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Bromination of Ethylenic Compounds. 39. Predominance of Steric Effects on the Reactivity of Tetrasubstituted Alkenes[1]

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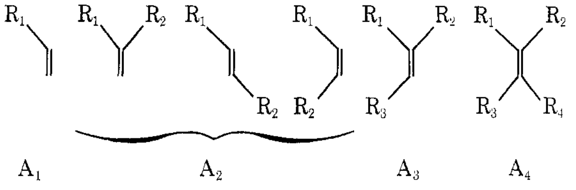
The bromination rate constants of 15 tetrasubstituted A_4 alkenes have been measured in methanol. Comparison of the effect of R in the trimethylalkylethylenes $Me_2C{=}CMeR$ with that of the same R in less substituted alkenes, $RCH{=}CH_2$, $RCH{=}CHMe$, or $Me_2C{=}CHR$, shows that the rate-diminishing steric effect is enhanced as the number of methyl on the double bond increases. Furthermore, the reactivity diminishes progressively when the methyls of tetramethylethylene are successively replaced by ethyl groups. Thus, substituent steric effects become more important than polar ones for the tetrasubstituted alkenes. Whereas for less substituted alkenes reactivity–structure correlations in terms of σ^* are obtained, a correlation with ΣE_s^c only accounts for the reactivity of tetrasubstituted alkenes. The importance of steric effects is further underlined by the absence of any relationship between the reactivity and the ionization potentials in the A_4 series and by the similarity of the substituent effects on bromination and on the addition reactions of bulky electrophiles whose rates are controlled by steric effects.

The systematic study of the bromination of ethylenic compounds has focused on several olefin populations: alkenes,[1,2] arylalkenes (styrenes and diphenylethylenes),[3] and cycloalkenes.[4] In order to complete previous studies on mono-, di-, and trisubstituted alkenes, we measured the reactivity of tetrasubstituted alkenes for which only the simplest structures, tetramethyl- and trimethylethylethylenes, have so far been studied.[2,9]

On the basis of early data of Dubois and Mouvier, the kinetic effect of different alkyl groups, their number, and their relative positions were evaluated.[2] Polar and steric effects, expressed in terms of linear free energy relationship, are additive for only a limited number of alkenes. The polar reaction constant has been determined from monoalkenes where it has been shown that steric effects are weak and negligible. The study of tetraalkylethylenes should allow us to determine the role of steric effects on their reactivity.

Results

We shall use the abbreviation A_4 for the tetrasubstituted alkenes and A_1, A_2, and A_3 for the mono-, di-, and trisubstituted ones, respectively.



For our study of the A_4 series, we have chosen 15 alkenes, either commercial or synthetized in the laboratory,[5] with substituents ranging from methyl to neopentyl. The rate constants, measured competitively[6] or directly[7] in our usual medium (methanol with 0.2 M NaBr at 25 °C), are given in Table I. In addition, we measured under the same conditions the rate constants of two *gem*-A_2 alkenes whose values were useful in the discussion which follows:

$$n\text{-Bu-MeC}{=}\text{CH}_2 \; k_{\text{exp}} = 2.27 \times 10^3 \text{ M}^{-1}\text{ s}^{-1}$$

$$n\text{-Pe-MeC}{=}\text{CH}_2 \; k_{\text{exp}} = 1.98 \times 10^3 \text{ M}^{-1}\text{ s}^{-1}$$

Table I shows distinct series in the A_4 population. The first group contains the trimethylalkylethylenes, $Me_2C{=}CMeR$, with variable R (compounds no. 1–8). The second one contains

Table I. Bromination Rate Constants of Tetrasubstituted Alkenes

Registry no.	No.	Alkene	k_{exp}[a]	Ref	Precision, %
563-79-1	1	$Me_2C{=}CMe_2$	9.16×10^5	b	4
10574-37-5	2	$Me_2C{=}CMe$-Et	6.5×10^5	c	9
7145-20-2	3	$Me_2C{=}CMe$-*n*-Pr	3.32×10^5	d	1
3074-64-4	4	$Me_2C{=}CMe$-*n*-Bu	3.55×10^5	d	1.5
19781-18-1	5	$Me_2C{=}CMe$-*n*-Pe	3.38×10^5	d	1
565-77-5	6	$Me_2C{=}CMe$-*i*-Pr	1.03×10^5	d	1
32540-07-1	7	$Me_2C{=}CMe$-*i*-Bu	3.76×10^4	d	1
33175-59-6	8	$Me_2C{=}CMe$-*neo*-Pe	1.78×10^3	d	1
10557-44-5	9	*cis*-Me-EtC=CEt-Me	3.83×10^5	c	8
19550-88-0	10	*trans*-Me-EtC=CEt-Me	3.66×10^5	c	8
19780-67-7	11	$Me_2C{=}CEt_2$	1.56×10^5	c	4
50787-13-8	12	$Et_2C{=}CMe$-Et	1.08×10^5	c	3
868-46-2	13	$Et_2C{=}CEt_2$	2.56×10^4	c	3
19780-61-1	14	$Me_2C{=}CEt$-*n*-Bu	8.83×10^4	c	6.5
50787-14-9	15	$Et_2C{=}CEt$-*n*-Pr	1.43×10^4	c	6

[a] Rate constants in $M^{-1}\ s^{-1}$ measured at 25 °C in methanol, 0.2 M NaBr. [b] Reference 2. [c] Couloamperometrically measured, ref 7. [d] Measured by competitive method described in Experimental Section and in ref 6.

only those A_4 alkenes with methyl and ethyl substituents (no. 1, 2, and 9–13).

The elementary rate constant[8] for the free bromine addition, k_{Br_2}, and Q ratio, $k_{Br_2}/k_{Br_3^-}$, have been measured elsewhere[9] for trimethylethylethylene. The Q value, 21.6, is higher than the limit of 16 established previously[10] and the rate constant k_{Br_2}, calculated by the relationship[8] $\log k_{r_2} = \log k_{exp} + 1.13$, is in satisfactory agreement with the experimental k_{Br_2} value, $1.23 \times 10^7\ M^{-1}\ s^{-1}$.[9]

Consequently, it can be assumed that the variations of k_{exp} parallel those of k_{Br_2} and that the structural effects measured on k_{exp} are representative of those on k_{Br_2}.

Specific Effect of a Variable Alkyl Group R on the Reactivity. In Figure 1 are shown the effects of a group R on the reactivity of the trimethylalkylethylenes (A_4) compared to the effect of the same R in ethylene- (series A_1) or methyl- (A_2) and dimethyl- (A_3) alkenes.[1,2]

The balance between the accelerating polar and retarding steric contributions is revealed when R is methyl and ethyl (left-hand side of Figure 1). The progressive introduction of methyl groups on ethylene increases the reactivity nonadditively, the last methyl giving the smallest acceleration. The replacement of methyl by ethyl enhances the reactivity by a factor of 1.5 for A_1 and A_2, of only 1.15 for A_3, and finally 0.60 for A_4. Thus, the replacement of methyl by ethyl in A_4 diminishes the reactivity: the steric contribution becomes more important than the polar one, even with a group as small as ethyl.

When R is a bulky group, the steric contribution is the most important factor (right-hand side of Figure 1). The greater the number of methyl substitutents, the greater the reactivity decreases. Thus, the neopentyl diminishes the reactivity by a factor of 5.3 for A_1, 32.7 for A_2, and 514 for A_4.

Therefore whereas steric effects exceed the polar ones in A_1, A_2, and A_3 only when R is bulky, they are preponderant in the A_4 series even when the methyl group is replaced by the small ethyl group: *consequently, tetramethylethylene is the most reactive acyclic alkene.*[11]

Predominant Steric Contribution of an Ethyl Group in A_4 Alkenes. Inspection of Table I shows a continuous decrease in reactivity of tetramethylethylene by progressive replacement of methyl by ethyl groups. If the increase in the electron-donating polar effect on passing from methyl to ethyl results in an acceleration of 1.5, as shown by uncrowded mono- and disubstituted alkenes,[2] we can calculate that reactivity of tetraethylethylene is reduced by a factor of 180 owing to the intervention of steric effects.

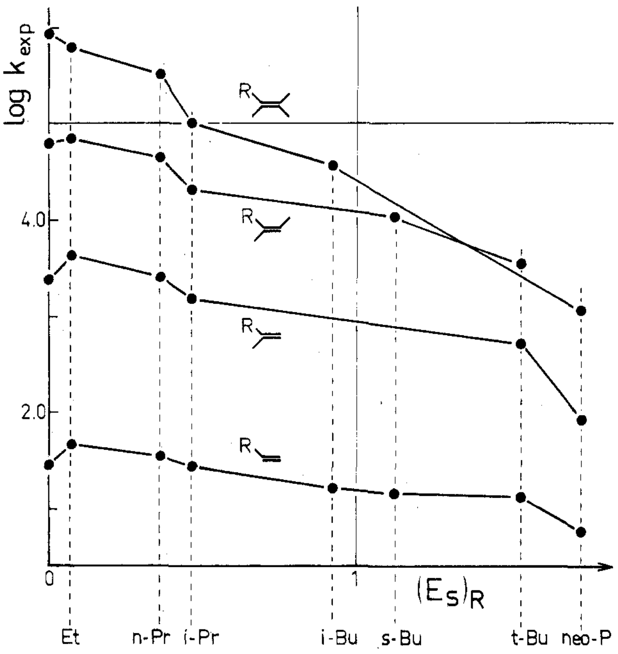


Figure 1. Increase in the steric deceleration by R of alkene bromination with the number of methyl groups on the double bond.

Analogous introduction of one or several ethyl groups in less substituted alkenes did not lead to similar attenuations in reactivity.[2] In Figure 2, we compare the effect of the replacement of the methyl groups by ethyl in the A_4 series with the effect of progressive replacement of the hydrogens of ethylene by ethyl groups. We observe a large increase in reactivity on passing from mono- to di- and triethylethylenes, the diminution being evident only with the introduction of the fourth ethyl, whereas in A_4 the decelerating effect is observed upon the first replacement of methyl by ethyl.

We observed generally[2,9] for disubstituted alkenes the reactivity sequence trans < cis < gem. However, if we compare compounds 9, 10, and 11, we obtain, considering only the relative positions of the ethyl groups, the sequence cis $\simeq$ trans $\gg$ gem: *the reactivity of the gem-dimethyldiethylethylene is* 3.4 times smaller than would be expected from the k_{gem}/k_{cis}

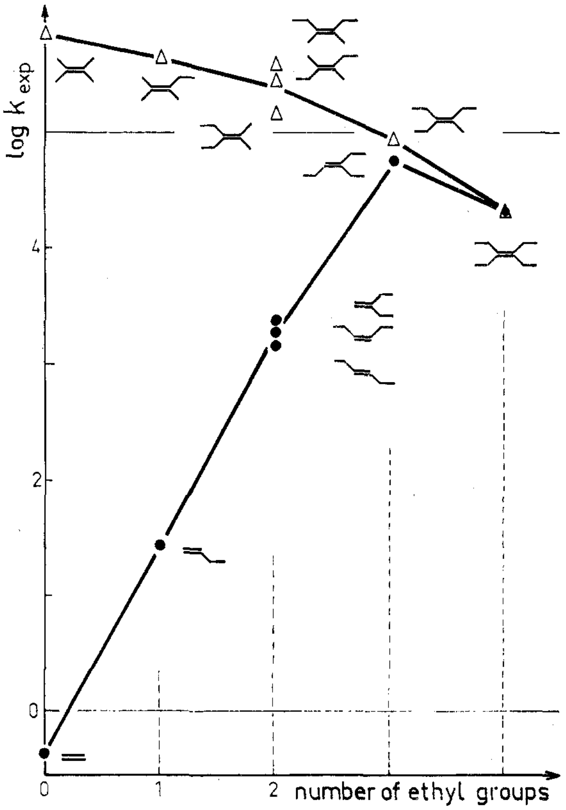


Figure 2. Effects of ethyl substituents on alkene reactivity: accelerating polar contribution in mono-, di-, or triethylethylenes; decelerating steric contribution in tetrasubstituted ethylenes.

ratio of the corresponding diethylethylenes. Thus, the accumulation of substituents affects not only the overall reactivity of the alkenes but also the relative reactivities of the geometric isomers.

The inversion of the reactivity sequence of geometric isomers could also result from the enhancement of substituent steric effects in the geminate position. The same effect was previously observed in disubstituted alkenes when the alkyl substituents are particularly bulky. For example for the di-*tert*-butylethylenes, the sequence is trans ≃ cis ≫ gem.[2,9]

Criteria for the Participation of Steric Effects. It can be confirmed by several criteria that the influence of steric effects on the reactivity of A_4 alkenes toward bromine is important. We examine successively a physicochemical criterion, the ionization potential, which is related to the substituent inductive effect, and two kinetic criteria based on the comparison of the bromination rate constants of A_4 with those of other addition reactions where steric effects have been identified as the rate-determining factor.

A. Ionization Potentials. Our recent photoelectron spectroscopic study of numerous alkenes allowed us to show that the electronic effects of substituents on the ionization potential (IP) are the most important, their steric effects having only a secondary effect.[13]

The increasing electron-donating effect of alkyl groups leads to a diminution of the IP and to an increase in electrophilic reactivity. Consequently, if there were an IP/log k_{exp} correlation, it should have a *negative slope.* Such correlation has been observed for the bromination of the less crowded methylalkenes.[14] For A_4 alkene bromination, there does not exist any linear relationship between IP and log k; at best, a tendency toward a positive correlation can be observed. This confirms our preceding conclusion that polar effects play only a minor role in bromination of A_4.

Table II. Steric Effects on Reactivity of Alkenes as a Function of the Electrophile

	Relative reactivities		
A_4	Br_2 this work	NO^{17}	$O_2{}^{18}$
$Me_2C{=}CMe_2$	1.0	1.0	1.0
$Me_2C{=}CMe\text{-}Et$	0.58	0.88	0.69
$Me_2C{=}CMe\text{-}n\text{-}Pr$	0.36	0.57	0.66

B. Kinetic Data on Various Additions to A_4. The addition of O_3 to very crowded olefins is very sensitive to steric effects of alkyl substituents[15] but the only study on A_4 is concerned with the reaction products alone[16] for compounds no. 1, 2, 9, 10, and 11. The only kinetic data on A_4 are the rates of photooxidation of NO in the presence of alkenes[17] and the deactivation of singlet oxygen O_2 ($^1\Delta_g$).[18] The *same reactivity decrease* is observed for the only three structures studied in the three reactions (Table II).

The steric effects of alkene substituents are less marked in NO addition and singlet oxygen deactivation because these electrophilic reagents are probably less voluminous than bromine. Therefore these data could signify that the electrophile–substituent interactions are an important rate-determining factor.

We have also compared the kinetic effect of an alkyl group R on the bromination of A_4 alkenes with the effect of the same R in the addition of two bulky reagents to less crowded R-substituted alkenes, since other data are not available. In these latter reactions, additions of bis-3-methyl-2-butylborane[19] and 2-4-dinitrobenzenesulfenyl chloride,[20] the steric effect very clearly predominates over the inductive one[21] because of the very large steric requirements of the electrophile. Between the A_4 bromination and these additions, we obtain (Figure 3) *four satisfactory linear correlations of the form*

$$\log k(\mathrm{R}) = a \log k_{\mathrm{exp}}(\mathrm{R}) + b$$

where R = Me, Et, *n*-Pr, *n*-Bu, *i*-Pr, *i*-Bu, *t*-Bu, and *neo*-Pe; $k_{exp}(R)$ is the rate constant for the bromination of $RMeC{=}CMe_2$; and $k(R)$ are the rate constants obtained by Pritzkow[20] and Brown[19] for 1-alkenes $RCH{=}CH_2$ and for the cis and trans 2-alkenes, $RCH{=}CHMe$.

This comparison of the kinetic data confirms that the contribution of steric effects to the reactivity of A_4 toward bromine is important.

Linear Free Energy Relationships, Log $k_{exp} = f(\Sigma E_s)$. For the bromination of alkenes mono-, di-, or trisubstituted by small linear groups, we have obtained[2] a linear free energy relationship with polar constants, σ^*, and thus determined the sensitivity of bromination to polar effects of substituents: $\rho = -3.10$. As expected from our qualitative observations on the substituent effects by crowding of the alkenes, we obtain *no relationship between* log k_{exp} *and* σ^* *for the* A_4 *alkenes,* even for *n*-alkyl substituents.

Since from the previous analysis of substituent effects, we established that steric effects are of considerable importance, we now attempt to correlate the reactivity of A_4 alkenes by means of the empirical E_s parameters. We have used two scales of steric constants, those of Taft,[22] E_s, and those of Hancock, $E_s{}^c$, calculated from the former so as to correct for hyperconjugation.[23] With Taft's E_s, we observe an almost correct linear relationship only for the trimethylalkylethylenes:

$$\log k_{\mathrm{exp}} = 1.55\ (\pm 0.10)\ E_s + 5.98\ (\pm 0.08)$$

$$(r = 0.986 \text{ and } \Psi = 0.13)$$

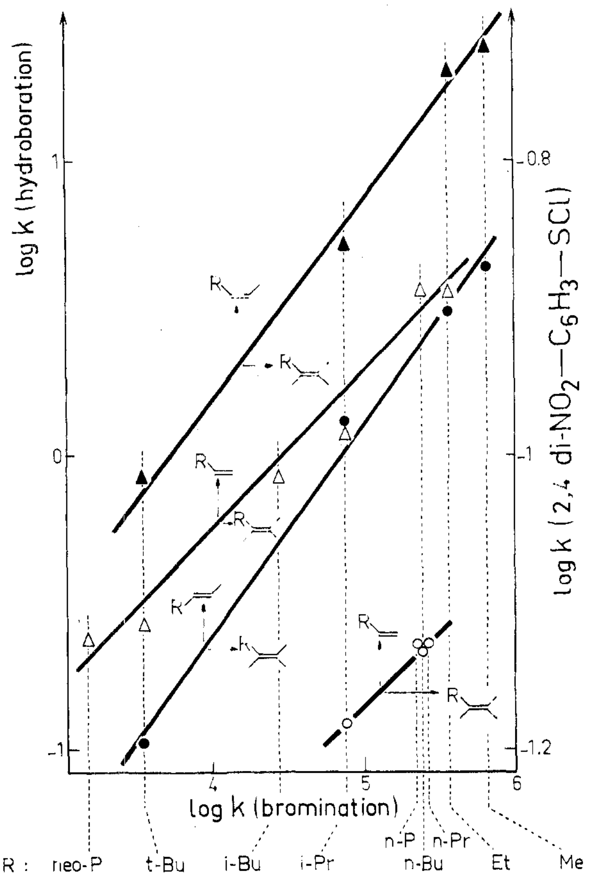


Figure 3. Effects of alkyl substituents on additions controlled by steric effects: hydroboration[18] of mono- (○), cis (▲), and trans (●) dialkylethylenes vs. bromination; addition of 2,4-dinitrobenzene sulfenyl chloride[19] to monoalkylethylenes (△) vs. bromination of tetraalkylethylenes. For trimethyl-*tert*-butylethylene, the bromination rate constant has been extrapolated from Figure 4.

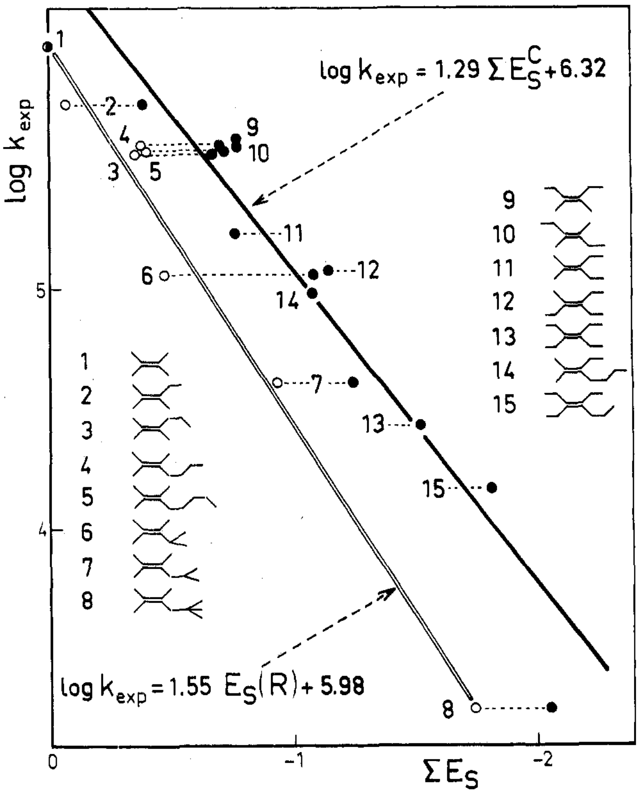


Figure 4. Correlation of the bromination rate constants for tetraalkylethylenes with steric parameters E_s.

The use of Hancock's constants allows us to include all the A_4 alkenes in a unique correlation:[24]

$$\log k_{\text{exp}} = 1.29\ (\pm 0.11)\ \Sigma E_s{}^c + 6.32\ (\pm 0.12)$$

$$(r = 0.962 \text{ and } \Psi = 0.29)$$

These relationships are shown in Figure 4.

Considering present and earlier data for the bromination of the various alkene sets, we obtain[2] very different free energy relationships: $\log k = f(\Sigma\sigma^*)$ for alkenes with a very few simple substituents, then $\log k = f(\Sigma\sigma^*, \Sigma E_s)$ for alkenes with bulkier substituents, and finally $\log k = f(\Sigma E_s)$ for the A_4.

The diversity of the structure–reactivity correlations in bromination exhibits clearly the increasing weight of steric effects as the degree of substitution of the alkene increases. Assuming, in the absence of contradictory data, that the mechanism of bromine addition is the same for all the alkenes, the absence of a general relationship shows that the classical structural parameters and the notions of independence and additivity of substituent effects, applied successfully to numerous reactions,[25] *cannot be transposed to a much more complex reaction center such as the ethylenic double bond.*

The initial hypothesis that the E_s values are additive, contested in particular by Miller[26] and by Shorter,[25] for polysubstituted compounds, fails to account adequately for all the observed reactivities of alkenes. On a very crowded reaction center, the interactions between the nonbonded alkyl groups are large[27] and the enhancement of the steric effects results from mutual hindrance to the free rotation of the alkyl groups. The calculation of these supplementary steric restrictions, for example, in the forms of increments

$$\Sigma E_s = \sum_{i=1}^{4} E_s(R_i) + \Delta E_s(R_1 - R_2) + \Delta E_s(R_2 - R_3) + \ldots$$

for a given reaction and a restricted set of compounds is possible but we think that it is only of limited interest.

Conclusion

The absence of stereochemical and thermodynamic data on A_4 prevents us discussing the reaction mechanism as we did for A_3.[1] It is nevertheless likely that for the A_4 as for the A_3, the importance of steric effects indicates a clear predominance of bromine-substituent interactions in the rate-determining step.

The synthesis and the kinetic, thermodynamic, and stereochemical studies of new A_4 are worthwhile in order to confirm these conclusions on the remarkable evolution of the balance between polar and steric effects.

Another important result of our study on crowded olefins is the demonstration that the steric effects of a given alkyl group depend markedly on the other substituents on the alkene, i.e. *on its environment.* Therefore, it is not possible to attribute a value to a steric parameter without defining its environment. This notion has already been advanced in the acid-catalyzed migration of alkyl groups in ketones.[28] If the environment influences the steric effect, it becomes impossible to obtain quantitative structure–reactivity relationships and it is, then, necessary to develop new approaches where these steric effects will be defined by taking into account the overall topology of the molecule. Developments of reactivity–topology treatment[29] might be more fruitful than the classical approach based on empirical parameters of individual alkyl groups.

Experimental Section

Starting Materials. The alkenes were either commercial samples (Chemical Samples) or were synthesized in the laboratory[5] (compounds no. 7, 8, 12, 13, and 15 of Table I). All the alkenes were purified by GLC (Intersmat IGC 12M apparatus) on the following columns: (a) 40% $AgNO_3$, saturated solution in ethylene glycol on Firebrick FBC 22 (length 1.50 m, diameter 6 mm); (b) 20% DEGS on FBC 22 (3 m × 6 mm).

The purity of the reactants as checked by GLC was always better than 99%. The retention times were determined on column b under the following conditions: H_2 20 ml/min; air 300 ml/min; He (carrier gas) 10 ml/min; oven temperature 25 °C; injector 150–200 °C. The structure of all the alkenes was checked by NMR, ir, and mass spectroscopy. The ir spectrum is not very useful, the C=C band at 1620–1670 cm^{-1} being always very weak and disappearing completely for the two symmetrical alkenes. Nevertheless, the absence of bands associated with vinylic protons is a good criterion of purity of the A_4. The NMR spectra (JEOL, solvent CCl_4, Me_4Si internal standard, 60 MHz) were always sufficient for the unambiguous verification of the structures of the alkenes. The mass spectra were used in support of the NMR spectra.

NaBr and MeOH were purified as described previously.[2,7]

Kinetic Measurements. Direct measurements were performed by couloamperometry.[7] For all the alkenes studied, the reaction is overall second order and the appropriate log plot is a straight line to at least 90% reaction. We have checked particularly the rate constant of tetramethylethylene, which was determined by another method, coulometric concentrostat,[2] and was substantially corrected after improvement of the method. The two values are in agreement: $k_{exp} = 9.16 \times 10^5$ M^{-1} s^{-1} (by couloamperometry, $\pm 3.6 \times 10^4$, that is, the standard deviation on 12 runs is 4%).

Competitive measurements were performed by GLC as described previously.[6] The partial order relative to the alkene is unity in all cases. The reactivities relative to tetramethylethylene (k_{TME}) are determined with an error always less than 2%. To improve the precision, alkenes 7 and 8 of Table I, of low reactivity, were studied in competition with two alkenes of known rate constant.

Precision. The time–concentration data (direct method) and *concentration data (competitive method)* were handled by a computer. The agreement between the values determined by the two methods is excellent and is in accord with the idea that there is a single mechanism for direct and competitive bromination of alkenes.[6] For these very rapid reactions, the competitive method is more precise than couloamperometry.

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