J. Am. Chem. Soc. **1981**, *103*, 5388-5392

The importance of the hydrophobic interactions of pyrroles I and II and aliphatic and/or aromatic amino acid side chains in myoglobins and hemoglobins is evidenced by the evolutionary conservatism of these amino acids.[10] Although heterogeneity in hemin orientation within the pocket of hemoproteins is now recognized in several cases[28-30] all cases involve permutating pairwise the two hydrophobic (I ↔ II) and the hydrophilic pyrroles (III ↔ IV). The difference in hydrophobicity of the perimeter of pyrroles I, II and III, IV makes it extremely unlikely that heme rotational heterogeneity about the β-γ-meso axis will occur in a protein environment.

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Substituent Dependence of the Selectivity in Alkene Bromination through Bromocarbenium Ions[1]

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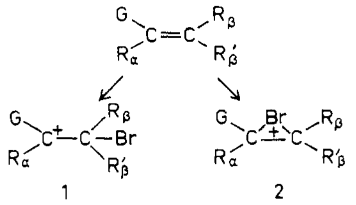
Abstract: Substituent effects on the rates of bromination of alkenes $G_\alpha R_\alpha C{=}CR_\beta R_\beta'$, where G is a conjugatively electron-donating group, are consistent with a carbenium ion like transition state, whereas by the same criteria the transition state for nonconjugated alkenes is bromonium type. The reactivities of compounds with the same substituent G are analyzed in terms of the sensitivity to structural and solvent effects. The lowest sensitivity is attributed to the earliest transition state. The dependence of the reaction constant on G leads to a general equation including cross terms: $\log k = -7.7\sum(\sigma_p{}^+)_\alpha - 13.7\sum(\sigma_m{}^+)_\beta - 7.0(\sigma_p{}^+)_{G_\alpha}(\sigma_p{}^+)_{R_\alpha} - 5.8\sum(\sigma_p{}^+)_\alpha\sum(\sigma_m{}^+)_\beta + 1.64$. The carbenium ion character, common to both bromination and hydration, results in highly dissymmetric α- and β-substituent effects. However, these two reactions respond differently to β substituents: a β methyl increases the bromination rate but decreases the hydration rate. Similarities and differences in the transition-state models are discussed; the kinetic data suggest that the transition state is earlier in bromination than in hydration.

Quantitative treatment of the effects of π-donor substituents on reactivity has been extensively developed in aromatic series, but most of the treatments of substituents in aliphatic series include only alkyl groups or substituted alkyl groups where conjugation between the substituent and the reaction center is excluded.[2] The linear free-energy relationships (LFER) therefore contain only polar, steric, and hyperconjugative terms.[2b] Nevertheless, a few correlations including resonance parameters (albeit defined from reactions of aromatic compounds) have been proposed,[3-5] and recently Tidwell[6] put the hydration rates of a large set of aromatic and aliphatic ethylenes into a single correlation.

In this article, we develop a quantitative reactivity treatment based on new data on the bromination of enolic derivatives (enols, enol ethers, and enol esters) and phenylalkenes (unsubstituted phenyl ring). The assumption, made for hydration,[6] that the effects of substituents borne by the two unsaturated carbons are independent proves to be valid only to a first approximation. We shall show that a general equation including interactions between substituents[7] performs much better. These interaction terms will be related to the variation of the transition-state position with the nature of the conjugated electron-donating substituent; this variation is confirmed by measurements of the solvent effects upon the reactivity.

Scheme I



It is also possible to confirm by correlation analysis that the transition state is carbenium ion like for the compounds considered here. Contradictory statements have been made as to the carbenium (**1**, Scheme I) or bromonium (**2**) character of the transition state for Ad_EC1 bromine addition.[8] On the basis of a free-energy relationship (FER) using σ_I and σ_R parameters, Charton[5] concludes that the transition state is carbenium type; comparison of bromination with hydration and sulfenylation "reaction models" leads Schmid[9] to the opposite conclusion, that the transition state

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Table I. Bromination Rate Constants (in MeOH, $T = 25$ °C)

compound	k, M^{-1} s^{-1}
1, $MeCOOCH{=}CH_2$	6.00×10^{2} [a]
2, $EtCOOCH{=}CH_2$	8.62×10^{2} [b]
3, $MeCOOC(Me){=}CH_2$	1.28×10^{4} [a]
4, $PhCH{=}CH_2$	1.53×10^{3} [c]
5, $Ph_2C{=}CH_2$	4.32×10^{4} [d]
6, $PhC(Me)C{=}CH_2$	1.62×10^{5} [c]
7, $EtOCH{=}CH_2$	2.26×10^{8} [e]
8, $EtOC(Me){=}CH_2$	2.30×10^{9} [e]
9, $MeCOOC(Me){=}CHBr$	1.53[a]
10, *trans*-$MeCOOCH{=}CHMe$	1.82×10^{3} [b,f]
11, *cis*-$MeCOOCH{=}CHMe$	3.70×10^{3} [b]
12, *cis,trans*-$PhCH{=}CHBr$	1.72×10^{-2} [b]
13, *trans*-$PhCH{=}CHCO_2Et$	2.20×10^{-2} [b]
14, *trans*-$PhCH{=}CHPh$	1.09×10[g]
15, *trans*-$PhCH{=}CHCH_2Cl$	1.17×10[c]
16, *trans*-$PhCH{=}CHCH_2OAc$	5.59×10[c]
17, *trans*-$PhCH{=}CHCH_2OMe$	2.68×10^{2} [c]
18, $PhC(Me){=}CHPh$	4.43×10^{2} [k]
19, *trans*-$PhCH{=}CHCH_2OH$	1.01×10^{3} [c]
20, *trans*-$PhCH{=}CHMe$	3.26×10^{3} [d]
21, *trans*-$PhCH{=}CHEt$	4.29×10^{3} [c]
22, $HOC(Me){=}CClCO_2Et$	2.51×10^{4} [h,f]
23, $HOC(Me){=}CBrCO_2Et$	2.82×10^{4} [i,f]
24, $HOC(Me){=}CHCOMe$	2.75×10^{6} [h,f]
25, $HOC(Me){=}CHCO_2Et$	3.31×10^{6} [i,f]
26, $HOC(Me){=}CHCO_2Me$	3.31×10^{6} [b,f]
27, $HOC(Et){=}CMeCO_2Et$	4.90×10^{6} [h,f]
28, *trans*-$EtOCH{=}CHMe$	9.17×10^{8} [e,f]
29, $HOC(Ph){=}CHCOPh$	7.41×10^{5} [b,f]
30, $HOC(Ph){=}CHCO_2Et$	2.04×10^{6} [j,f]

[a] Reference 1. [b] This work. [c] Reference 11b. [d] Dubois, J. E.; Marie de Ficquelmont-Loizos, M. *Tetrahedron* 1978, *34*, 2247-2257. [e] Poupard, D., unpublished results. [f] Value calculated from the equation $\log k = \log k_g + 1.39$; see supplementary material. [g] Dubois, J. E.; Garnier, F. *Bull. Soc. Chim. Fr.* 1967, 4512-4514. [h] Reference 4. [i] Reference 47. [j] Dubois, J. E.; Alcais, P. *C. R. Acad. Sci.* 1965, *260*, 887-890. [k] Dubois, J. E.; Ruasse, M. F.; Argile, A. *Tetrahedron* 1975, *31*, 2921-2926.

is bromonium ion like. We, however, maintain that the wide variety of structures studied makes it highly probable that there will be mechanistic plurality in bromination.[10,11] Applied to the present set of derivatives with conjugatively electron-donating substituents, several criteria lead unequivocally and consistently to the conclusion that the transition state is carbenium ion like.

Results

Bromination rate constants are first order relative to each reactant, bromine and olefin. Since they cover 11 powers of 10, several kinetic methods had to be used. Rate constants higher than 10^5 M^{-1} s^{-1} were determined by the couloamperometric method,[12] those lower than 1 M^{-1} s^{-1} by arseniometric titration,[13] and the intermediate ones by potentiommetry.[14]

Except for arseniometric titration, all the methods require the presence of an alkali metal bromide. The equation relating the rate constants to the salt concentration is well established:[15]

$$Y = k_g(1 + K[Br^-]) = k + p[Br^-] \qquad (1)$$

K is the equilibrium constant for $Br_2 + Br^- \rightleftharpoons Br_3^-$; its values are 177 and 16.3 in methanol[16] and water,[17] respectively. The constant

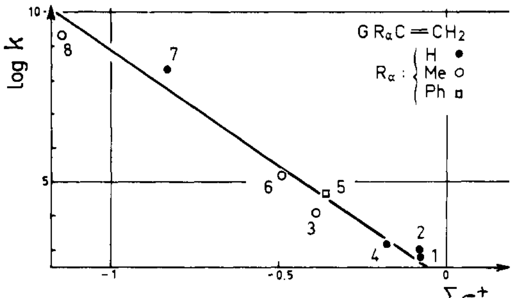

Figure 1. Correlation of the reactivities of conjugated vinylic compounds against the sum of the substituent constants σ_p^+. The numbering of the compounds is the same as in Table I.

k corresponds to the rate constant without added salt and consequently is the rate constant for the addition of molecular bromine. The k value is either obtained by extrapolating the linear plot of Y against $[Br^-]$ to $[Br^-] = 0$ or estimated from k_g values at 0.2 M salt concentration through eq 2. All k_g values along

$$\log k = \log k_g(0.2 \text{ M NaBr}) + d \qquad (2)$$

with k, p, and d values (Tables IV and V) and comments are available in the supplementary material. The constant p was often identified with $Kk_{Br_3^-}$ on the assumption of concurrent attack by bromine and the tribromide ion. This interpretation remains controversial;[13] p probably includes a salt effect.[18] Our discussion will be based exclusively on the k values for the addition of molecular bromine. The available data for bromination of conjugated polysubstituted alkenes in methanol are collected in Table I; those in water are given in Table III.

Discussion

Carbenium Nature of the Transition State for Conjugated Alkenes. We showed that bromine adds to alkylalkenes through a bromonium type transition state[10] but to α-phenylalkenes through a carbenium-type transition state[11] (at least when there is no deactivating substituent on phenyl). The bromophenylcarbenium ion is stabilized, in preference to the corresponding bromonium ion, by charge delocalization on the aromatic ring. Analogously, the replacement of an alkyl substituent by an aryl substituent shifts the transition state from bridged to open in alkyne bromination.[19] In the case of enol derivatives the carbenium ion can also be stabilized[20] by the donor contribution associated with the conjugation of the groups -OR and -OCOR. The strong electron-delocalizing ability of the ethoxy and phenyl groups does not lead *necessarily* to an open transition state, since a bridged sulfonium transition state is observed for these two groups in ArSCl addition.[21] However, the values of the σ_R^+ constants of the acetoxy, ethoxy, and phenyl groups (-0.48, -1.10, and -0.29) indicate that the first two groups are best able to stabilize positive charge. If, therefore, the bromination of phenylalkenes goes through a carbenium transition state, it is reasonable to assume the same type of transition state for enol esters and ethers.

For α-arylalkenes[22] and enol ethers[23] the carbenium character of the intermediate is confirmed by the nonstereospecificity of bromine addition.[24] In contrast, when the intermediate is bridged,

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(23) Dana, G.; Convert, O.; Perrin, C. *J. Org. Chem.* **1975**, *40*, 2133-2135; Peterson, P. E.; Indelicato, J. M. *J. Org. Chem.* **1970**, *35*, 531-532; Lemieux, R. U.; Fraser-Reid, B. *Can. J. Chem.* **1965**, *43*, 1460-1475.

addition is always stereospecifically anti, both for alkylalkene bromination[25] and for sulfenylation[21] (including that of enol ethers).

The carbenium nature of the transition state has several kinetic consequences, in particular, on the identity of the most appropriate resonance parameter for the treatment of the data. The investigation of charged intermediates by LFER is based on analogy between the reaction studied and certain model reactions which are used to define different types of substituent constants. Thus, a LFER containing the parameter σ_p^+ implies that the substituent is, as in the defining reaction for σ_p^+, conjugated with a positively charged reaction center, whereas a LFER with σ_p excludes this direct conjugation.[2a] The carbenium-type mechanism is favored for the bromination of vinylic compounds $GR_\alpha C{=}CH_2$, since correlation 3 (Figure 1) with σ_p^+ (correlation coefficient R =

$$\log k = -6.7\sum\sigma_p^+ + 2.12 \qquad (3)$$

0.988) is better than correlation with σ_p (R = 0.934). It should be noted that Charton's analysis,[5,26] based on the use of the parameter σ_R, leads to the conclusion that there is a single carbenium ion mechanism for conjugated alkenes *and* alkylalkenes. We claim that there are *two* mechanisms with distinct intermediates, bromonium being always associated with nonconjugated alkenes[10] and carbenium with conjugated alkenes. In view of this difference in opinion, the point merits further discussion.

To test the hypothesis that there are different intermediates depending on the type of compound, we have performed correlations with two different data sets: (i) conjugated alkenes only and (ii) conjugated alkenes plus linear[27] nonconjugated *gem*-alkenes (see Table VI, supplementary material). The poor quality of all the "lumped" correlations and the drastic modification of the coefficients of the various parameters are associated with a mechanistic difference within the second data set.

The "kinetic effect of methyl"[11a,28] illustrates also the distinct substituent sensitivities associated with the two types of transition state. In the case of a bromonium intermediate,[10] the ratio $k_{\beta Me}/k_0$ (k_0, the rate constant of the reference compound $GCH{=}CH_2$; $k_{\beta Me}$, the rate constant of trans $GCH{=}CHMe$) is about 30. For all the compounds with a conjugated electron-donating substituent, the ratio $k_{\beta Me}/k_0$ is about 10 times smaller (2.1, 3.0, and 4.1 for G=Ph, -OCOMe, and -OEt, respectively).

Dissymmetry of Substituent Effects. Additive Reactivity–Structure Correlation. Starting with the parameter σ_p^+ selected for the limited vinyl model, $GR_\alpha C{=}CH_2$, we shall now study the general model $GR_\alpha C{=}CR_\beta R_{\beta'}$ by means of structure–reactivity correlations.

In a carbenium-type transition state the charge is localized at the carbon (C_α) to which the electron-donating substituent G is attached. Thus, the effects of α and β substituents (Scheme I) are not expected to be similar. Indeed, a correlation vs. the sum $\sum\sigma_p^+$ of the effects of the four substituents does not work (R = 0.85) for conjugated olefins.[29]

Given the substituent effects at C_α (correlation 3), it remains for us to measure β-substituent effects separately. We previously studied[11b] alkyl substituents β to a phenyl ring (G = Ph) and showed that the reactivity correlates with their inductive effects. We include here β substituents capable of resonance and adopt σ_m^+ constants[30] as a measure of the substituent effect, instead of the σ^* constants[2b] previously used, in order to make the scales more homogeneous and to facilitate comparison with work on hydration.[6,31] The reactivities of compounds $PhCH{=}CHR$ are a linear function (eq 4; correlation coefficient R = 0.993) of the

$$\log k = -11.8(\sigma_m^+)_\beta + 2.78 \qquad (4)$$

σ_m^+ value of R_β. In contrast to hydration, double bond stabilization in the initial state, expressed by the parameter D, is unimportant in the correlation. Thus, substituents R_β = Br (**12**) and R_β = CO_2Et (**13**), which have very different D values,[32] both fit correlation 4 very well (Figure 2).[33]

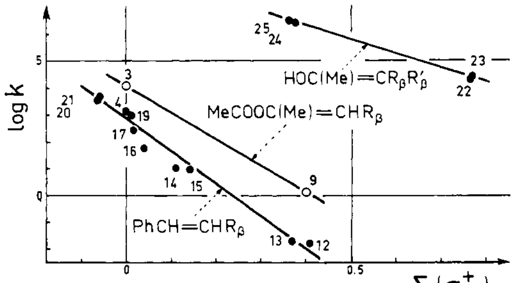

Figure 2. Correlation of the reactivities of compounds with β substituents against the sum of the substituent constants $(\sum\sigma_m^+)_\beta$. Each line corresponds to a fixed α substituent.

Table II. Reaction Constant Dependence on Reference Substituent G

G	hydration[a] ρ_α^+	bromination ρ_α^+	bromination ρ_β^+
F_3C	−27		
H	−11.8[b]	−7.4	
Ph	−12	−6.5	−11.8
MeCOO	−11	−4.2	−9.2
HO			−5.0
EtO	−8.6	−3.2	

[a] Values calculated from data of ref 6. [b] Value calculated by eliminating the deviating alkylalkene values.

With the assumption that both α- and β-substituent effects are independently additive, the correlations obtained for terminal alkenes (eq 3) and phenylalkenes (eq 4) can be melded into one. We obtain correlation 5, including all compounds in Table I. This

$$\log k = -7.4\sum(\sigma_p^+)_\alpha - 9.7\sum(\sigma_m^+)_\beta + 1.50 \qquad (5)$$

correlation reproduces the reactivities very well and the correlation coefficient (R = 0.967) is of the customary magnitude for LFER. However, there is a noticeable variation in the coefficients on going from the subsets (correlations 3 and 4) to the general correlation. The coefficient of $\sum(\sigma_p^+)_\alpha$ goes from −6.7 for *gem*-alkenes to −7.4 for the general correlation; the coefficient of $\sum(\sigma_m^+)_\beta$ goes from

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(24) In both cases, however, the reaction is stereoselective, and the same mixture of dibromides is not obtained from the cis and the trans isomers. Free rotation of the α-bromocarbenium ion is hindered by weak bridging or by an interaction between bromine and the cationic center.

(25) Fahey, R. C. *Top. Stereochem.* **1968**, *3*, 237–342; Dubois, J. E.; Chrêtien, J. R. *J.* Fahey, *Chem. Soc.* **1978**, *100*, 3506–3513.

(26) Two premises of this treatment appear to be unjustified: (a) Charton uses only the parameter σ_R, which according to its defining reaction should not be employed for carbenium type reactions. (b) Charton affirms that the coefficient of the resonance effect should be much greater than that of the polar effect when the reaction is carbenium type. In fact, for known reactions of this type, both in aromatic series and in the hydration of aliphatics, parameter σ_p^+ fits, i.e., the coefficients of the two effects are identical.

(27) We restrain our choice to linear substituents so as to avoid steric effects.[10]

(28) Dubois, J. E.; Toullec, J.; Barbier, G. *Tetrahedron Lett.* **1970**, 4485–4488.

(29) For alkylalkenes we obtained[10] an excellent correlation of the reactivity in terms of the sum of the polar effects of the four substituents, implying a symmetrically bridged transition state.

(30) The substituent constants σ_m^+ are taken from Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1958**, *80*, 4979–4987; σ_m values (from Exner, O. "Correlation Analysis in Chemistry"; Chapman, N. B., Shorter, J., Ed.; Plenum Press: London, 1978; p 439) are used in the place of the unknown σ_m^+ values.

(31) Knittel, P.; Tidwell, T. T. *J. Am. Chem. Soc.* **1977**, *99*, 3408–3414; we introduce the revised ρ_α^+, given later by Nowlan, V. J.; Tidwell, T. T. *Acc. Chem. Res.* **1977**, *10*, 252–258.

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(33) The agreement between measured and calculated data for the series $PhCH{=}CHR$ is slightly improved by introducing D in eq 4; but when the whole data set is considered the parameter D is not significant. A referee pointed out the fact that the D values of Hine are correlated with electrical and steric effects. If steric effects are negligible, which appears to be the case here, D should not be significant when the correlation equation already contains two electrical effect parameters.

Table III. Influences of Conjugated Substituents on the Solvent Effect

compd[a]	$k(H_2O)$[b]	$\Delta \log k$[b]	G, R_α[c]	compd[a]	$k(H_2O)$[b]	$\Delta \log k$[b]	G, R_α[c]
13	2.20×10^2 [d]	4.00	Ph, H (4.31)	**1**	7.50×10^5 [e]	3.11	MeCOO, H (3.34)
14	4.36×10^5	4.60		**2**	1.18×10^6	3.18	
16	6.71×10^5	4.08		**10**	2.88×10^6	3.58	
4	4.10×10^7	4.43		**11**	5.35×10^6	3.50	
22	4.63×10^6	2.41	HO (2.41)	**9**	1.73×10^3 [e]	3.05	MeCOO, Me (2.79)
				3	4.33×10^6 [e]	2.53	

[a] Numbers are those from Table I. [b] k in $M^{-1}\ s^{-1}$; $\Delta\log k = \log k(H_2O) - \log k(MeOH)$. [c] Mean $\Delta\log k$ indicated in parentheses. [d] Bell, R. P.; Pring, M. *J. Chem. Soc.* B **1966**, 1119–1126. [e] Reference 1.

−11.8 for the phenylalkenes to -9.7. These differences lead us to doubt whether substituent effects are really additive. We shall show that this assumption is only valid to a first approximation.

One should also consider the possible occurrence of steric effects. However, in the bromonium-type mechanism, such an effect does not operate for linear substituents;[10] it appears only when at least one substituent is highly ramified (e.g., *tert*-butyl) and originates from electrophile–substituent interactions.[34] Owing to the dissymmetry of the carbenium-type transition state, the interactions between the entering bromine and α substituents (G, R_α) are expected to be lower and those between bromine and R_β could be higher. But inspection of Table I shows that compound **23**, which possesses a much bulkier group than compound **22** along with similar polar effects, reacts at the same rate.

Reaction Constant Dependence on Reference Group G. Multiple-Substituent Effect Correlation Including Cross Terms. Close inspection of Figure 1, where we have plotted the reactivities of vinylic compounds against $\sum\sigma_p^+$, shows that the deviations of the disubstituted compounds $GCMe{=}CH_2$ are small but always in the same direction. The kinetic effect of a methyl group α to the G group of the monosubstituted compound $GCH{=}CH_2$ is smaller than the value of 110 predicted by eq 3. The $k_{\alpha Me}/k_0$ values are 106, 21, and 10 for G = Ph, -OCOMe, and -OEt, respectively. In particular, this effect depends on G, decreasing as G becomes more strongly conjugatively electron donating.[35] (Note that the behavior of alkylalkenes[10] is quite different: $k_{\alpha Me}/k_0$ oscillates about a mean value of 90).

The reaction constant for β-substituent effects also depends on G. Figure 2 shows that ρ_β^+ decreases, in the same way as the ρ_α^+ values, following the sequence G = Ph, –OCOMe, and –OH (slopes −11.8, −9.2, and −5.0, respectively; cf. Table II).

The decrease of the reaction constant, when the electronic demand at the carbenium ion center decreases because of the presence of a strong electron donor, is frequently encountered in work on aromatic compounds[36] but has rarely been detected in aliphatic series. In electrophilic bromination of aromatics[7] the variation of the reaction constant appears to be linearly related to the σ_p^+ constant of the GPA (group of principal activation). In our case, the order of ρ^+ follows σ_R^+ rather than ρ_p^+, but the limited number of groups makes it impossible to generalize.

In the case of electrophilic bromination of aromatics (addition as well as substitution), a precise correlation based on the additivity of substituent effects is out of the question, since the reaction constants depend on the GPA. Dubois et al.[7] have shown that it is necessary to introduce cross terms, also referred to as "interaction terms", into the classical equation in order to account for the nonadditivity.

It can be shown mathematically[7b] that these terms are proportional to the products of substituent constants taken two by two and that the general reactivity–structure equation is on the following form, as proposed previously:

$$\log k/k_0 = \sum_{i=1}^{i=4}\rho_i\sigma_i + \sum_{i=1}^{i=4}q_i\sigma_i\sigma_j \qquad (6)$$

Apart from aromatic electrophilic substitution, there are few examples of the application of this equation with cross terms since it requires a large number of homogeneous data.[7,37] For addition to an ethylenic double bond, four substituents would lead to six cross terms; we therefore propose certain simplifications in order to reduce this number. Since few compounds contain a substituent R_β', we shall assume that interactions between R_β and R_β' can be disregarded. Moreover, it is reasonable to assume that all interactions between an α substituent (G or R_α) and a β substituent have the same coefficient $q_{\alpha\beta}$. The simplified general equation then becomes:

$$\log k/k_0 = \rho_\alpha{}^+\sum(\sigma_p{}^+)_\alpha + \rho_\beta{}^+\sum(\sigma_m{}^+)_\beta + q_\alpha(\sigma_p{}^+)_{G_\alpha}(\sigma_p{}^+)_{R_\alpha} + q_{\alpha\beta}\sum(\sigma_p{}^+)_\alpha\sum(\sigma_m{}^+)_\beta \qquad (7)$$

From the reactivities of Table I the following coefficients and standard errors (in parentheses) are calculated: $\rho_\alpha = -7.7$ (0.5), $\rho_\beta = -13.7$ (0.9), $q_\alpha = -7.0$ (2.3), $q_{\alpha\beta} = -5.8$ (1.1), and $\log k_0 = 1.64$. All coefficients are statistically significant; the correlation coefficient is 0.986; the mean deviation between the calculated and experimental values goes from 0.67 log unit for the additive correlation 5 to 0.45 log unit for correlation 7, which therefore performs much better. Cross terms like those in eq 6 also account remarkably well for the rate constants of bromine addition to aryl-substitued stilbene derivatives[7b] and allow a unifying description of carbenium-type bromination.

Bromination–Hydration Comparison. It is interesting to compare our results with those for hydration, accepted as the archetype[9] of an addition reaction with a carbenium-type transition state. Knittel and Tidwell[31] proposed correlation 8 for this reaction. The carbenium character common to both reactions is

$$\log k = -10.5\sum(\sigma_p{}^+)_\alpha - 6.3\sum(\sigma_m{}^+)_\beta - 0.50D - 8.39 \qquad (8)$$

expressed by the use, in correlations 7 and 8, of different structural parameters for the substituents at the carbenium center (σ_p^+) and for those at C_β (σ_m^+).

Just as we observe interactions of the substituent effects in bromination, Koshy et al.[6b] note that for hydration of the styrene series $XC_6H_4CG{=}CH_2$ (X variable and G constant) σ^+ varies significantly with the stabilizing effects of G. However, they neglect these interactions in the general correlation which is strictly additive.[38]

Note that the absolute values of ρ_α^+ are systematically smaller for bromination than for hydration.[39] Charge development at

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(34) Ruasse, M. F.; Argile, A.; Bienvenüe-Goetz, E.; Dubois, J. E. *J. Org. Chem.* **1979**, *44*, 2758–2760.

(35) The ratio $k_{\alpha Me}/k_{\beta Me}$ seems a priori to be a good test of the transition state. A value close to unity is expected for a symmetrical bromonium-type transition state, and a much greater value for a carbenium transition state where the α substituent, unlike the β substituent, is atached directly to the charged carbon. This ratio varies from 1.9 to 3.9 for alkylalkenes[10] and rises to 7 and 50 for G = OCOMe and Ph, respectively. However, in the limiting case of the strongly electron-donating substituent –OEt, $k_{\alpha Me}/k_0$ is very small and $k_{\alpha Me}/k_{\beta ME}$ falls to 2.5 (see ref 28).

(36) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1973**, *95*, 2397–2399; Brown, H. C.; Ravindranathan, M.; Rho, M. M. *Ibid.* **1976**, *98*, 4216–4218.

(37) Miller, S. I. *J. Am. Chem. Soc.* **1959**, *81*, 101–106.

(38) In reality, if the results are examined more closely, one finds (Table II) for the complete set of substrates—going beyond styrenes alone—that the ρ_α^+ values depend on G (ρ_α^+ measured with G constant and R_α variable). They range from −8.6 to −27, while the ρ_α^+ value in the additive correlation is −10.5. The amplitude of the effect of electronic demand is, however, smaller in hydration than in bromination (Table II); this motivates the use of a cross-term treatment for the second reaction and not for the former.

(39) For ring-substitued styrenes the reverse order has been observed (see ref 22b). We have no explanation but would point out that the ρ^+ value for styrene hydration varies considerably from one author to another (see ref 6b).

C_α in the transition state is therefore smaller for the former reaction. The essential difference between the two reactions lies in the relative importance of the term *D*, which expresses the loss of double-bond stabilization. This term is negligible for bromination; that is, the resonance stabilization of the olefin arising from the β substituent is almost entirely retained in the transition state. This is not the case for hydration, where the loss of stabilization of the initial state (*D* term) can outweigh the gain in stability of the positive charge (σ_m^+ term). Thus, in bromination a β methyl always accelerates the reaction, while it decelerates hydration.[31] The coefficient ρ_β^+ of the parameter σ_m^+ is either greater or smaller than the ρ_β^+ of -6.3 calculated for hydration, depending on the substituent G (Table II). Whatever G, however, the ratio $\rho_\beta^+/\rho_\alpha^+$ is seen to be greater than that of 0.6 calculated for hydration.

It is possible to rationalize the results obtained by assuming that the transition state is earlier for bromination than for hydration. This is in line with the generally accepted idea[40] that the hydration transition state is late.[41] The earlier transition state for bromination leads to a lesser charge development and therefore to a smaller reaction constant for α substituents. Furthermore, the partial double bond remaining in the transition state conserves to a certain extent the double bond–substituent conjugation (negligible *D* term) and transmits the electronic effect of the β substituent better than a saturated carbon. In other words, the C_α–C_β distance is smaller for bromination and therefore the effects of β substituents on the transition state are relatively greater.

Solvent Effect and Transition-State Position. The lower selectivity of compounds with strongly electron-donating groups G, observed in bromination, can be interpreted either by an earlier transition state or by delocalization of the transition-state charge. If this delocalization were the only factor, the solvent effect would be constant because basically it relates to solvation of the leaving Br^- anion.[42] The later the transition state, the more charge is developed and the higher the solvent effect is. Table III presents data on the differences in reactivity, $\Delta \log k$, which occur when the reaction is transferred from MeOH to water. The solvent effect is approximately constant for given α substituents[43] but changes significantly from one G to another. According to the solvent effect, the transition state becomes progressively earlier on going from Ph to MeCOO to HO.[44] Consequently, structure effects (ρ_α^+ and ρ_β^+ in Table II) are expected to decrease in the same order, which is indeed observed. However a more conclusive analysis awaits further data.

Experimental Section

Materials. Propenyl acetate was prepared from acetic anhydride and propionic aldehyde in the presence of *p*-toluenesulfonic acid.[45] Cinnamyl acetate was prepared from the corresponding alcohol and acetic anhydride.[46] Other reagents were obtained commercially. The various compounds were purified by VPC on SE 30 or Carbowax 20 M columns. Methanol was twice distilled over bromine and dried by distillation over Mg. Water was distilled from potassium permanganate.

Kinetics. Reagent concentrations ranged from 5×10^{-7} to 5×10^{-4} M for bromine; from 10^{-7} to 2×10^{-2} M for the alkene, depending on the methods and the reactivities.

In the case of enol bromination,[47] the corresponding keto ester or diketone is added to the bromine solution. Only the enol part of the keto compound reacts. The rate of equilibration of the keto compound is slow compared with the rate of bromine addition and does not perturb the measurements. The enol concentration is reckoned to be the difference between the initial (in excess) and final bromine concentrations.

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Supplementary Material Available: Table IV, bromination rate constants k_g at various sodium bromide concentrations; Table V, relationship between *k* and k_g (0.2 M NaBr) values; comments on eq 1 and 2; Table VI, reactivity–structure correlations for *gem*-alkenes (6 pages). Ordering information is given on any current masthead page.

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(40) Noyce, D. S.; Schiavelli, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 1020–1022 and 1023–1026.

(41) This statement is no more than a mean indication; in fact, the position of the transition state varies from one compound to another; see ref 26 and next paragraph.

(42) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 1977–1978.

(43) Despite large differences in reactivity, e.g., 10^5 between styrene and ethyl cinnamate.

(44) A referee pointed out that hydrogen-bonding effects in water render the solvent effect for the OH group ambiguous and required data for G = EtO. Due to the high reactivity of the ethers studied here, their rate constants in water are at present inaccessible.

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(48) Dubois, J. E.; Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1436–1441.

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