions and over a large reactivity range are available and (ii) despite the high endergonicity of its rate-determining step, the intrinsic kinetic contribution is not small with respect to the thermodynamic one. In this paper we have emphasized that the selectivity differences between the formation of benzylic bromocations bearing resonant or nonresonant substituents R arise from differences in thermodynamic contributions. This interpretation does not exclude the probability that resonance also modifies the kinetic contribution by decreasing the intrinsic barrier. Unfortunately, a Marcus model,[41] developed for electron-transfer reactions and successfully applied to proton[42] and methyl[27b] transfer reactions, is not strictly applicable to the kinetic contribution in bromination: α is probably close to 1, identity reactions of bromination do not exist, and thermodynamic data for the rate-determining step are not at present available. Further work in progress will enable the evaluation of more general models[27a,30,43] in bromination.

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Trajectory Analysis. 1.[1] Theoretical Model for Nucleophilic Attack at π-Systems. The Stabilizing and Destabilizing Orbital Terms

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Abstract: A simple model is proposed for qualitatively describing the trajectory along the reaction coordinate of an attacking nucleophile at a π-electrophilic center. Two sets of first-order interactions are considered: (1) the *stabilizing* (charge transfer) interactions of the nucleophile HOMO with the lowest unoccupied π^* and σ^* molecular orbitals of the electrophile and (2) the *destabilizing* (repulsive) interactions of the nucleophile HOMO with the highest occupied π and σ molecular orbitals of the electrophile. A more complete analysis involving all unoccupied and occupied molecular orbitals on the π-electrophile is also presented.

In a classic series of papers, Burgi, Dunitz, et al.[2-5] were able to map portions of the reaction coordinate for the addition of oxygen- and nitrogen-centered nucleophiles to carbonyl groups by correlating structural regularities found in a large number of solid-state structures. From this elegant analysis, the trajectory followed by such nucleophiles in the course of addition to a carbonyl group was described by an angle θ with respect to the C–O bond axis (Figure 1). Values of θ ranging from 70° to 80° were observed at nucleophile–substrate distances of 2.5–3.5 Å. An ab initio SCF calculation of the trajectory of hydride ion attacking formaldehyde gave similar results.[2] More recently, trajectory calculations of hydride attacking acetylene and ethylene[6,7] likewise characterized a transition state described by an acute angle θ. In these cases θ values of 54° and 56° were reported for acetylene and ethylene, respectively. The authors of these studies suggest that the calculated trajectories are de-

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(1) In the context of this research, the word "trajectory" means the minimum-energy path through the multidimensional geometrical space characterizing the approach of two reacting species in the immediate vicinity of the "transition state" geometry. In the sense used here, the word has a meaning substantially different from that used in classical mechanics where it represents the dynamic path through classical phase space of a system characterized by well-defined initial conditions or the usage in statistical analysis of reactions that follow paths across a well-defined potential surface from initial reactants in precisely defined states to final products in similarly well-defined states.

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