

# Reactivity of Ethylenic Compounds. 42. The Multipathway Mechanism in Styrene Bromination: Competition between Bromonium and Carbonium Ion Intermediates<sup>1</sup>

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**Abstract:** The structure of transition states and intermediates in styrene bromination is reinvestigated on the basis of the multipathway scheme where bromonium and carbonium ions are formed via competitive pathways. From the bromination in methanol of ring substituted styrenes **1**,  $\alpha$ -methylstyrenes **2**, and *trans*- $\beta$ -methylstyrenes **3**, several criteria have been devised to estimate the relative importance of the different paths: dependence of the  $k_{\alpha\text{-Me}}/k_{\text{H}}$  ratio on the substituents; demonstration of curvature in the  $\rho\sigma$  plot by extension of the substituent scale; stereochemistry of product formation. Results lead to a coherent view of kinetic and stereochemical data. Bromination of styrenes and  $\beta$ -methylstyrenes goes through carbonium ion intermediates only when they bear electron-donating substituents. The intermediate of **1** and **3** substituted by the most electron-attracting group is almost exclusively the bromonium ion. For the other substituents, there is competition between the two intermediates. The reaction constants of each pathway are determined. For styrene bromination in methanol,  $\rho_{\text{C}}$  of the carbonium ion pathway is  $-4.36$  and  $\rho_{\text{B}}$  of the bromonium ion one is about  $-2.8$ ; in acetic acid,  $\rho_{\text{C}}$  is as high as  $-5.6$ . For *trans*- $\beta$ -methylstyrenes in methanol, these  $\rho_{\text{C}}$  and  $\rho_{\text{B}}$  values are attenuated by a factor of 0.94. Whereas a methyl group in the  $\beta$  position does not change the relative stabilities of the two intermediates, a methyl group in the  $\alpha$  position enhances the stability of the carbonium ion substantially more than that of the corresponding bromonium ion. Thus,  $\alpha$ -methylstyrene bromination goes through carbonium ions exclusively, with a  $\rho$  value of  $-4.26$ , whatever the substituent. The stereochemistry of dibromide formation in the bromination of **3** confirms the scheme deduced from the kinetic data: from nonstereoselective for *trans*-4-methoxy- $\beta$ -methylstyrene, the reaction passes to antistereoselective for 3,5-bis(trifluoromethyl) **3**. Extensive comparisons of substituent effects on bromination and on other electrophilic additions to styrene, hydration and sulfenylation in particular, lead us to discuss the different factors (charge magnitude at the transition state, distance between the ring and the cationic center) which control the  $\rho$  value.

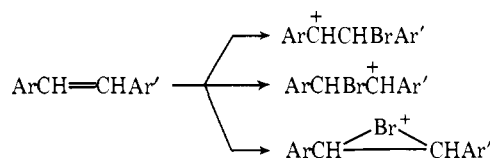
## Introduction

Among electrophilic additions, olefin bromination appears as an atypical system since its cationic intermediates are not in all cases cyclic ions but can also be open carbonium ions.<sup>2,3</sup> From stereochemical and kinetic data, empirical rules have been inferred: aliphatic alkenes react through bromonium ions since their bromination is generally stereospecifically anti; electron-donating aromatic rings directly attached to the double bond make bromination nonstereoselective and favor carbonium ion intermediates. However, these rules are too rough to take into account all the data and even in the case of styrenes, the simplest aromatic olefins, there exist arguments for and against a unique free carbonium ion structure of the transition states and intermediates.

Kinetic ring substituent effects on styrene bromination<sup>4,5</sup> afford an apparently linear Hammett-Brown relationship with a  $\rho$  value in the  $-4.5$  range corresponding to the formation of a benzylic carbonium-ion-like transition state. The high solvent effect on styrene bromination<sup>6</sup> ( $m = 1.20$ ) indicates that the transition state closely resembles the intermediate and makes it possible, therefore, to extrapolate the structure of the intermediate from that of the rate-determining transition state. Consequently, kinetic data apparently support a carbonium ion structure for the intermediates. However, thermodynamic data<sup>7</sup> on pairs of *cis* and *trans* olefins, including the strained  $\beta$ -*tert*-butylstyrenes, show that ground-state tensions are retained or even enhanced in the transition state. This is, in principle, in disagreement with a carbonium-ion-like transition state since minimization of substituent-substituent interactions should be expected in a free carbonium ion. The stereochemistry of *trans*- $\beta$ -methylstyrene bromination,<sup>8</sup> which is nonstereoselective when the ring substituent X is 4-OMe but stereoselective for X = H, reveals that the carbonium ion intermediate tends to a bromonium ion when the donor ability of the ring is decreased. This variable stereochemistry has been explained by weakly bridged intermediates. However, neither

the magnitude of the bridging nor the charge distribution in the intermediate has ever been determined.

On the other hand, in stilbene bromination,<sup>9</sup> kinetic substituent effects and regiochemistry of the solvent-incorporated products were finally interpreted in terms of competitive pathways with carbonium or bromonium ion intermediates in a scheme analogous to that involved in solvolysis<sup>10</sup> where neighboring group assisted and solvent-assisted pathways compete.



Carbonium ion pathways predominate for strongly electron-donating substituents, the bromonium ion one for strong electron attractors. In intermediate cases, the three pathways can compete.

In order to show that the bromination of styrene can also be interpreted on the basis of such a multipathway scheme, we undertook a reinvestigation of this system.

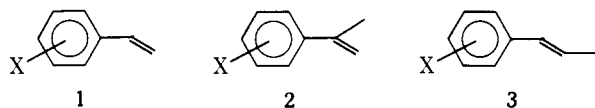
Previous measurements of kinetic substituent effects have been carried out in different solvents: methanol for electron-donating ones<sup>4</sup> and acetic acid for electron attractors.<sup>5</sup> Since solvent effects on  $\rho$  values for reactions via cationic intermediates cannot be excluded, the similarity of the  $\rho$  values for both sets of substituents in different media does not necessarily mean that there is a linear relationship for all the substituents. Consequently, we carried out kinetic experiments on a large reactivity scale, from 4-OMe to 3,5-(CF<sub>3</sub>)<sub>2</sub>, in a single solvent, methanol. By extending the substituent range up to the strongly electron-attracting 3,5-bis(trifluoromethyl) group, we intended to favor charge stabilization by the bromine atom over stabilization by the aromatic ring. This substituent has already been successfully used<sup>11</sup> in solvolysis to enhance the electron demand

Table I. Rate Constants<sup>a</sup> for Free Bromine Addition to Ring-Substituted Styrenes at 25.0 °C

X	<i>k</i> , M <sup>-1</sup> s <sup>-1</sup> in AcOH		<i>k</i> , M <sup>-1</sup> s <sup>-1</sup> in MeOH	
	styrenes 1	styrenes 1	α-methylstyrenes 2	<i>trans</i> -β-methylstyrenes 3
a 4-OH				(1.95 ± 0.04) × 10 <sup>7</sup>
b 4-OMe	5.53 × 10 <sup>5</sup>	(3.37 ± 0.03) × 10 <sup>6c</sup>	6.60 × 10 <sup>7</sup>	3.02 × 10 <sup>6</sup>
c 4-Me	1.07 × 10 <sup>3b</sup>	(1.98 ± 0.10) × 10 <sup>4c</sup>	(2.17 ± 0.03) × 10 <sup>6</sup>	3.46 × 10 <sup>4</sup>
d 3,4-C <sub>4</sub> H <sub>4</sub> <sup>d</sup>		7.59 × 10 <sup>3</sup>		
e 3-Me		3.32 × 10 <sup>3</sup>	3.81 × 10 <sup>5</sup>	6.30 × 10 <sup>3</sup>
f 4-F	25.3 <sup>b</sup>	(1.54 ± 0.09) × 10 <sup>3c</sup>		
g H	14.3 <sup>b</sup>	(1.53 ± 0.08) × 10 <sup>3c</sup>	(1.38 ± 0.04) × 10 <sup>5</sup>	(3.23 ± 0.06) × 10 <sup>3c</sup>
h 4-Cl		(3.84 ± 0.25) × 10 <sup>2c</sup>	3.40 × 10 <sup>4</sup>	
i 4-Br	2.53 <sup>b</sup>	(2.52 ± 0.10) × 10 <sup>2c</sup>		4.79 × 10 <sup>2</sup>
j 3-Cl	2.15 × 10 <sup>-1b</sup>	(4.78 ± 0.20) × 10 <sup>c</sup>	4.16 × 10 <sup>3</sup>	
k 3,4-Cl <sub>2</sub>	8.33 × 10 <sup>-2b</sup>	19.1		
l 3-CF <sub>3</sub>		11.8 ± 0.09	(9.17 ± 0.03) × 10 <sup>2</sup>	33.5 ± 0.08
m 3-NO <sub>2</sub>	9.61 × 10 <sup>-3b</sup>	2.82		
n 4-NO <sub>2</sub>	3.58 × 10 <sup>-3b</sup>	1.20		3.16
o 3,5-(CF <sub>3</sub> ) <sub>2</sub>		0.25 ± 0.02	12.1 ± 0.02	0.60 ± 0.02

<sup>a</sup> Absolute errors are given when *k*<sub>Br<sub>2</sub></sub> is experimentally measured from bromide ion effects. When they are not tabulated, *k*<sub>Br<sub>2</sub></sub> is obtained from empirical relationships between log *k*<sub>Br<sub>2</sub></sub> and log *k*<sub>exp</sub> at 0.2 M NaBr; in these cases, the errors on log *k*<sub>Br<sub>2</sub></sub> are less than 0.05 log unit (see Experimental Section). <sup>b</sup> Reference 5c. <sup>c</sup> M. de Fiequelmont and J. E. Dubois, *Tetrahedron*, **34**, 2247 (1978). <sup>d</sup> β-Naphthylethylene.

on poor neighboring groups. Moreover, the magnitude of the charge borne by each olefinic carbon atom in the transition state was estimated by the *k*<sub>Me</sub>/*k*<sub>H</sub> ratio method,<sup>12</sup> which constitutes a more sensitive approach than a classical ρσ analysis. To this end, we measured the ring substituent effects on the bromination of α-methylstyrene **2** and *trans*-β-methylstyrene **3**. Finally, the ring substituent effects on the ste-



reochemistry of *trans*-β-methylstyrene **3** were determined so as to measure the magnitude of bromine bridging in the intermediates and to render our interpretation coherent with both kinetic and stereochemical data.

## Results

**Kinetics.** The bromination rate constants, *k*<sub>exp</sub>, of the ring-substituted styrenes **1**, α-methylstyrenes **2**, and *trans*-β-methylstyrenes **3** listed in Table I were measured in methanol containing 0.2 M NaBr at 25 °C by various coulometric and amperometric methods.<sup>13</sup> In this medium, two brominating agents, free bromine Br<sub>2</sub> and tribromide ion Br<sub>3</sub><sup>-</sup>, formed in the equilibrium



add to the olefin.<sup>14</sup> Owing to doubts about the nature of the “*k*<sub>Br<sub>3</sub><sup>-</sup></sub> mechanism”,<sup>15</sup> we shall only consider substituent effects on the constant *k*<sub>Br<sub>2</sub></sub>.

The rate constants *k*<sub>Br<sub>2</sub></sub> have been obtained in two ways: either from experimental bromide ion effects or from empirical relationships between *k*<sub>exp</sub> and *k*<sub>Br<sub>2</sub></sub>.

The first method, described in the Experimental Section, was used to measure the *k*<sub>Br<sub>2</sub></sub> values for a set of styrenes chosen to cover the entire reactivity range within each series **1**, **2**, and **3**. These experimental values are then used to establish empirical relationships between log *k*<sub>Br<sub>2</sub></sub> and log *k*<sub>exp</sub> at 0.2 M NaBr. Finally, the *k*<sub>Br<sub>2</sub></sub> values for the remaining styrenes were calculated from *k*<sub>exp</sub> (0.2 M NaBr) (Table IV) by means of these relationships (see Experimental Section). All these *k*<sub>Br<sub>2</sub></sub> constants, which will be reduced to *k* in the following discussion, are given in Table I, where the rate constants for styrene bromination in acetic acid are also shown.

### Substituent Effects and ρσ Relationships in Styrene Bro-

mination. For bromination in methanol of the ring substituted styrenes **1** (Table I), the ρσ<sup>+</sup> plot is approximately linear:

$$\log k_1 = -3.92\sigma^+ + 3.18 \quad (2)$$

$$\text{correlation coefficient } R = 0.996$$

$$\text{standard deviation on the slope } s = 0.10$$

However, this relationship is not homogeneous: partial correlations either for electron-donor substituents (**1b–g**), eq 3, or for electron attractors (**1h–o**), eq 4, lead to very different slopes.

$$\log k_{1b-g} = -4.36\sigma^+ + 3.10 \quad R = 0.992 \quad s = 0.27 \quad (3)$$

$$\log k_{1h-o} = -3.53\sigma^+ + 2.96 \quad R = 0.995 \quad s = 0.13 \quad (4)$$

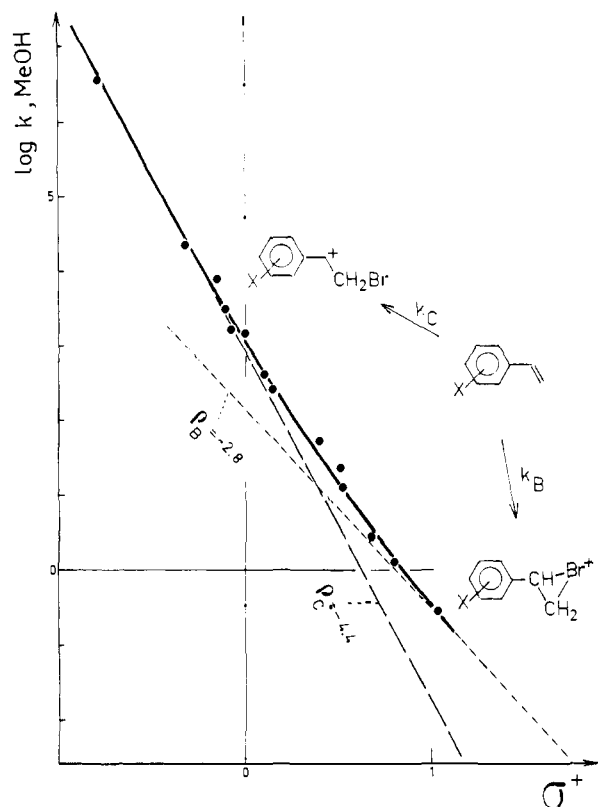
The fact that the slope of the ρσ<sup>+</sup> plot is 20% greater for donor than for attractor substituents is significant relative to the errors on log *k* and on the slopes. Thus the ρσ<sup>+</sup> plot for styrene bromination in methanol can be either a poor straight line or a curve<sup>16</sup> (Figure 1). Consequently, none of the slopes of eq 2, 3, or 4 can be considered as the true ρ value for styrene bromination.

For *trans*-β-methylstyrenes **3a–o**, a similar situation is observed: the ρσ relationship for all the substituents gives a slope of -3.82 but partial correlations for electron-donating or electron-attracting substituents lead to slopes of -4.08 and -3.31, respectively. On the other hand, there exists a very accurate linear relationship between the substituent effects on substrate **1** and **3**. Plotting log *k*<sub>3</sub> against log *k*<sub>1</sub> for each substituent, we obtain

$$\log k_3 = 0.94 \log k_1 + 0.04 \quad R = 0.9995 \quad s = 0.012 \quad (5)$$

Such log *k*/log *k* correlations between reactivities of closely related substrates measured under similar conditions are more accurate and more instructive than the classical ρσ relationships. The slope of eq 5 shows that the introduction of a *trans*-β-methyl group attenuates the ρ value for the ring substituents by a factor of 0.94.

For α-methylstyrenes **2b–o**, the ρσ<sup>+</sup> plot is concave downward as expected from geometrical factors. In the ground state,<sup>17</sup> the aromatic ring is rotated out of the plane of the double bond by a 32° angle. The passage to the transition state cannot greatly change this geometry since the hybridization remains sp<sup>2</sup> if the intermediate is a carbonium ion and near sp<sup>2</sup> if it is a dissymmetrical bromonium ion. Therefore, a Yu-



**Figure 1.** The  $\rho\sigma^+$  relationship for styrene bromination. Is the plot a poor straight line or a curve? The trend of the  $k_{\alpha\text{-Me}}/k_{\text{H}}$  ratio supports a curve which indicates a change in the structure of the intermediate.

kawa-Tsuno equation is more appropriate. The  $\rho$  value was established from the five meta-substituted compounds **2e,g,j,l,o** and the  $r$  value from the deviations of the para-substituted ones **2b,c,h** (Figure 2).

$$\log k_2 = -4.26(\sigma + 0.65\Delta\sigma^+) + 5.18$$

$$R = 0.998 \quad s_\rho = 0.120 \quad (6)$$

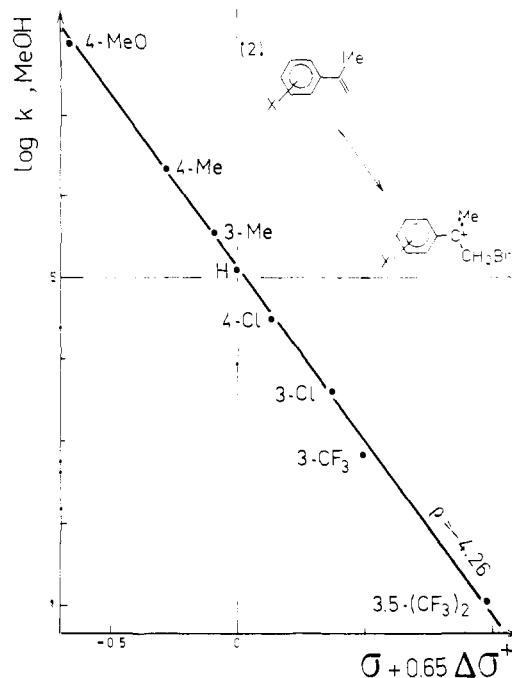
$$s_r = 0.205$$

Direct comparison between substituent effects on styrene and  $\alpha$ -methylstyrene bromination can only be made from non-conjugating meta substituents since resonance effects differ in the two olefinic substrates.

$$\log k_2 = 1.07 \log k_1 + 1.77 \quad R = 0.9996 \quad s = 0.016 \quad (7)$$

Thus meta-substituent effects on  $\alpha$ -methylstyrene appear to be greater than those on styrene bromination, a rather unexpected result, as we shall see further.

**Product Formation.** The product composition was investigated in the case of the *trans*- $\beta$ -methylstyrene system **3**. In hydroxylic solvents, bromination leads to dibromides and solvent incorporated products. Diastereoisomeric dibromides were identified by their NMR spectra.<sup>8</sup> Substituent effects on the chemical shifts of the aliphatic protons are negligible. The stereochemistry of dibromide formation was determined by integration of the methyl group and  $\text{H}_\alpha$  proton signals. "Erythro" and "threo" methoxy bromides<sup>18</sup> were obtained predominantly by bromination of *trans*- and *cis*- $\beta$ -methylstyrenes ( $\text{X} = \text{H}$ ), respectively, in pure methanol. Chemical shifts of methine and methyl protons of these mixed adducts are readily distinguishable from those of the dibromo adducts. NMR spectra of the diastereoisomeric methoxy bromides differ essentially in the position of the doublet corresponding to the methyl protons. Assuming that chemical shifts of aliphatic protons are insensitive to ring substituents, we can de-



**Figure 2.** The Yukawa-Tsuno plot of  $\alpha$ -methylstyrene bromination. The  $\rho$  value is established from nonconjugating meta substituents.

**Table II.** Dependence of the Dibromide Stereochemistry<sup>a</sup> on the Ring Substituents in  $\beta$ -Methylstyrene Bromination in Methylene Chloride

	% erythro	% threo
<b>3b</b> <i>trans</i> -4-OMe <sup>b</sup>	63	37
<b>3g</b> <i>trans</i> -H	81	18
<i>cis</i> -H	28	72
<b>3l</b> <i>trans</i> -3-CF <sub>3</sub>	91	9
<b>3o</b> <i>trans</i> -3,5-(CF <sub>3</sub> ) <sub>2</sub>	100	0

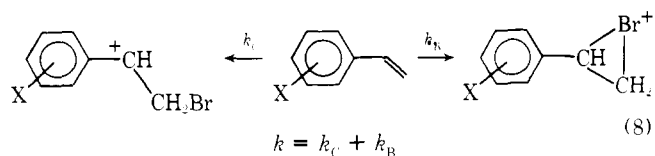
<sup>a</sup> Reproducibility is within 2%. <sup>b</sup> Reference 8 in  $\text{CCl}_4$  at 5 °C.

termine the configuration of the methoxy bromides from **3l** and **3o**. NMR data on these adducts are given in the Experimental Section.

The stereoselectivity of the dibromide formation in methylene chloride depends on the substituent (Table II). In methanol, the major products are the solvent-incorporated adducts; the dibromides represent only 5% of the total products for **3g** and 12% for **3o**. The mixed adducts are formed stereospecifically and regioselectively: the methanol attacks in all cases the benzylic carbon atom so that the methoxy bromides obtained are the 1-methoxy-1-aryl-2-bromopropanes.

## Discussion

A quantitative separation between carbonium and bromonium ion pathways has been made in stilbene bromination<sup>9</sup> on the basis of the curvature in the  $\rho\sigma^+$  plot which indicates changes in the transition state structure with changes of the substituents. In the case of styrenes **1**, our results show that a curvature in the  $\rho\sigma^+$  plot cannot be definitely ruled out but the magnitude of the curvature, if it exists, is too small to be interpreted in terms of competitive pathways as in the scheme of eq. 8.



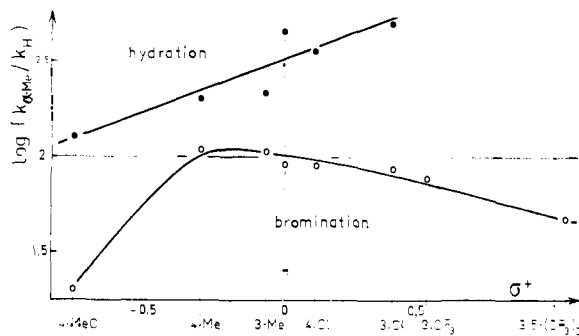
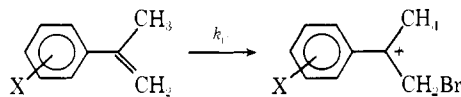


Figure 3. The comparison of the trend in the  $k_{\alpha\text{-Me}}/k_{\text{H}}$  ratio in bromination and in hydration (data from ref 21). In hydration the charge on the  $\text{C}_{\alpha}$  carbon atom increases as the  $\sigma^+$  increases, whereas in bromination it decreases.

The  $\rho\sigma^+$  analysis of bromination of  $\alpha$ -methylstyrenes **2** does not show such an ambiguity and we can consider that there is no change in the bromination mechanism for these substrates. Therefore, we shall firstly identify the transition states and intermediates in the bromination of  $\alpha$ -methylstyrenes **2**. Then we shall deduce, from the observed methyl effects in bromination, the structure of intermediates for styrenes **1** and  $\beta$ -methylstyrenes **3**. Finally we shall discuss the substituent effects on various other additions to styrenes compared to bromination.

**Carbonium Ion Structure of the Transition States in  $\alpha$ -Methylstyrene Bromination.** In addition to the  $\rho$  value of the Yukawa-Tsuno relationship the carbonium-ion-like structure of the transition state is justified by several arguments.

The introduction of an  $\alpha$ -methyl group on the double bond of stilbenes<sup>19</sup> transforms the curved  $\rho\sigma^+$  plot of stilbene bromination into a strictly linear one for substituents varying from 4-OMe to 4-CF<sub>3</sub>. Thus, the donor  $\alpha$ -methyl stabilizes the benzylic carbonium ion much more than the corresponding bromonium ion so that the bromonium ion pathway is made negligible, even when the substituent is as electron attracting as 4-CF<sub>3</sub>. Consequently, it is reasonable to assume that bromination of  $\alpha$ -methylstyrenes substituted by groups varying from 4-OMe to 4-CF<sub>3</sub> goes through carbonium ions. For the least reactive compound **2o**, we can assume that the transition state is carbonium-ion-like since this olefin does not deviate from the  $\rho\sigma$  correlation (eq 6). Spectroscopic observations of  $\beta$ -bromocumyl cations<sup>20</sup> show that bromine participation is negligible in these tertiary ions. In solvolysis also,<sup>10</sup> a methyl group directly attached to a tertiary cationic center is sufficiently electron donating to eliminate neighboring group participation or solvent assistance. Thus the  $\rho$  value,  $-4.26$ , found in eq 6 for  $\alpha$ -methylstyrene bromination can be taken as the measure of the sensitivity to substituent effects of the carbonium ion pathway.



**The  $\alpha$ -Methyl Effect and the Competition between Two Pathways in Bromination of Styrenes **1**.** Since we know the structure of the intermediates of  $\alpha$ -methylstyrene bromination, we attempt to deduce from it the structure of styrenes **1** by comparing the methyl effect expected for reactions via carbonium ions with that observed in bromination. The introduction of an  $\alpha$ -methyl group on substrates which react via arylcarbonium ions diminishes the electron demand on the aromatic ring so that substituent effects are reduced, the  $k_{\alpha\text{-Me}}/k_{\text{H}}$  ratio diminishing as the substituents become more electron donating. In styrene bromination, this effect is com-

pletely different: except for the 4-OMe substituent, the  $k_{\alpha\text{-Me}}/k_{\text{H}}$  ratio decreases as the substituent becomes more and more electron attracting (Table I). As shown by the negative slope of Figure 3, the variation of the methyl effect in bromination is in the opposite direction to that in hydration,<sup>21</sup> an addition via carbonium ions. Insofar as the trend in hydration can be considered as the normal trend for reactions via carbonium ions, these ions cannot be the intermediates both in the bromination of styrenes and of  $\alpha$ -methylstyrenes. Since it can be demonstrated that they are reasonably involved in  $\alpha$ -methylstyrene bromination, it is in styrene bromination that some deviation from the carbonium ion mechanism occurs for the electron-attracting substituents. According to the methyl effects, in styrene reactions via carbonium ions, the benzylic carbon atom is more and more charged as the ring substituent becomes more and more electron attracting; in bromination, this carbon atom becomes less and less charged. Therefore, it is reasonable to assume that a bromonium ion competes increasingly with a carbonium ion; the charge would be, then, stabilized by the bromine atom rather than by the aromatic ring.

#### The Carbonium Ion Pathway in the Bromination of Styrenes

**1.** The effect of the  $\alpha$ -methyl substituent on  $\rho$  for bromination via carbonium ions was measured in stilbene bromination:<sup>19</sup>  $\rho_{\alpha\text{-Me}}/\rho_{\text{H}} = -4.87/-5.05 = 0.96$ . Since we know the  $\rho$  value of  $-4.26$  for  $\alpha$ -methylstyrene bromination, we can estimate that for styrene bromination via carbonium ions. This calculation leads to a  $\rho$  value of  $-4.43$ , very near to that found in eq 3 for styrenes with electron-donating substituents only. The  $\rho\sigma$  plot for styrene bromination must consequently be considered as a curve and not a straight line, the curvature suggesting that a bromonium ion pathway competes with the carbonium ion one in the case of strongly electron-attracting substituents. In methanol, the substituent effects on the carbonium ion pathway can, therefore, be expressed<sup>25</sup> by eq 3' with a  $\rho$  value of  $-4.36$ .

$$\log k_{\text{C}} = -4.36\sigma^+ + 3.10 \quad (3')$$

The carbonium-ion-like transition state in styrene bromination has been previously rejected<sup>7</sup> because of the absence of rotation in this state, tensions of the ground state being retained. Our present and previous<sup>26</sup> results indicate that the charge distribution is carbonium-ion-like. These observations are not necessarily contradictory if we admit that the spatial layout of the substituents is frozen in the carbonium-ion-like transition states of bromination. Recent findings in hydration<sup>21b</sup> justify the assumption of a locked conformation for the carbonium-ion-like transition states in electrophilic additions; in hydration as in bromination, ground state tensions are retained in these states.

#### The Bromonium Ion Pathway in Bromination of Styrenes **1**.

Equation 3' expresses the substituent effects on the carbonium ion pathway; the deviations, from this equation, of styrenes with electron-attracting substituents enable us to obtain the rate constants for the bromonium ion pathway by eq 8,  $k_{\text{B}} = k - k_{\text{C}}$ . Owing to the uncertainties in eq 3, the calculation is only very approximate. Rough estimates obtained in this way are given in Table III for the most electron-attracting substituents: the bromonium ion pathway could contribute to the extent of 85% for compound **1o**, although eq 2 is fairly good to a first approximation. An analogous situation is found in the now-resolved controversy concerning the existence of the phenonium ion: a large phenonium contribution to the mechanism leads to only a small deviation from the  $\rho\sigma$  plot.<sup>10</sup> The solution of this latter problem was found in the curvature of an extended  $\rho\sigma$  plot. In styrene bromination, no great curvature can be detected. To find readily interpretable deviations, it would be interesting to deactivate the aromatic ring even more. Unfortunately, substituents much more electron attracting

**Table III.** Estimated Importance of the Bromonium Ion Pathway  $k_B$  in Bromination of Styrenes **1**

	$k_B^a$	% $k_B^b$
3-CF <sub>3</sub>	5.0	40
3-NO <sub>2</sub>	1.3	45
4-NO <sub>2</sub>	0.74	60
3,5-(CF <sub>3</sub> ) <sub>2</sub>	0.21	85

<sup>a</sup> Calculated from eq 8 where  $k_C$  is measured by eq 3'. <sup>b</sup> %  $k_B = k_B/k \times 100$ .

than 3,5-(CF<sub>3</sub>)<sub>2</sub> do not exist at present.<sup>29</sup> From the available estimates of the bromonium rate constants (Table III), we appraise the parameters of the bromonium ion pathway. Since the bromine atom rather than the benzylic carbon atom bears most of the charge in this pathway,  $\sigma$  should be the appropriate substituent constant. There exists a satisfactory  $\rho\sigma$  relationship ( $R = 0.999$ ) for the four estimated  $k_B$  values with a  $\rho_B$  value of  $-2.8$  ( $s_\rho = 0.065$ ).

Thus, the kinetic data for styrene bromination are quantitatively interpreted by the multipathway scheme where bromonium and carbonium ions were formed competitively. The choice of this scheme is based essentially on its ability to account quantitatively for the substituent effects. However, such a competition between two discrete intermediates is kinetically and stereochemically indistinguishable from the more classical model of bromination intermediates in which the charge delocalization between the olefinic carbon and bromine atoms would depend on the substituents.<sup>2</sup> This latter model, although often suggested, cannot at present be tested quantitatively.

**The  $\beta$ -Methyl Effect and the Structure of the Intermediates in Bromination of the *trans*- $\beta$ -Methylstyrenes **3**.** Whereas the  $\alpha$ -methyl effect is high and variable, the  $k_{\beta\text{-Me}}/k_H$  ratio, in the range of 1.5–2.5, is persistently small.<sup>27</sup> Therefore, the C <sub>$\beta$</sub>  carbon atom is not significantly charged either for electron-donating substituents or for strongly electron-attracting ones. The decrease in charge on the C <sub>$\alpha$</sub>  atom shown by the  $k_{\alpha\text{-Me}}/k_H$  trend is consequently compensated only by an increase in charge on the bromine atom. Therefore, the bromonium-ion-like transition state, which competes with the carbonium ion one in the case of the least reactive styrenes **1**, should not be significantly charged on C <sub>$\beta$</sub> .

The fact that substituent effects on styrene and  $\beta$ -methylstyrene are linearly correlated by eq 5 suggests that a  $\beta$ -methyl group stabilizes the bromonium and the carbonium ions to a similar extent. Small  $\beta$ -methyl effects in reactions via carbonium ions are usual;<sup>10</sup> they are not surprising for additions via cyclic ions. In styrene sulfonylation,<sup>28</sup> an addition via a cyclic episulfonium ion, the  $\beta$ -methyl effect is 2.

For bromination of *trans*- $\beta$ -methylstyrenes **3**, the results can be analyzed by the method applied in bromination of styrenes **1** for separating the carbonium and bromonium ion pathways. However, since there is an accurate correlation between substituent effects on bromination of **3** and **1** (eq 5), it is not necessary to repeat the complete analysis. As shown by the slope of eq 5, the ring substituent effects on **3** are attenuated by a factor of 0.94 whatever the structure of the intermediate.

**Solvent Effects on  $\rho$  Value in Styrene Bromination.** Previous results<sup>5</sup> have shown that in acetic acid, the  $\rho\sigma^+$  relationship for styrene bromination is linear. However, we observe that the data in acetic acid (Table I) correlate linearly with those in methanol. The curvature obtained in methanol must, therefore, also exist in acetic acid. Various  $\rho$  values for styrene bromination in this solvent have been published:  $-4.21$ ,<sup>5a</sup>  $-4.71$ ,<sup>5b</sup>  $-4.83$ .<sup>5c</sup> From the slope of eq 9 and from the  $\rho_C$  value ( $-4.36$ )

$$\log k (\text{MeOH}) = 0.77 \log k (\text{AcOH}) + 2.06$$

$$R = 0.9992 \quad s = 0.011 \quad (9)$$

in methanol, we calculate a  $\rho_C$  in acetic acid of  $-5.65$ . Such a high solvent effect on  $\rho$  is expected for a reaction via a cationic intermediate: the  $\rho$  value increases as the polarity decreases. The calculated value in acetic acid is also in agreement with that of  $-5.69$  found by Bodrikov<sup>30</sup> for styrene bromination by *N*-bromosuccinimide in acetic acid. An important solvent effect on  $\rho$  is observed in sulfonylation also:  $\rho$  passes from  $-2.66$  in acetic acid<sup>31</sup> to  $-3.74$  in tetrachloroethane.<sup>28</sup>

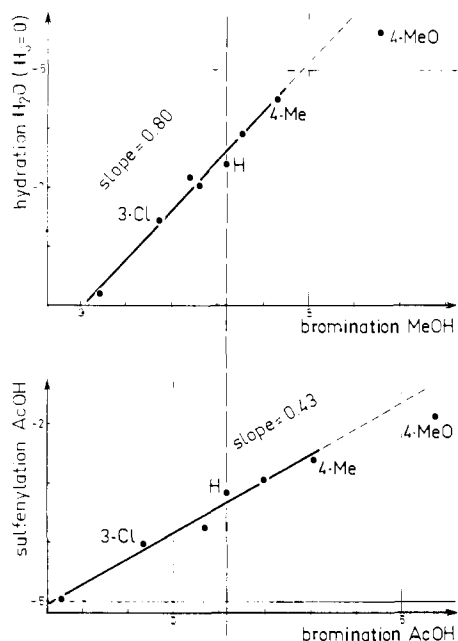
An important consequence of the linearity of eq 9 is that the relative magnitude of the bromonium and carbonium pathways does not change from methanol to acetic acid. This confirms our analysis of kinetic solvent effects in bromination:<sup>6</sup> solvent changes cannot lead to a significant variation in the charge distribution in the transition state.

**Dependence of the Stereochemistry on the Substituents.** In the apolar methylene chloride, the bromide ion addition changes from near nonstereoselective for the most reactive styrene (**3b**) to antistereoselective for the least reactive one (**3o**) (Table III). For **3b**, the low stereoselectivity observed corresponds to that of the corresponding  $\beta$ -bromo cation as demonstrated by Fahey.<sup>8</sup> Thus in methylene chloride, bromine bridging is absent in the intermediate of **3b** and becomes complete in that of **3o**. Therefore, these data show that the intermediate in styrene bromination changes from  $\beta$ -bromo-carbonium ions for the most electron-donating substituents to a bridged bromonium ion for the most electron-attracting substituents.

The stereochemistry of dibromide formation from **3g** depends little on the solvent: the erythro/threo dibromide ratio is almost unchanged<sup>32</sup> when the solvent passes from methylene chloride and chloroform<sup>8</sup> to acetic acid.<sup>33</sup> Therefore, the stereochemical results on dibromide formation obtained in methylene chloride can reasonably be transposed to methanol<sup>34a</sup> so that stereochemical and kinetic data are in rough agreement: the intermediate changes from carbonium ion for electron-donating substituents to essentially bromonium ion for the strongest electron attractor. However, precise rate-product correlation,<sup>35</sup> analogous to those found in solvolysis, cannot be established because the relative rates of the bromonium and carbonium ion pathways<sup>25</sup> are not known accurately.

On the other hand, in methanol as in acetic acid, the solvent-incorporated products are formed stereospecifically. In methanol, the amount of dibromide formed is so small<sup>34b</sup> that we cannot say whether this also formed stereospecifically. In acetic acid, whereas the attack of the solvent on **3g** is stereospecific (100% *trans*), that of the bromide ion is only stereoselective (80% *trans*, 20% *cis*). It is therefore reasonable to assume that, in methanol as well, dibromides are formed stereoselectively and methoxy bromides stereospecifically. Since dibromides and solvent-incorporated products are formed from the same intermediate, the interpretation is rather difficult if bromine bridging is the sole reason for stereospecificity in these ions. In fact, the stereospecific formation of methoxy bromides could only be explained by a strongly bridged bromonium ion. But this interpretation is inadequate since it is coherent neither with the regiospecificity of the solvent attack nor with the absence of stereospecificity in dibromide formation.

**Comparison of Substituent Effects in Bromination and Related Electrophilic Additions. Charge Distribution in the Transition States.** Abundant kinetic data on electrophilic additions to styrenes have been published.<sup>2</sup> Most of these additions, except hydration and bromination, go through cyclic intermediates. Bromination appears to be atypical: it is at present the only reaction where ring substituents are able to change the structure of the intermediate from open to cyclic cation. A comparison between substituent effects on bromination and hydration<sup>36</sup> or sulfonylation,<sup>37,31</sup> taken as models



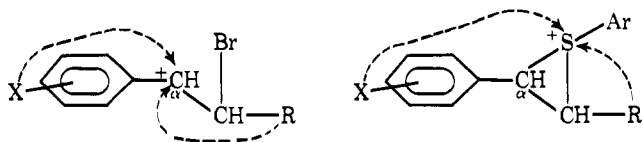
**Figure 4.** Comparison of substituent effects in bromination, hydration, and sulfenylation of styrenes. Ring substituent effects in bromination are substantially larger than those in sulfenylation; they are only apparently larger than those in hydration because the solvent differs for both reactions.

for additions with open or cyclic intermediates, respectively, is instructive.<sup>38</sup> Plots of  $\log k^{\text{Br}_2}$  (bromination) against  $\log k^{\text{H}^+}$  (hydration) and  $\log k^{\text{ArSCl}}$  (sulfenylation), substituent by substituent, avoiding the use of  $\sigma$  or  $\sigma^+$  constants defined from different reactions, are given in Figure 4. Eliminating the 4-OMe substituent,<sup>39</sup> approximately linear correlations for the common substituents are obtained:

$$\log k^{\text{H}^+} = 0.80 \log k^{\text{Br}_2} - 8.95 \quad R = 0.991 \quad s = 0.047 \quad (10)$$

$$\log k^{\text{ArSCl}} = 0.43 \log k^{\text{Br}_2} - 3.83 \quad R = 0.984 \quad s = 0.039 \quad (11)$$

Since the correlation coefficients are so similar, it is impossible to deduce directly from these equations that the charge distribution in the bromination transition state is carbonium-ion-like as in hydration or onium-like as in sulfenylation. The comparison between hydration and bromination is not very instructive, because the solvents (water and methanol, respectively) differ and medium effects on both reactions are large.<sup>36</sup> For this reason, the less than unit slope of eq 10 does not necessarily signify that substituent effects are higher in bromination than in hydration. On the other hand, comparison of sulfenylation and bromination (eq 11) is made in the same solvent: acetic acid.<sup>37</sup> It can be deduced, therefore, that substituent effects are higher in bromination than in sulfenylation. This result is inconsistent with the recent interpretation of Schmid et al.<sup>40</sup> On the basis of almost identical R effects in bromination and sulfenylation of  $\beta$ -R substituted styrenes,  $\text{C}_6\text{H}_5\text{CH}=\text{CHR}$ , these authors conclude that both transition state structures should be cyclic. In fact, similar R effects with dissimilar ring substituent effects are only consistent with a carbonium-ion-like transition state for bromination where R is in the  $\beta$  position and  $\text{XC}_6\text{H}_4$  in the  $\alpha$  position relative to the



charge and with an episulfonium-ion-like transition state in sulfenylation (R and  $\text{XC}_6\text{H}_4$  both in  $\beta$  positions relative to the charge).

The slopes of such  $\log k/\log k$  correlations must be interpreted with caution.<sup>38b</sup> Strictly speaking, the  $\rho$  values to which these slopes are equivalent measure the sensitivity of the reaction to substituent effects:  $\rho$  expresses at the same time the position of the transition state along the reaction coordinate (charge magnitude) and the way in which substituent effects are transmitted (charge location). In particular, the observed trend of  $\rho$  values for chlorination<sup>41</sup> ( $-3.22$ ), bromination ( $-5.7$ ), and sulfenylation<sup>37</sup> ( $-2.41$ ) of styrenes **1** in acetic acid results from a combination of these two factors: bromination and probably chlorination also go through transition states in which the benzylic carbon atom is charged; the differences between their  $\rho$  values would reflect differences in the magnitude of this charge. Sulfenylation, on the other hand, goes through an episulfonium ion and the attenuation of  $\rho$  is partly due to the greater distance between the charge and the ring substituents; in fact, the  $\rho$  for sulfenylation should be compared to the  $\rho_{\text{B}}$ , for bromination via bromonium ion. Previous attempts to interpret<sup>40</sup> the  $\rho$  trend for these reactions based on the relative magnitude of assistance by neighboring chlorine, bromine, and sulfur atoms have not succeeded because the variation of the charge magnitude was neglected.

## Conclusion

Although a sharp curvature in the free-energy relationship, analogous to that observed in stilbene bromination, does not exist in styrene bromination, it has been possible to analyze quantitatively the data for this system by the multipathway scheme. This analysis explains coherently the kinetic ring-substituent effects, the kinetic  $\alpha$ - and  $\beta$ -methyl effects, and the stereochemistry of dibromide formation. Moreover, it has the merit of clearly showing the limiting cases—pure bromonium or pure carbonium ions—and to specify the charge distribution in the intermediate situations. Thus, the multipathway scheme leads to rational and quantitative interpretations whereas the weakly bridged intermediate usually proposed is a vague model which can account only for a qualitative discussion of data but precludes a quantitative one.

Furthermore, our analysis emphasizes that the  $\rho\sigma$  relationships are unsuitable for determining variations of mechanism or intermediate structure involving only slight free-energy changes. In fact, small deviations of the order of 0.3–0.5 log unit can be minimized or completely hidden in large-scale  $\rho\sigma$  correlations. Thus, complementary data must be associated with these analyses in order to detect a minor pathway compared to a predominant one.

Another consequence of our treatment follows from the carbonium ion structure of the transition states and intermediates in aryl olefin bromination. Until now, solvolysis was the exclusive reaction model for structural studies of carbocations. However, there exist numerous problems concerning these ions which are difficult to resolve on the basis of solvolysis data and which might be considered from the viewpoint of bromination. For example, vinylic cations are more readily obtained from bromination than from solvolysis;<sup>6b</sup> secondary aryl cations which are not generated in solvolysis due to the solvent participation have already been examined<sup>42</sup> in the nonnucleophilically assisted bromination. Thus, bromination is an interesting model, complementary to solvolysis, for generating carbocations.

## Experimental Section

**Synthesis of Styrenes.** Styrenes **1**, **2**, and **3** were prepared by conventional methods;<sup>21,31,33</sup> dehydration of the corresponding arylcarbinols obtained by condensation of arylmagnesium halides on the appropriate ketones. They were purified by preparative LPC or VPC

**Table IV.** Experimental Bromination Rate Constants<sup>a</sup> of Styrenes in Methanol (0.2 M NaBr) at 25 °C

	styrenes 1	$\alpha$ -methyl- styrenes 2	<i>trans</i> - $\beta$ - methyl- styrenes 3
a			$8.06 \times 10^5$
b	$1.07 \times 10^5$	$2.08 \times 10^6$	$1.32 \times 10^4$
c	$1.07 \times 10^3$	$8.09 \times 10^4$	$1.88 \times 10^3$
d	$3.48 \times 10^2$		
e	$1.59 \times 10^2$	$1.45 \times 10^4$	$3.66 \times 10^2$
f	$7.55 \times 10$		
g	$6.72 \times 10$	$5.87 \times 10^3$	$1.68 \times 10^2$
h	$1.85 \times 10$	$1.43 \times 10^3$	
i	$1.23 \times 10$		$3.12 \times 10$
j	2.73	$1.88 \times 10^2$	
k	1.18		
l	0.87	$3.88 \times 10$	2.72
m	0.22		
n	$8.67 \times 10^{-2}$		0.30
o	$4.1 \times 10^{-2}$	0.74	0.135

<sup>a</sup> In  $M^{-1} s^{-1}$ ; reproducibility, generally in the range of 2–3%, is always below 5%.

and characterized by their spectral properties (NMR and IR). Purity was checked by analytical VPC.

**Product Analysis.** To a stirred solution ( $5 \times 10^{-3} M$ ) of styrene 3 in methanol, a slight excess (5%) of bromine diluted ( $10^{-2} M$ ) in the same solvent is added drop by drop slowly so that only a pale yellow color is developed. During the addition, the reactant solution is maintained at 25 °C. When the addition is ended, the solvent is evaporated under vacuum at room temperature. The residue is extracted in ether. The ethereal solution is washed successively with sodium thiosulfate and sodium bicarbonate solutions and dried over magnesium sulfate. The solvent is then evaporated under vacuum at room temperature. The final residue is analyzed by NMR spectroscopy. Integration of signals corresponding to methyl,  $H_\alpha$  and  $H_\beta$  protons gives the product composition. For the additions in methylene chloride, the same experimental procedure is followed. The residue obtained after elimination of the reaction solvent is dissolved in  $CCl_4$  and analyzed by NMR spectroscopy. The NMR spectra of the dibromides have already been described.<sup>8</sup> For the threo methoxy bromide,  $C_6H_5CH_\alpha(OMe)CH_\beta BrMe$ , the chemical shift of the methoxy protons is at 3.25 ppm, that of  $H_\alpha$  is at 4.15 ppm (doublet,  $J = 3.75$  Hz), that of  $H_\beta$  is a multiplet, and that of the methyl protons is at 1.45 ppm (doublet,  $J = 6.3$  Hz). For the erythro isomer, the chemical shift of the methoxy protons is at 3.36 ppm, that of  $H_\alpha$  is at 4.4 ppm (doublet,  $J = 5.3$  Hz), and that of the methyl protons is at 1.65 ppm (doublet,  $J = 6.3$  Hz). The change in the ring substituents does not alter these chemical shifts.

**Kinetic Methods.** Three kinetic methods have been used to measure the experimental rate constants,  $k_{exp}$ : coulometry<sup>43</sup> for rate constants higher than  $10^4 M^{-1} s^{-1}$ , potentiometry<sup>13a</sup> for those in the range  $10^{-1}$ – $10^4 M^{-1} s^{-1}$ , and UV spectroscopy<sup>13b</sup> for the smaller ones.

**Experimental  $k_{Br_2}$  Determinations.** Experimental rate constants,  $k_{exp}$ , are measured at three bromide ion concentrations and are given in Table V only for styrenes whose experimental  $k_{Br_2}$  values are not published elsewhere. As shown previously,<sup>14</sup> the bromide ion effect follows the equation  $k_{exp}(1 + K[Br^-]) = \alpha + \beta[Br^-]$  where  $\alpha$  and  $\beta$  are constants and  $K$  is the equilibrium constant of the  $Br_2/Br_3^-$  equilibrium.  $\alpha$  is the  $k_{Br_2}$  rate constant since, when  $[Br^-] = 0$ , then  $k_{exp} = k_{Br_2}$ . Thus, the plot of the function  $k_{exp}(1 + K[Br^-])$  vs.  $[Br^-]$  gives  $k_{Br_2}$  at  $[Br^-] = 0$ .

**Empirical  $k_{exp}/k_{Br_2}$  Relationships and  $k_{Br_2}$  Calculations.** A set of experimental  $k_{Br_2}$  values is used to establish empirical relationships between  $\log k_{Br_2}$  and  $\log k_{exp}$  at 0.2 M NaBr. For styrenes 1, the  $\log k_{Br_2}/\log k_{exp}$  relationship is accurately linear from X = 4-OMe to 3-CF<sub>3</sub>.

$$\log k_{Br_2} = 1.056 \log k_{exp} + 1.200 \quad (12)$$

correlation coefficient,  $R = 0.997$

standard deviation on slope,  $s = 0.010$

**Table V.** Dependence of the Experimental Rate Constants<sup>a</sup> of Styrene Bromination on Bromide Ion Concentration

	0.2 M	[Br <sup>-</sup> ] 0.1 M	0.05 M
1l	0.87	1.18	1.7
1o	$4.10 \times 10^{-2}$	$4.45 \times 10^{-2}$	$5.81 \times 10^{-2}$
2c	$7.48 \times 10^4$	$1.30 \times 10^5$	$2.35 \times 10^5$
2g	$5.87 \times 10^3$	$9.47 \times 10^3$	$15.9 \times 10^3$
2l	45.4	69.5	112
2o	0.74	1.06	1.60
3a	$8.05 \times 10^5$	$1.32 \times 10^6$	$2.23 \times 10^6$
3l	2.72	3.56	5.14
3o	$1.35 \times 10^{-1}$	$1.48 \times 10^{-1}$	$1.68 \times 10^{-1}$

<sup>a</sup> In  $M^{-1} s^{-1}$ ; reproducibility, generally in the range of 2–3%, is always below 5%.

For  $\alpha$ -methylstyrenes 2, the relationship is linear over the whole reactivity range:

$$\log k_{Br_2} = 1.037 \log k_{exp} + 1.251 \quad (13)$$

$$R = 0.9998 \quad s = 0.014$$

For  $\beta$ -methylstyrenes 3, only the least reactive compound deviates from linearity:

$$\log k_{Br_2} = 1.050 \log k_{exp} + 1.109 \quad (14)$$

$$R = 0.9998 \quad s = 0.020$$

The relationships are excellent: average differences between experimental and calculated reactivities are 0.03 log unit with a maximum of 0.06 log unit. Equations 12, 13, and 14 have, therefore, been used to calculate  $\log k_{Br_2}$  for styrenes where only  $k_{exp}$  has been measured.

These calculated  $\log k_{Br_2}$  values are reported in Table I. It can be reasonably assumed that the errors are less than 0.05 log unit, i.e., the errors on calculated  $\log k_{Br_2}$  are not higher than those on experimental values.

For styrenes 1 and  $\beta$ -methylstyrenes 3, the  $\log k_{Br_2}/\log k_{exp}$  plots are slightly curved in the low reactivity range between the 3-CF<sub>3</sub> and 3,5-(CF<sub>3</sub>)<sub>2</sub> substituents. Consequently, the  $\log k_{Br_2}$  values for the 3-NO<sub>2</sub> and 4-NO<sub>2</sub> compounds have been graphically interpolated rather than calculated by eq 12 or 14. Errors for these three points could be at the most 0.08 log unit.

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$$\log k = -3.92(\sigma + 1.13\Delta\sigma^+) + 3.02$$

$$R = 0.984 \quad s_p = 0.13 \quad s_r = 0.36$$

The statistical coefficients are not better than those of the  $\rho\sigma^+$  analysis (eq 2); the Yukawa-Tsuno  $\rho$  value is not different from that of the  $\rho\sigma^+$  treatment. As demonstrated by analysis of  $\alpha$ -methylstyrene data (vide infra), a valid Yukawa-Tsuno treatment must give a  $\rho$  value different from that of the  $\rho\sigma^+$  plot and must improve significantly the correlation. For this reason, we do not retain the Yukawa-Tsuno analysis of data for bromination of 1.

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 (25) The adoption of eq 3 for the carbonium ion pathway supposes that the bromination of the unsubstituted styrene 1g goes through the carbonium ion exclusively. This may be incorrect since 3g is brominated with some stereoselectivity (vide infra). Therefore, the  $\rho$  value for the  $k_C$  pathway could be somewhat underestimated. However, we have at present no other method of obtaining a more precise  $\rho$  value.  
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 (27) As eq 7 expresses the  $\alpha$ -methyl effect, eq 5 represents the  $\beta$ -methyl one. The  $b$  term of these equations,  $\log k_i = a \log k_1 + b$ , denotes the magnitude of these effects; coefficient  $a$  that of their variation as a function of  $\log k_1$ . Although these  $a$  coefficients are similar in magnitude (+7% for the  $\alpha$  effect, -6% for the  $\beta$  one), they represent very different variations in absolute value.  
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 (29) We regret that Gassman et al. have never published in detail their method for the synthesis of the strongly electron-attracting 4-CN-3,5-Cl<sub>2</sub>-phenyl group whose  $\sigma^+$  is 1.22 (P. G. Gassman and A. F. Fentiman, *Tetrahedron Lett.*, 1021 (1970)).  
 (30) I. V. Bodrikov, N. G. Bronnikova, and I. S. Okrokov, *Zh. Org. Khim.*, 9, 953 (1973).  
 (31) K. Izawa, T. Okuyawa, and T. Fueno, *Bull. Chem. Soc. Jpn.*, 47, 1480 (1974); sulfonylation of *trans*- $\beta$ -methylstyrene in acetic acid.  
 (32) Stereochemistry of dibromide formation for *trans*- $\beta$ -methylstyrene is 84% *trans* in  $CDCl_3$  and 83% in acetic acid.  
 (33) J. H. Rolston and K. Yates, *J. Am. Chem. Soc.*, 91, 1469 (1969).  
 (34) (a) The amount of dibromide formed in methanol is too small for its stereochemistry to be determined. For example, for *trans*- $\beta$ -methylstyrene 3g, the 5% of dibromide obtained in MeOH is shown by NMR to be erythro. If the formation of dibromide in MeOH were as stereoselective as in  $CH_2Cl_2$  (81% erythro and 19% threo) the threo dibromide would amount to only 0.9% of the total products and could not be detected by NMR. (b) For a discussion on the dibromide/methoxy bromide ratio, see J. E. Dubois and J. C. Chrétien, *J. Am. Chem. Soc.*, 100, 3506 (1978).  
 (35) Whereas addition to 3o is 100% *trans*, the kinetic data indicate that the carbonium ion pathway can account for 15% of the total rate of 1o and consequently of 3o. This carbonium pathway could lead to a very small amount (0.75% if absence of stereoselectivity is 50/50) of threo isomer not detected by NMR analysis.  
 (36) G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, *J. Am. Chem. Soc.*, 99, 3392 (1977).  
 (37) N. Kharasch and W. L. Orr, *J. Am. Chem. Soc.*, 78, 1201 (1956). Comparison with the data of Izawa<sup>31</sup> gives a fairly good correlation:  $\log k_{styr} = 0.97 \log k_{\beta-Mestyr} - 0.37$  ( $R = 0.9998$ ). Orr's data concerning only 4 substituents are extended by those of Izawa using the above question.  
 (38) (a) Since this paper was submitted, an article was published, (G. H. Schmid and T. T. Tidwell, *J. Org. Chem.*, 43, 460 (1978)) where it is proposed that sulfonylation and hydration be taken as mechanistic models of bromination. This proposition, when applied to alkene bromination, falls to determine the transition state structure because the hydration-bromination and sulfonylation-bromination correlations are both poor. On the other hand, for styrene bromination, these correlations (eq 10 and 11) are equally good. Therefore, the existence of a linear relationship either with sulfonylation or with hydration is not a sufficient criterion by which to demonstrate the structure of the transition state. (b) J. E. Dubois, A. Bienvenue, G. Barbier, and H. Tavernier, *C. R. Acad. Sci., Ser. C*, 266, 997 (1968).  
 (39) The two plots are curved in the region of the 4-OMe substituent due to variable resonance effects.  
 (40) G. H. Schmid, A. Modro, and K. Yates, *J. Org. Chem.*, 42, 871 (1977).  
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 (42) J. E. Dubois, M. F. Ruasse, and A. Argile, *Tetrahedron Lett.*, 1713 (1976).  
 (43) J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, 8, 359 (1964).