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ETHYLENIC COMPOUNDS REACTIVITY: BROMINATION—XLI[1]

RELATIVE REACTIVITIES OF $R^1CMe{=}CH_2$ AND $R^1CH{=}CMe_2$ SERIES AS A CRITERION FOR DISTINGUISHING BETWEEN BRIDGED AND ACYCLIC TRANSITION STATES. DEGREE OF SYMMETRY OF THE BROMONIUM ION-LIKE TRANSITION STATE

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Abstract—Reactivities of homogeneous series of ethylenic compounds $R^1CH{=}CH_2$ **1**, *trans* $R^1CH{=}CHMe$ **2**, $R^1MeC{=}CH_2$ **3** and $R^1CH{=}CMe_2$ **4** have been measured in methanol at 25°C (R^1 = Me, Et, *n*-Pr, $-CH_2C_6H_5$, $-CH_2OCOCH_3$, $-CH_2Cl$). The criterion developed to decide between a bridged and a carbonium ion-like transition state is based on an internal comparison of the series and avoids resorting to external structural scales. Even in the case of alkenes **3** and **4** which are very dissymmetric with respect to polarity, the sensitivity to polar effects remains constant and the transition state behaves like a symmetric entity; only a slight secondary effect, attributed to hyperconjugation, is detectable.

For years, alkene bromination has been considered as a reaction with a cyclic transition state (T.S.) resembling intermediate: (Br^+) in Fig. 1. That this T.S. model could not be extended to arylolefins came to mind and was proven quite early;[2,3] but the aliphatic compounds were not implicated in the carbonium ion mechanism devised for the aryl ones. However, recently, Charton[4] and Pritzkow[5] stated that for alkylalkenes, bromination goes through a carbonium ion-like T.S., (resembling intermediate C_α^+ or C_β^+ in Fig. 1); de la Mare in his review[6] favored a very dissymmetric bromonium ion-like T.S. In the latter case, "the attack proceeds simultaneously in separate processes at the two olefinic carbon atoms". Such a dissymmetric bromonium ion-like T.S. may lead to reaction products differing in stereochemistry from those expected on the basis of competing open carbonium ions. But, as concerns the free energy relationships, the two models imply the same equations.

Numerous criteria have been devised to determine the cyclic or acyclic character of the T.S. in electrophilic addition reactions.[7] They fall into two main groups: one based on the free energy relationships, and the other based on the stereochemistry of the reaction, the anti sense of the bromination of 1,2-disubstituted ethylenes[8] supporting a cyclic T.S. The second group rests on the hypothesis of the similarity of the T.S. and the charged intermediate following it. The latter hypothesis has been suspected in the case of bromination[9] and we prefer to confine ourselves to the group of kinetic criteria.

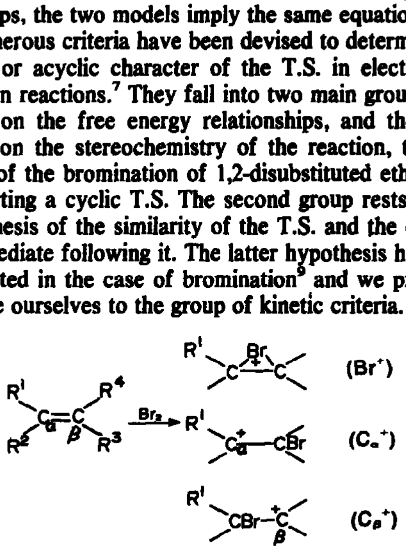

Fig. 1. Possible bromination intermediates. R^1 = Me, Et, *n*-Pr, $-CH_2C_6H_5$, $-CH_2OCOCH_3$ or $-CH_2Cl$: series 1: $R^2 = R^3 = R^4 = H$; series 2: $R^2 = R^4 = H$; R^3 = Me; series 3: R^2 = Me, $R^3 = R^4 = H$; series 4: R^2 = H; $R^3 = R^4$ = Me.

Each kinetic criterion taken alone is insufficient, and contradictory conclusions may sometimes be drawn from the same data. Thus, Pritzkow *et al.*[5] interpreted our previous results on the bromination rates of aliphatic alkenes as implying a carbonium ion-like T.S. even though we favored[10] a bromonium ion-like T.S. It appeared to us that the question of the nature of the T.S. in alkene bromination deserved reexamination, and that it would be useful to find a better criterion for distinguishing between open and bridged ions.

RESULTS

Numerous kinetic results are already in hand,[1,10,11] but it was desirable to extend data concerning alkenes where a carbonium ion might be favored, i.e. where one carbon is disubstituted. The four analogous series shown on Fig. 1 were studied, where only R^1 varies and the other fixed substituents tend to favor one of the two distinct possible carbonium ions C_α^+ or C_β^+. In series **1** and **2** the stabler carbonium ion may change from C_α^+ to C_β^+ according to the electron-donating or electron-attracting character of R^1. The situation is clearer in series **3** and **4**; the α-carbonium ion is favored in the series $R^1CMe{=}CH_2$ where only C_α is substituted, the β-carbonium ion in the series $R_1CH{=}CMe_2$ where C_β is disubstituted. Unbranched substituents with small steric effects and including heteropolar substituents were chosen to obtain a large variation of the polar effect. The σ^* polar substituent constants relative to the R^1 substituents are comprised between -0.115 (*n*-Pr) and $+1.05$ ($-CH_2Cl$) covering more than 40% of the σ^* polar scale.[12] The steric substituent constants vary only between 0 (Me) and -0.38 ($-CH_2C_6H_5$), thereby corresponding to 7% of the whole E_s steric scale.[12] The omission of substituents -Me and -Et would further narrow the E_s variation (3%) without changing the relationships shown later.

Rate constants (see experimental section) were measured in methanol at 25°C with added NaBr; they follow equation 1 in which k_g is the rate constant at a bromide ion concentration $[Br^-]$; K is the equilibrium

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

Table 1. Bromination rate constants[a] of alkenes of series 1–4[b]

Series	Compound	R^1	k
1	a	CH_2Cl	1.67×10^{-1},[f]
	b	CH_2OCOMe	8.50×10^{-1},[f]
	c	$CH_2C_6H_5$	5.33×10,[f]
	d	Me	4.03×10^2,[e]
	e	Et	4.98×10^2,[e]
	f	*n*-Pr	4.51×10^2,[e]
2	a	CH_2Cl	4.13[c]
	b	CH_2OCOMe	2.32×10,[c]
	c	$CH_2C_6H_5$	1.55×10^3,[c]
	d	Me	1.30×10^4,[g]
	e	Et	1.60×10^4,[g]
	f	*n*-Pr	1.15×10^4,[d]
3	a	CH_2Cl	7.97[c]
	b	CH_2OCOMe	8.96×10[c]
	c	$CH_2C_6H_5$	4.70×10^3,[c]
	d	Me	3.69×10^4,[d]
	e	Et	6.03×10^4,[d]
	f	*n*-Pr	3.63×10^4,[d]
4	a	CH_2Cl	2.95×10^2,[c]
	b	CH_2OCOMe	1.58×10^3,[c]
	c	$CH_2C_6H_5$	1.30×10^5,[c]
	d	Me	1.29×10^6,[g]
	e	Et	1.35×10^6,[d]
	f	*n*-Pr	8.95×10^5,[d]

[a] In M^{-1} sec^{-1}. [b] See Fig. 1. [c] Table 3. [d] Value calculated by the equation: $\log k = \log k_g$ (0.2 M NaBr) + 1.13; J. E. Dubois and X. Q. Huynh, Bull. Soc. Chim. Fr., 1436 (1968). [e] Ref. 20. [f] Ref. 10. [g] M. de Ficquelmont-Loïzos, Doctoral Thesis No. AO 8355, Paris (1973).

constant for the formation of tribromide ion;[13] k is the rate constant for the addition of molecular bromine. The discussion will be based on the k values reported in Table 1.

DISCUSSION

General reactivity-structure correlation

Equation (2) is obtained when the rate constants of series 1–4

$$\log k = -3.19\,\Sigma\sigma^* + 7.30$$

$$\text{correlation coefficient } R = 0.991 \qquad (2)$$

are put into one correlation of log k against the sum of the polar constants σ^* of the alkyl substituents R. Equation (2) does not greatly differ from eqn (3) ($R = 0.994$) based on an earlier set of data.[10]

$$\log k = -3.10\,\Sigma\sigma^* + 7.02 \qquad (3)$$

The Hammett–Taft ρ-value lies in the $|\rho| \sim 3$ region where numerous cyclic but some acyclic reactions (such as hydration of styrenes) are found.[7] Thus, the criterion which relates an absolute ρ-value lower than 4 to a cyclic T.S. and a larger value to a carbonium ion-like T.S., is not absolutely decisive here. The additivity of substituent polar effects shown by eqns (2) or (3) seems to be a more convincing criterion. Such additivity is expected in the case of a symmetrical bromonium ion-like T.S., but unexpected for competing carbonium ion-like T.S., where the substituents on each ethylenic carbon atom must have dissymmetric influences. However, general correlations (2) or (3) may be criticized from the two standpoints of accuracy and validity of the chosen structural parameter. Although correlation (2) is statistically significant, the deviations reach 0.48 log units, which is far beyond the experimental error. Insofar as the choice of the polar effect scale is concerned, both σ^* and σ_I scales are well established and often indifferently used since they are linearly related.[12,14] However, as Levitt and Widing[15] have pointed out, this correlation does not apply to alkyl groups for which another linear correlation has been proposed. Measurement of the polar effect of alkyl groups is still a subject of controversy.[15,16]

In the present case where both alkyl and electron-attracting substituents have been retained, σ^* and σ_I scales cannot be used indifferently; correlation (2) is found between log k and $\Sigma\sigma^*$ but no correlation is found between log k and $\Sigma\sigma_I$. Up to now,[10,17,18] for the bromination of aliphatic alkenes, we have used the σ^* constants because they arise directly from a model reaction including aliphatic derivatives. However, it is still better to avoid the polar effect scale problem applying the method we now propose to analyze the data. With such a method we are able to determine the bromonium or carbonium ion-like nature of the T.S. without resorting to the substituent constants.

Consideration of independent, isosubstituted series

Usually all available kinetic data are put into one reactivity vs structure correlation.[4–7,10] In contrast, our treatment is based upon the organization of the compounds into series where the number of various possible structural influences is reduced to a minimum and/or some of them (and consequently the interactions between them) are kept constant. In the present case, the steric environment is maintained quasi constant along a series (see Results). The isosubstituted series are compared to an internal reference, series 1; this series is the least substituted one, and is thus free from interactions between substituents. The straight lines observed (Fig. 2), fitted by the least squares method,[19] follow eqns (4)–(6).

$$\log k_2 = 1.02 \log k_1 + 1.42 (R = 0.9997\ s_p = 0.012\ s_0 = 0.025) \qquad (4)$$

$$\log k_3 = 1.05 \log k_1 + 1.85 (R = 0.9975\ s_p = 0.037\ s_0 = 0.075) \qquad (5)$$

$$\log k_4 = 1.05 \log k_1 + 3.28 (R = 0.9991\ s_p = 0.022\ s_0 = 0.045) \qquad (6)$$

(s_p standard error of the slope; s_0 standard error of the intercept).

The slopes do not significantly differ from unity and the lines may be considered as straight lines parallel to the reference line, at distances† of 1.45, 1.93 and 3.36 log units, respectively. This treatment of the data fits the experimental data much better than does the global correlation (2); the deviations do not exceed 0.17 log unit. However, rather than the improvement of the fit, the main point is the significance of the relative positions of the lines, which we shall now discuss.

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†Setting $\log k = \log k_1 + b$, the least squares treatment involves $b = (\Sigma \log k - \Sigma \log k_1)/n$, n being the number of k values.

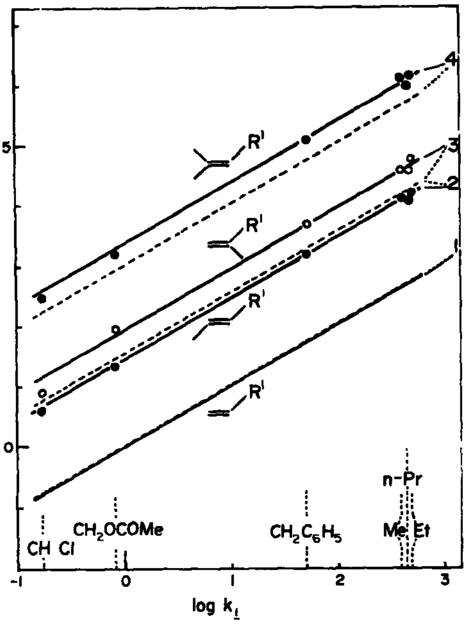

Fig. 2. Symmetrical bromonium ion hypothesis. Comparison of the experimental (continuous lines) and the theoretical eqn 7′ (broken lines) data. To a given abscissa corresponds a given substituent R^1 shown on the ordinate. Data come from Table 1.

Criterion for choosing between bridged and carbonium ion-like T.S.

We shall focus our attention on series 3 and 4 which seem the most likely to go through a carbonium ion intermediate. Independently of any other data and of any polar effect scale, the relative slopes of lines 3 and 4 provides information regarding the T.S. character. If the T.S. is bridged, the reactivities of series 3 and 4 should be equally sensitive to the polar effect of the group R^1, and lines 3 and 4 are expected to be parallel. If the T.S. were carbonium ion-like, pathway C_α^+ would be favored for series 3, and pathway C_β^+ for series 4. The sensitivity of series 4 to the polar effect of R^1 should thus be smaller than that of series 3; the attenuation coefficient should be about 0.43, as found for the $-CH_2-$ group.[20] The experimental proportionality coefficient is equal to unity (ratio of the slopes of series 3 and 4) and proves therefore the bromonium ion character of the T.S. Thus, comparison of series 3 and 4 is convincing, without the knowledge of any ρ- or σ^*- value.

The criterion for distinguishing cyclic and acyclic T.S. proposed here cannot at present be applied systematically to other addition reactions on the double bond, due to the lack of comparable results for series of type 3 and 4. Nevertheless in a few cases an incomplete log k vs log k array may be drawn (Fig. 3). The relative positions of the lines corresponding to series 2 and 3 are closely similar in chlorination[21] and bromination and suggest therefore that the T.S. is of the same type.† In the case of hydroxymercuration,[24a] the lower reactivities of *trans* $R^1CH{=}CHMe$ compounds 2 compared to $R^1CH{=}CH_2$ compounds 1 are unexpected. For both bromonium ion and carbonium ion-like T.S. models the replacement of a hydrogen by a methyl group should enhance the reactivity. A large steric effect of the incoming reactant is suspected.

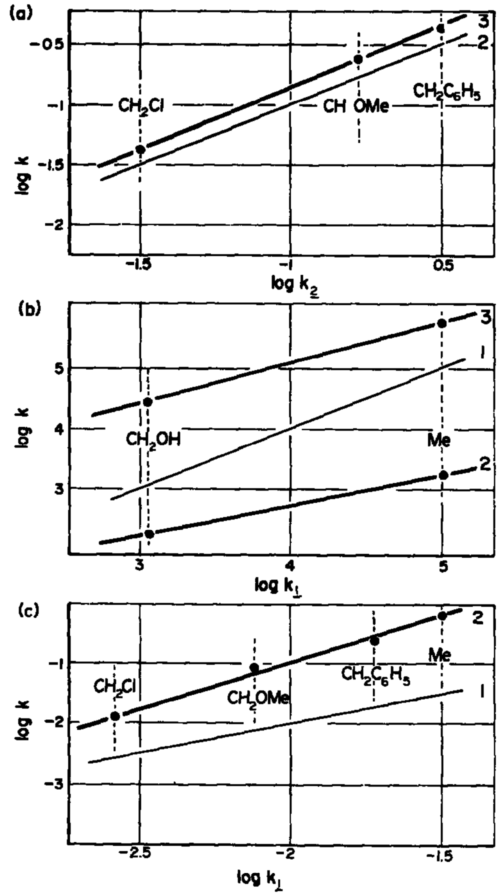

Fig. 3. Experimental arrays for some electrophilic additions to alkenes: (a) chlorination;[21] (b) hydroxymercuration;[24a] (c) peracetic acid addition;[24b] the line numbers refer to the same series as in Fig. 2.

Bromonium ion array

Now we propose to examine the relative experimental positions of the lines in Fig. 2 to see if they are in accord with those which can be expected theoretically for bromonium ion intermediates. If we assume a symmetrical bromonium ion and additive polar effects only, eqn (7) relates the reactivities of series n and series 1.

$$\log k_n = \log k_1 + \sum_{R^2}^{R^4} \text{polar effects relative to H} \qquad (7)$$

The last term in eqn 7 is a constant for a given series since R^2 to R^4 do not vary (Fig. 1). Thus, if the T.S. is bromonium ion-like, the lines are expected to be parallel; the distances between them are related to the replacement of one of two vinylic hydrogen atoms in series 1 by a methyl group. Blended lines should correspond to series 2 and 3, where one vinylic hydrogen atom in series 1 is replaced by one methyl group. Going from series 2 or 3 to series 4, one more H atom is replaced by one methyl group; thus, the distance between lines 2 or 3 and line 4 should be identical to the distance between line 1 and lines 2 or 3.

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†The very low selectivity observed in the chlorination case,[21] much lower than that observed by Poutsma,[22] may be due to the high concentrations used. One of us has shown[23] that, for concentrations higher than 10^{-3} M, the relative reactivities of alkenes diminish when the concentration increases.

As expected, the experimental lines (Fig. 2) are parallel and equivalent distances are found between lines 1 and 2 and also between lines 3 and 4. However, lines 2 and 3 are not blended. This substituent effect deviation from strict additivity was not perceptible in the general reactivity-structure treatment (eqn 2) because the 0.48 log unit separation between lines 2 and 3 is of the order of magnitude of allowed errors in LFER. Our treatment based on separate series reveals that some of the deviations from eqn (2) are systematic and should therefore be justified.

If we choose for polar effects the σ^* scale, eqn (7) turns to eqn (7'). The theoretical lines, calculated from the previously published[10] ρ-value for series 1, are shown as dashed lines in Fig. 2.

$$\log k_n = \log k_1 + \sum_{R^2}^{R^4} (\sigma^* - \sigma_H) \qquad (7')$$

Notice that the parallelism of the lines in Fig. 2 is relevant to the reactivity-selectivity controversy.[25] The selectivity may be considered as the reactivity variation induced by a given structural change (e.g. from R = *n*-Pr to R = $-CH_2Cl$). The selectivities of bromine reacting with series 1 and series 4 are identical, in spite of a reactivity difference of more than 3 log units between the two series. The present example is particularly appropriate since the structural differences between one series and another are limited and the medium unchanged.

Further criticism of the carbonium ion hypothesis

Our new criterion (relative slopes of lines 3 and 4) fully corroborates our previous hypothesis of a bromonium ion pathway, but is inconsistent with the conclusions of other authors.[4-6] We shall try to explain these contradictions.

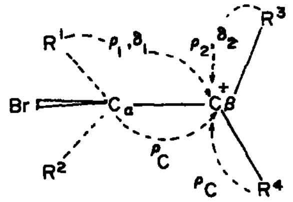
Charton and Charton[4] apply to electrophilic additions to olefins the Hammett equation in the form (8). For the authors the relative values of the coefficients α and β are a criterion of the nature of the T.S. To a relatively large β value corresponds a carbonium ion-like T.S. Equation (8) applied to the bromination of a set of 8 alkenes,

$$\log k_X = \alpha \Sigma \sigma_{I,X} + \beta \Sigma \sigma_{R,X} + h \qquad (8)$$

including 6 monosubstituted alkylalkenes and 2 enolic derivatives, gives $\alpha = +0.33$ and $\beta = -13.2$. The authors conclude that the bromination T.S. is carbonium ion-like. The correlation obtained is probably an artefact attributable to the consideration of a very small set of compounds which possibly react through different mechanisms. The small positive non-significant coefficient of the polar effect is in contradiction with the large reactivity differences (more than 3 log units) prompted by our various R[1] substituents. The σ_R variation along the R[1] substituents can only be due to hyperconjugation (difference between C–X and C–C hyperconjugation) and not to direct resonance effects. The observed reactivity differences must then be essentially attributed to polar effects. The coefficient of the polar effect should be negative: deceleration is observed with electron-attracting substituents (positive σ_I).

The observed reactivity differences must then be essentially attributed to polar effects. The coefficient of the polar effect should be negative: deceleration is observed with electron-attracting substituents (positive σ_I). If eqn (8) with Charton and Charton's coefficients is applied to allylchloride (**1a**) for instance, the calculated log k value is more than 1.7 log units larger than the experimental one.

Pritzkow *et al.*[5] used as a criterion of the nature of the T.S. the relative values of ρ_1 and ρ_2 in eqn (9). This expression takes in account only the C_β^+ carbonium ion pathway, where C_β is the more substituted carbon (Scheme 1).



Scheme 1.

$$\log k = \log k_0 + \rho_1(\sigma^*_{R^1} + \sigma^*_{R^2}) + \rho_2(\sigma^*_{R^3} + \sigma^*_{R^4}) + \delta_1(E_{s,R^1} + E_{s,R^2}) + \delta_2(E_{s,R^3} + E_{s,R^4}). \qquad (9)$$

The E_s and δ values[12] describe the steric effects of the substituents and are analogous to σ^* and ρ values respectively. The difference in the sensitivity of C_β^+ to the substituents linked to C_α and C_β is expressed by two distinct ρ values, ρ_1 and ρ_2 respectively. As R[1] and R[2] are more distant from the charged carbonium centre than R[3] and R[4], ρ_1 is expected to be smaller than ρ_2. If $\rho_1 = \rho_2$, eqn (9) no longer describes a carbonium ion pathway, but the bromonium ion pathway. Thus, Pritzkow *et al.* base their hypothesis of a carbonium ion-like T.S. on the very different values they obtain for ρ_1 and ρ_2 ($\rho_1 = 0.00$; $\rho_2 = -5.44$). But, if their treatment is applied to our data (excepting our data for the compounds including the substituent $-CH_2OCOCH_3$ for which the E_s value is not known), not only are ρ_1 and ρ_2 identical† ($\rho_1 = -3.14 \pm 0.29$; $\rho_2 = -3.24 \pm 0.28$), but also δ_1 and δ_2 are nearly null ($\delta_1 = 0.05 \pm 0.15$, $\delta_2 = -0.24 \pm 0.18$). The fact that the results are so sensitive to the set of compounds considered casts serious doubt upon the validity of the numerical values of the parameters obtained. There appear to be two reasons to question the set of data used by Pritzkow *et al.*: (i) the variations of R[1] and R[2] on one hand, R[3] and R[4] on the other hand are quite unbalanced; in all cases R[1] = H and, for 19 compounds among 23, R[2] = H or Me; on the other hand R[4] varies from $ClCH_2-$ to H and *neo*-Pe; (ii) as we showed elsewhere some artificial coefficients may arise from f (E_s, σ^*) correlations when they include only alkyl substituents, due to the relationship between E_s and σ^* for some of these substituents[10] (among the 23 compounds only 2 have a heteropolar substituent).

From the formal kinetic point of view, the hypothesis of two concurrent dissymmetric T.S. proposed by de la Mare[6] closely resembles the hypothesis of two concurrent carbonium ions. De la Mare's treatment suffers from the exclusive consideration of H and Me substituents. The rate enhancement linked to the replacement of an H atom by a methyl group is in fact not exactly constant,

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†The 95% confidence intervals are reported after the various parameters.

but this inconstancy is specific of the H atom. The parallelism of the lines in Fig. 2 shows that for $R^1 = H$ the replacement of one R^1 substituent by another one produces the same rate enhancement whatever the series. The imperfect additivity of the structural effects of the replacement of an H atom by a methyl group in the methylethylene series is directly linked to the discrepancy between the experimental and theoretical arrays in Fig. 2, but is an epiphenomenon insufficient to question the bromonium ion-like T.S. Instead of 2 concurrent dissymmetric T.S., an alternative hypothesis is one single dissymmetric T.S. Such a T.S. might be more or less dissymmetric depending on the substituents, and might explain the differences between the experimental array and the array based on the simple symmetrical bromonium ion model.

Degree of symmetry of the bromonium ion-like T.S.

Several approaches to the geometry of the bromonium ion have already been explored. Theoretical extended Hückel calculations have been performed[26] on the consequences of a dissymmetrization of the normally symmetric ethylene-bromonium ion. For 2,2-dimethyl and trimethyl-ethylenebromonium ions, on the basis of ^{13}C NMR spectra, Olah *et al.*[27] concluded in favor of an equilibrating mixture of the unsymmetrically bridged ion and an open ion. As concerns alkene bromination, the regioselectivity of solvent incorporated addition products suggests also a dissymmetrical intermediate.[28] Up to now, the quantitative involvements of such a dissymmetry on the free energy relationships have not been studied. The effects of the dissymmetrization of a bromonium ion may be analyzed in terms of the total $(\sigma + \pi)$ charges on carbons C_α and C_β or of the π charges alone. The first are linked to polar effects, the second to hyperconjugative effects.

A difference in the total charges on carbons C_α and C_β could lead to different sensitivities ρ_α and ρ_β of the two carbon centres to substituents, as in eqn 10. This equation resembles eqn 9 but is fundamentally different; ρ_1 and ρ_2 are constants whereas ρ_α and ρ_β are supposed to vary with the partial charges on C_α and C_β and consequently with the nature of the substituents. Since the selectivity is here constant (parallelism of the lines in Fig. 2) the total charge developed at the T.S. and consequently the total sensitivity $(\rho_\alpha + \rho_\beta)$ are assumed to be constant. Then, $\rho_\alpha = \rho - \Delta\rho$ and $\rho_\beta = \rho + \Delta\rho$, the ρ value corresponding to symmetrical compounds, whence eqn (11) may be derived from eqn 10, with $\Delta\sigma^* = (\sigma^*_{R^3} + \sigma^*_{R^4}) - (\sigma^*_{R^1} + \sigma^*_{R^2})$. Equation (11) corresponds to an acceleration for dissymmetrical compounds relative to symmetrical ones, the term $\Delta\rho\Delta\sigma^*$ being positive. Taking into account symmetrical compounds only (**5a–d** in Table 2 and **2d** in Table 1), the terms ρ and $\log k_0$ are calculated to be −3.09 and 6.99 respectively. The term $\Delta\rho$ is not a constant, but is expected to be related to $\Delta\sigma^*$, therefore $\Delta\rho\Delta\sigma^*$ should be proportional to $(\Delta\sigma^*)^2$. A search for a correlation between the reactivity and parameters $\Sigma\sigma^*$ and $(\Delta\sigma^*)^2$ gives for the coefficient of $(\Delta\sigma^*)^2$ a non-significant value; the hypothesis that C_α and C_β have different sensitivities is therefore to be rejected. Either the charge dissymmetry which is deduced from NMR observations or regioselectivity is too small to have a repercussion on these sensitivities, and/or the T.S. is more symmetrical than the intermediate.

$$\log k = \log k_0 + \rho_\alpha(\sigma^*_{R^1} + \sigma^*_{R^2}) + \rho_\beta(\sigma^*_{R^3} + \sigma^*_{R^4}) \quad (10)$$

$$\log k = \log k_0 + \rho\Sigma\sigma^* + \Delta\rho\Delta\sigma^* \quad (11)$$

Table 2. Bromination rate constants of some symmetrical alkenes

Compound	$R^1 = R^3$,[b]	$R^2 = R^4$,[b]	k[a]
a	CH_2Cl	H	4.17×10^{-3},[f]
5 b	H	H	4.65[h]
c	Et	H	2.60×10^4,[g]
d	Me	Me	1.24×10^7,[d]

[a–g]See Table 1. [h]Ref. 18.

At the same time as it differentiates the total charges on C_α and C_β, the dissymmetrization of a bromonium ion differentiates the overlap populations[26] of Br and C_α on the one hand and of Br and C_β on the other hand. When for instance the overlap population of Br and C_α (which may be taken as an estimate of the relative bond order between the two atoms) is small, the π orbital of C_α^+ can interact with σ orbitals belonging to R^1 and R^2. Such a stabilization would, moreover, explain the fact that *cis* and *trans* dimethylethylene bromonium ions rearrange to the *gem*-dimethylethylenebromonium ion.[27] The experimental observations, that series **1–4** are parallel and the reactivities of series **3** and **4** are enhanced, are in agreement with this hyperconjugative hypothesis† on 2 conditions: (i) compared to the stabilization difference between R^1 (or R^2) = H and R^1 (or R^2) = $-CH_2R$, the stabilization differences between one $-CH_2R$ group and another are negligible; (ii) the stabilization does not intervene when C_α and C_β are equally substituted. The expected reactivity equation is then (12), where i characterizes the series and $d_i = 0$ when C_α and C_β are equally substituted. Fitting by least squares gives $\rho = -3.06 \pm 0.15$, $d_1 = 0.05 \pm 0.22$; $d_3 = 0.48 \pm 0.20$; $d_4 = 0.40 \pm 0.22$. Only parameters d_3 and d_4 are significant and may be considered as identical. Equation (12) becomes eqn (13) with d = 1 for *gem*-disubstituted and trisubstituted compounds and d = 0 for the others.

$$\log k = \log k_0 + \rho\Sigma\sigma^* + \Sigma d_i \quad (12)$$

$$\begin{gathered}\log k = 6.89 - 3.03\,\Sigma\sigma^* + 0.43\,d \\ (R = 0.997)\end{gathered} \quad (13)$$

The influence of the last term in eqn (13) is small compared to the influence of polar effects. The order of magnitude is similar to that of replacing a methyl group by an ethyl group. That the reactivity is experimentally sensitive to the π charge differentiation and not to the total $(\sigma + \pi)$ charge differentiation is in line with recent work by one of us; as regards carbonium ions it has been noted[31] that a substituent change makes the π charge vary more than the total charge.

Finally, we have shown here that for aliphatic alkenes with non-conjugating substituents a bromonium ion pathway accounts reasonably well for the bromination rate constants. We pointed out the crucial importance of the chosen set of compounds to apply the various criteria

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†The hyperconjugative stabilization of the alkene has been neglected here relative to the T.S. stabilization; according to Dewar[29] and Traylor *et al.*,[30] $\sigma - \pi$ conjugation contributes very little to the stabilities of neutral molecules.

Table 3. Dependence of bromination rates[a] on NaBr concentration at 25° in MeOH ($M^{-1}\ sec^{-1}$)

		NaBr[b]					
	Compound	0.05	0.10	0.20	k[c]	$k_{BR_3^-}$[c]	Q[d]
2a	*trans* $MeCH{=}CHCH_2Cl$	7.72×10^{-1}	6.12×10^{-1}	5.05×10^{-1}	4.13	4.04×10^{-1}	10
2b	*trans* $MeCH{=}CHCH_2OCOMe$	3.64	2.62	2.04	2.32×10	1.45	16
2c	*trans* $MeCH{=}CHCH_2C_6H_5$	2.28×10^{2}	1.65×10^{2}	1.24×10^{2}	1.55×10^{3}	8.41×10	18
3a	$CH_2{=}C(Me)CH_2Cl$	1.33	9.82×10^{-1}	7.87×10^{-1}	7.97	5.84×10^{-1}	14
3b	$CH_2{=}C(Me)CH_2OCOMe$	1.23×10	7.92	5.78	8.96×10	3.40	26
3c	$CH_2{=}C(Me)CH_2C_6H_5$	6.38×10^{2}	4.42×10^{2}	3.10×10^{2}	4.70×10^{3}	1.89×10^{2}	25
4a	$Me_2C{=}CHCH_2Cl$	3.95×10	2.73×10	1.91×10	2.95×10^{2}	1.15×10	26
4b	$Me_2C{=}CHCH_2OCOMe$	2.02×10^{2}	1.30×10^{2}	8.92×10	1.58×10^{3}	4.72×10	33
4c	$Me_2C{=}CHCH_2C_6H_5$	1.63×10^{4}	1.12×10^{4}	7.74×10^{3}	1.30×10^{5}	4.18×10^{3}	31

[a] Standard deviation less than 2.5%. [b] Concentration in M. [c] Values determined by eqn 1,[18] with $k_{Br_3^-} = \beta/K$; the $k_{Br_3^-}$ value is often attributed to the rate constant for the addition of Br_3^-. The standard deviation is about 2% on k and about 3% on $k_{Br_3^-}$. [d] $Q = k/k_{Br_3^-}$. The values are of the same order of magnitude as those observed for alkenes. The tendancy of Q to diminish when the rate constant falls below 10 is again observed.[10]

used to test the nature of the T.S. The criterion we propose necessitates the choice of clearly defined compounds (series **3** and **4**), but presents the advantage of avoiding recourse to external structural scales.

The fit of the bromonium ion model can be improved by the introduction of some dissymmetry, plausibly due to hyperconjugation. In the present discussion we supposed a unique type of T.S., bromonium or carbonium ion-like. Recent studies of our group[2] have shown that the reaction scheme may be more complicated; the reaction may follow different paths simultaneously. Thus, in the case of substituted stilbenes, competing bromonium and carbonium ion pathways have been identified. Our criterion and the closeness of the experimental and theoretical bromonium arrays make clear the paramount importance of the bromonium ion pathway; however, we point out that we limited ourselves to compounds with minor steric requirements (unbranched substituents). The possibility remains of a carbonium ion pathway for strained or crowded alkenes. Thus, in the particular case of cis-cyclo-octenes[17] the T.S. was shown to be carbonium ion-like. The examination of crowded alkenes is under way.

EXPERIMENTAL

Chemicals. Compounds were obtained commercially, except **2b** and **4b** which were prepared as described previously[32,33] and **4c** prepared by condensation of 1-chloro-3-methylbut-2-ene on phenyl magnesiumbromide in tetrahydrofuran. Compounds were purified by GLC on ODPN, Apiezon L or GESF 96 columns. Methanol was twice distilled over Br_2 and dried by distillation over Mg.

Kinetic measurements. Except for compound **4c** where, owing to the low solubility of the compound, the couloamperometric method was used, the rate constants were determined by potentiometry, as described previously[2,18] (Table 3).

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