Formation of Bromocarbenium Bromide Ion Pairs in the Electrophilic Bromination of Highly Reactive Olefins in Chlorinated Aprotic Solvents†

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The kinetics and the products of bromination of several substituted stilbenes with tetrabutylammonium tribromide (TBAT) have been investigated in aprotic solvents at different temperatures. Stilbenes bearing electron-withdrawing or moderately electron-donating substituents gave stereospecifically the anti addition products. The reactions followed a second-order rate law, and an inverse kinetic isotope effect (KIE), $k_H/k_D = 0.85(0.05)$, was found for the bromination of *cis*-stilbene. The reactions of *cis*- and *trans*-4,4-dimethoxystilbenes yielded mixtures of meso and *d*,*l* dibromides both in chloroform and 1,2-dichloroethane. The rate constants ($k_{Br_3^-}$) measured for the latter olefins deviated considerably from the Hammett correlations, and added bromide had a significant effect on the rates. The reactions of these activated stilbenes with molecular Br_2, carried out at low Br_2 concentration, followed a mixed second/third-order rate law. The kinetic and product distribution data for the reaction, with TBAT, of stilbenes bearing electron-withdrawing or moderately electron-donating substituents are interpreted on the basis of the known mechanism involving a product- and rate-determining nucleophilic attack by bromide on the olefin−Br_2 π-complex. The data related to the bromination of the more activated methoxystilbenes are rationalized considering that, for these olefins, even in aprotic solvents, the ionization of the initially formed 1:1 π-complex to a bromocarbenium bromide ion pair can compete both with the formation of a bromonium-tribromide ion pair and with the nucleophilic attack by Br^-. For this second-order process (first order in Br_2), the kinetic constants and the activation parameters have been measured in chloroform and 1,2-dichloroethane and the activation parameters have been compared with those related to the third-order Br_2 addition and to the reaction with TBAT.

Introduction

Sixty years after the postulation of bromonium ions as the intermediate of the electrophilic bromination of olefins by Roberts and Kimball,[1] important features concerning the formation of transient species are still under discussion and the object of extensive investigations.[2] Not only has the involvement of olefin−Br_2 π-complexes prior to the rate-determining step leading to the ionic intermediate been established[3] but also the nature of the interaction has recently been revealed.[4] Furthermore, evidence for the reversibilty of the ionization step has been presented, and the factors affecting this process have been extensively discussed.[5] The effect of the addition of bromide ion in protic and aprotic solvents has also been investigated.[2,6]

At least three alternative nonradical mechanistic pathways, all of which involve olefin−Br_2 π-complexes, were identified for the bromination of olefins (Scheme 1). In particular the first pathway (path a) has been proposed for the reaction with molecular bromine in aprotic solvents of modest polarity and consists in the ionization of a 1:2 π-complex to give a bromonium−bromocarbenium tribromide ion pair intermediate, which then collapses to dibromide and molecular Br_2.[3,5b,6,7] This pathway, involving a second-order dependence of the rate on Br_2, has been clearly demonstrated for brominations in several chlorinated hydrocarbon solvents.

A similar ionic mechanism, where a solvent-assisted bromine−bromine bond breaking occurs in a 1:1 π-complex and the reaction is first-order in Br_2 (path b), has been established for the bromination at low Br_2 concentrations in hydroxylic solvents[8,9] which provide specific electrophilic solvation by hydrogen bonding to the leaving bromide ion.[10] At higher Br_2 concentration, a third-order process of type *a*, has been reported also in acetic acid.[9b]

In the presence of added bromide salts, which in low polarity nonprotic solvents bind Br_2 as the highly stable

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† Dedicated to the memory of Professor Giuseppe Bellucci (d. March 3, 1996).

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Scheme 1

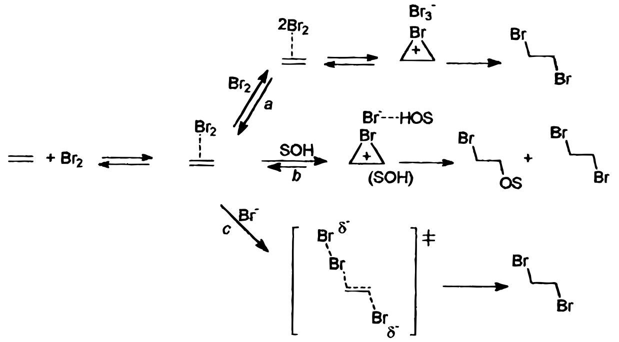


Table 1. Rate Constants for the Bromination of Stilbenes 1b−g and 2b−g in DCE with TBAT at 25 °C

olefin	$k_{Br_3^-}$ (M^{-1} sec^{-1})	**3**:**4**
1a	6.00(0.05) × 10^{-2}	*a*
1b	3.30(0.05) × 10^{-3}	>99:1
1c	7.90(0.1) × 10^{-4}	>99:1
1d	3.64(0.05) × 10^{-4}	>99:1
1e	3.20(0.05) × 10^{-4}	>99:1
1f	1.35(0.05) × 10^{-4}	>99:1
1g	6.25(0.1) × 10^{-5}	>99:1
2a	3.30(0.05) × 10^{-2}	*a*
2b	1.05(0.05) × 10^{-3}	<1:99
2c	3.20(0.05) × 10^{-4}	<1:99
2d	2.30(0.07) × 10^{-4}	<1:99
2f	9.95(0.15) × 10^{-5}	<1:99
2g	6.20(0.1) × 10^{-5}	<1:99

[a] See Table 2.

Br_3^- ion,[11] or when preformed Br_3^- salts are used as the brominating reagents, the bromination has been shown[7] to proceed through rate- and product-determining nucleophilic attack by Br^- on the 1:1 π-complex (path c).

The possibility that all three pathways can contribute to the overall bromination process has been taken into account only for the reactions carried out in protic solvents. In particular it is considered that in chlorinated solvents solely path a is involved in the absence of Br^-, while when bromide salts are added, in an at least stochiometric amount with respect to Br_2, the brominating agent is exclusively the Br_3^- species and path c alone is involved.

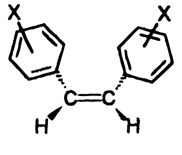
In the present paper we report evidence for the formation of bromocarbenium bromide ion pairs in chlorinated solvents during the bromination with Br_2 and tetrabutylammonium tribromide (TBAT) of *cis*- and *trans*-4,4′-dimethoxystilbenes, showing that path b can compete, depending on the olefin reactivity, with paths a and c also in these solvents. We also report the activation parameters in 1,2-dichloroethane and chloroform for all these processes.

Results

Table 2. Product Distribution for the Bromination of 1a and 2a with Br2 and TBAT in DCE and Chloroform at 25 °C

olefin	electrophile	solvent	product **3**:**4**
1a	Br_2	DCE	16:84
2a	Br_2	DCE	15:85
1a	TBAT	DCE	65:35
2a	TBAT	DCE	10:90
1a	Br_2	$CHCl_3$	15:85
2a	Br_2	$CHCl_3$	15:85
1a	TBAT	$CHCl_3$	55:45
2a	TBAT	$CHCl_3$	13:87

The bromination of the *cis*- and *trans*-stilbenes **1b**−**g** and **2b**−**g** with TBAT in 1,2-dichloroethane (DCE) gave, in a stereospecific way (>99%), only the anti addition products (Table 1). The pure *d,l* dibromides, **3b**−**g**, were thus obtained from the cis olefins, whereas the corresponding trans olefins gave the pure meso isomers **4b**−**g**. A lower stereoselection was instead observed in the reactions of TBAT with the *p*-methoxy-substituted stilbenes **1a** (55−65%) and **2a** (87−90%) both in DCE and chloroform (Table 2). In order to investigate the origin of this behavior the stability of the dibromides **3a** and **4a** in the reaction medium was checked. The product ratios reported in Table 2 for **1a** and **2a** were found to be practically independent of the conversion rate; only a small increase in the *d,l* dibromide during the reaction was observed in the bromination of **1a**. Furthermore, dibromides **3a** and **4a** were quantitatively recovered after exposure to tetrabutylammonium bromide (TBAB) or TBAT under conditions identical to those employed in all of the bromination runs of Table 2. This excluded any Br^--promoted dibromide interconversion during the reactions and assured that the measured **3**/**4** ratios were actually obtained under kinetic control. On the other hand, longer reaction times or higher Br^- concentrations produced a slow **3** → **4** conversion. Table 2 also reports the product distribution for the reaction of **1a** and **2a** with free Br_2. Under these conditions a stereoconvergent formation of dibromides **3**:**4**, in a 15:85 ratio, was observed both in DCE and chloroform.



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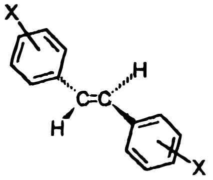

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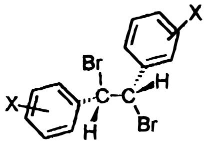

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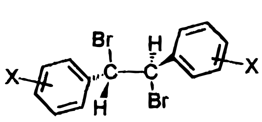

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a: X = *p*-OCH_3; **b**: X = *p*-CH_3; **c**: X = H; **d**: X = *p*-Cl;
e: X = *p*-Br, **f**: X = *m*-Cl **g**: X = *p*-CF_3

The rates of bromination of all olefins **1** and **2** by TBAT were measured spectrophotometrically at 25 °C by monitoring the disappearance of Br_3^-. All reactions obeyed the second-order rate law (first order in Br_3^-) of eq 1,

$$-d[Br_3^-]/dt = k_{Br_3^-}[Br_3^-][Ol] \qquad (1)$$

and the $k_{Br_3^-}$ values found for olefins **1a**−**g** and **2a**−**g** are reported in Table 1. An upward curved Hammett plot was obtained when the kinetic constants $k_{Br_3^-}$ for the bromination of **2a**−**g** were plotted against the σ^+ values. A very similar behavior was observed for the cis olefins.

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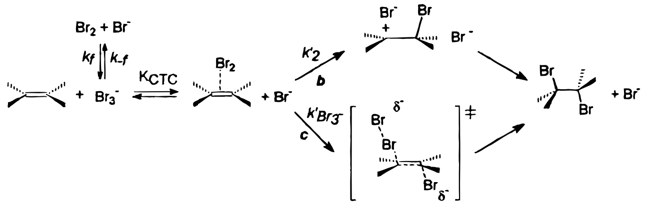
Scheme 2



In particular, the rate constants, $k_{Br_3^-}$, measured for the bromination of **1a** and **2a** deviated from a linear correlation.

The kinetic and product distribution data for the bromination of **1a** and **2a** with TBAT could be due to the concurrence of two processes (Scheme 2), respectively the direct ionization of the olefin$-$Br$_2$ π-complex (path b) or the trapping of this complex by Br$^-$ (path c), both first order in the brominating reagent. Considering that every step preceding the transformation of the olefin$-$Br$_2$ π-complex (CTC) is very fast, eq 2 can be written for the bromination of **1a** and **2a**, where k'_2 is the kinetic constant for the ionization of the CTC and $k_{Br_3^-}$ is the kinetic constant for the trapping of the π-complex by Br$^-$. Introducing the formation constant of the π-complex,

$$-d[Br_3^-]_t/dt = k'_2[CTC] + k'_{Br_3^-}[Br^-][CTC] \quad (2)$$

$$[CTC] = K_{CTC}[Ol][Br_2]$$

K_{CTC}, eq 2 can be rewritten in the form of eq 3, which, considering the equilibrium between Br$_3^-$ and Br$_2$, eq 4, gives eq 5, where $k_2 = k'_2 K_{CTC}$ and $k_{Br_3^-} = k'_{Br_3^-} K_{CTC}$. [Br$_3^-$] can be expressed as function of the $[Br_3^-]_t$

$$-d[Br_3^-]_t/dt = k'_2K_{CTC}[Ol][Br_2] + k'_{Br_3^-}K_{CTC}[Ol][Br_2][Br^-] \quad (3)$$

$$[Br_3^-] = K_f[Br^-][Br_2] \quad (4)$$

$$-d[Br_3^-]_t/dt = ((k_2 + k_{Br_3^-}[Br^-])/K_f[Br^-])[Br_3^-][Ol] \quad (5)$$

to give eq 7. In this equation $k_{Br_3^-}$ and k_2 are the second-

$$[Br_3^-]_t = [Br_3^-] + [Br_2]$$

$$[Br_3^-]_t = [(K_f[Br^-] + 1)/K_f[Br^-]][Br_3^-] \quad (6)$$

$$-d[Br_3^-]/dt = (k_2 + k_{Br_3^-}K_f[Br^-])/(1 + K_f[Br^-])[Br_3^-][Ol] \quad (7)$$

order rate constants for the bromination of **1a** or **2a** with Br$_3^-$ and free Br$_2$, respectively, and K_f is the formation constant of Br$_3^-$ species from Br$_2$ and Br$^-$ in the used solvent, respectively 2×10^7 M^{-1} in DCE and 2.44×10^4 M^{-1} in chloroform.[11]

Under the hypothesis of the dual pathway, for **1a** and **2a** the observed global second-order rate constant for the disappearance of Br$_3^-$ (k_{obsd}) can be expressed by eq 8.

$$k_{obsd} = (k_2 + k_{Br_3^-}K_f[Br^-])/(1 + K_f[Br^-]) \quad (8)$$

This is exactly the familiar Bartlett equation established for protic solvents. The only difference is that in halogenated solvents $K_f[Br^-] \gg 1$.

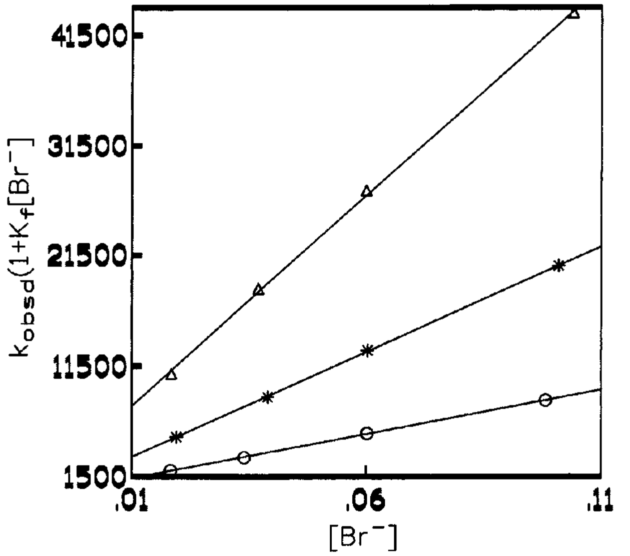


Figure 1. Plots of $k_{obsd}(1 + K_f[Br^-])$ vs [Br$^-$] for the bromination of **2a** in DCE at 10 (○), 25 (*), and 40 (△) °C.

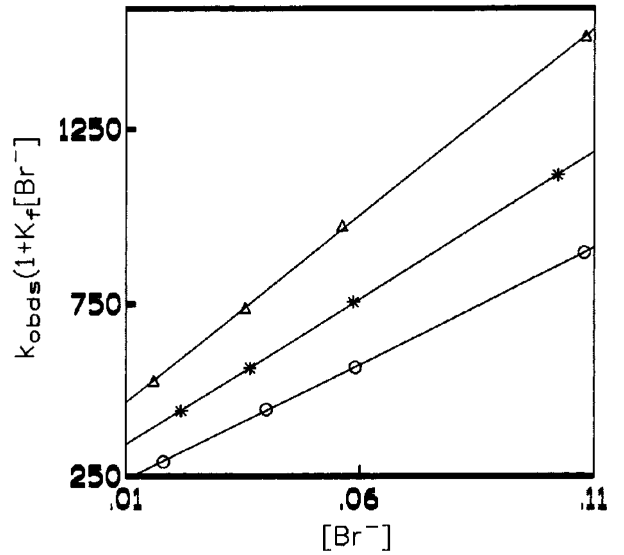


Figure 2. Plots of $k_{obsd}(1 + K_f[Br^-])$ vs [Br$^-$] for the bromination of **2a** in chloroform at 10 (○), 25 (*), and 40 (△) °C.

The reactions of **2a** were then carried out under pseudo-first-order conditions (olefin 10^{-2} M) with Br$_2$ (10^{-3} M) in the presence of a large excess of Br$^-$ (TBAB between 10^{-2} and 10^{-1} M), and a plot of k_{obsd} $(1 + K_f[Br^-])$ vs [Br$^-$], where [Br$^-$] was the concentration of the added Br$^-$, gave k_2 and $k_{Br_3^-}$ respectively from the intercept and slope (Figures 1 and 2). The calculated rate constants k_2 and $k_{Br_3^-}$ in DCE and chloroform at three different temperatures are reported in Table 3.

Taking into account the olefin concentration, on the basis of the k_2 value, a pseudo-first-order rate constant of 14 s^{-1} can be evaluated for the bromination of **2a** at 25 °C, via path b. A value of k_{-f} (between 5×10^2 and 5×10^3 s^{-1}) for the tribromide dissociation (Scheme 2) can be calculated assuming that k_f is diffusion-controlled. The difference between these two rate constants is then large enough to satisfy the initial assumption that all steps before the CTC transformation are sufficiently fast. Furthermore, the same k_2 values were found when the

Table 3. Second-Order Rate Constants for the Bromination of 2a by Br_2 in the Presence of TBAB in DCE and Chloroform

solvent	T (°C)	k_2 (M^{-1} s^{-1})	$k_{Br_3^-}$ (M^{-1} s^{-1})
DCE	10	$7.30(0.2) \times 10^2$	$4.00(0.2) \times 10^{-3}$
DCE	25	$1.40(0.1) \times 10^3$	$9.50(0.3) \times 10^{-3}$
DCE	40	$3.90(0.1) \times 10^3$	$1.90(0.1) \times 10^{-2}$
$CHCl_3$	10	$1.80(0.1) \times 10^2$	$2.75(0.2) \times 10^{-1}$
$CHCl_3$	25	$2.55(0.1) \times 10^2$	$3.45(0.2) \times 10^{-1}$
$CHCl_3$	40	$3.50(0.1) \times 10^2$	$4.40(0.2) \times 10^{-1}$

Table 4. Apparent Activation Parameters for the Second-Order Reaction of 2a with Br_2 in DCE and Chloroform

solvent	$E_{a,obsd}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (eu)
DCE	9.85(0.05)	9.25(0.05)	−12.8(0.5)
$CHCl_3$	3.88(0.05)	3.28(0.05)	−36.5(1)

Table 5. Apparent Activation Parameters for the Second-Order Reaction of 2a and 2c with TBAT in DCE and Chloroform

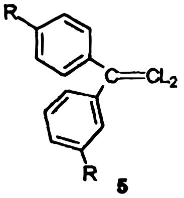
	solvent	$E_{a,obsd}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (eu)
2a	DCE	9.25(0.1)	8.65(0.1)	−39.5(1)
2a	$CHCl_3$	2.75(0.05)	2.17(0.05)	−53(1)
2c	DCE	9.85(0.1)	9.25(0.1)	−44(1)

brominations of **2a** were carried out with free Br_2, confirming that the Br_3^- dissociation cannot affect the rate of bromination with TBAT.

The values of the activation parameters for the two pathways, obtained from a fitting of the kinetics constants to the Arrhenius equation, are also reported in Tables 4 and 5.[12]

The rate constant, $k_{Br_3^-}$, obtained from eq 8 very satisfactorily fit in the log−log plot between the rates of bromination of **2a**−**g** with Br_3^- and with Br_2,[5e] which shows a slope (0.22 ± 0.02) significantly smaller than unity (Figure 3).

Finally an inverse kinetic isotope effect (KIE), $k_H/k_D = 0.85$ (0.05), was found for the second-order bromination of **1c** with TBAT. Very similar values, respectively 0.85 (0.05) and 0.80 (0.05), were measured in the reaction of 1,1-diphenylethylene (**5a**) and 3,4′-bis(trifluoromethyl)-1,1-diphenylethylene (**5b**) under identical conditions.



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a: R = H; L = H or D; **b**: R = CF_3; L = H or D

The kinetics of bromination of **2a** were measured in a stopped-flow apparatus by monitoring the disappearance of Br_2 in the presence of a 10-fold excess of olefin at $[Br_2]$ 10^{-3} M or at equal reagent concentration at $[Br_2]$ 10^{-2} M, both in DCE and chloroform. In agreement with the k_2 values calculated for the first-order reaction in Br_2 in the bromination of **2a** in the presence of Br^-, neither a clean second-order nor a first-order dependence on the halogen was found, particularly when the reactions were carried out at the higher temperatures and at low bromine concentrations ($[Br_2]$ 10^{-3} M). Therefore, for the reactions carried out under these conditions, the kinetic constants k_2 and k_3, related respectively to the first- and second-order (Br_2) process, were obtained by a fitting procedure applied to eq 9, which is the integrated form of eq 10 when the olefin is present in a large excess, and $[Br_2]$ is expressed as a function of the absorbance.

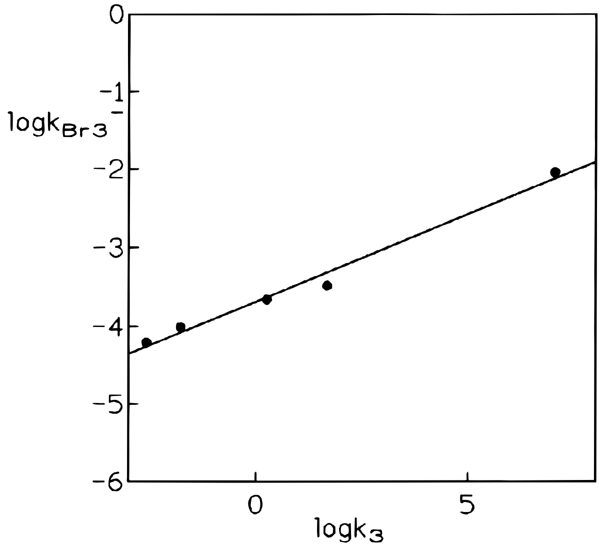

Figure 3. Comparison of the rate constants for the bromination of *trans*-stilbenes **2a**−**g** with Br_3^- and Br_2.

$$t = \frac{1}{k_2[\mathrm{Ol}]}\left[\left(\ln \frac{A_0}{\frac{k_3[\mathrm{Ol}]}{\epsilon c}A_0 + k_2[\mathrm{Ol}]}\right) - \left(\ln \frac{A}{\frac{k_3[\mathrm{Ol}]}{\epsilon c}A + k_2[\mathrm{Ol}]}\right)\right] \quad (9)$$

$$-\mathrm{d}[Br_2]/\mathrm{d}t = k_2[\mathrm{Ol}][Br_2] + k_3[\mathrm{Ol}][Br_2]^2 \quad (10)$$

A very satisfactory fitting ($R^2 > 0.998$) was obtained in both DCE and chloroform. The values of the kinetic constants are reported in Table 6, which also includes the activation parameters of the third-order process. Practically identical values of k_2 were obtained from the fitting procedure to eq 9 and from eq 7 when the reactions were carried out in the presence of variable amounts of TBAB (see Tables 6 and 3). Furthermore, the k_3 values obtained from eq 9 ($k_3 = 1.1(0.7) \times 10^7$ M^{-2} s^{-1} in DCE at 25 °C) are in good agreement with those independently found working at high Br_2 concentrations under conditions in which practically only the third-order term of eq 10 contributes to the rate ($k_3 = 1.3(0.5) \times 10^7$ M^{-2} s^{-1} in DCE at 25 °C).

Discussion

It has long been known[3] that in chlorinated solvents, of even modest polarity, the overall third-order Br_2 addition (Scheme 1, path a) involves the formation of olefin−Br_2 π-complexes, which undergo a cleavage of a bromine−bromine bond to give a bromonium (bromocarbenium)−tribromide ion pair intermediate, which then collapses to dibromide and molecular bromine. In solvents giving no electrophilic assistance to the Br^- formation in the ionization step, the second molecule of bromine is indeed believed to aid the Br−Br bond breaking by

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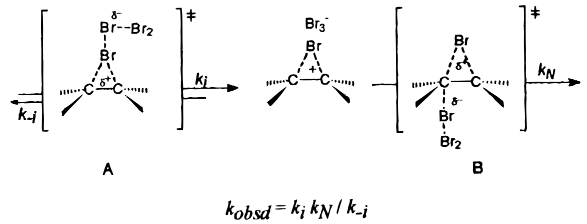
[12] It must be remembered that these values are not to be considered as true activation parameters but as a combination of kinetic and thermodynamic quantities involved in multistep reactions.

Table 6. Second-Order and Third-Order Rate Constants and Activation Parameters of the Third-Order Process in the Br_2 Addition to 2a in DCE[a] and Chloroform

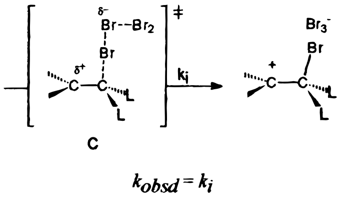
solvent	T (°C)	k_2 (M^{-1} s^{-1})	k_3 (M^{-2} s^{-1})	$E_{a,obsd}$ (kcal mol^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (eu)
DCE	15	$7.7(0.2) \times 10^2$	$1.5(0.2) \times 10^7$			
DCE	25	$1.70(0.1) \times 10^3$	$1.1(0.1) \times 10^7$			
DCE	40	$3.60(0.2) \times 10^3$	$5.9(0.2) \times 10^6$	−6.50(0.5)	−7.00(0.5)	−50(1)
$CHCl_3$	15	$1.80(0.1) \times 10^2$	$1.6(0.2) \times 10^6$			
$CHCl_3$	25	$2.35(0.2) \times 10^2$	$1.15(0.1) \times 10^6$			
$CHCl_3$	40	$5.15(0.2) \times 10^2$	$9.0(0.2) \times 10^5$	−5.00(0.5)	−5.4(0.5)	−49(1)

[a] For **2c**, $E_{a,obsd} = 1.54(0.05) \times 10^{-2}$ kcal mol^{-1}, $\Delta H^{\neq} = -0.6(0.05)$ kcal mol^{-1}, $\Delta S^{\neq} = -52(1)$ eu.

Scheme 3



Scheme 4



forming a charge-dispersed tribromide ion, and no evidence of second-order electrophilic bromination in chlorinated solvents has been reported.

In the presence of added bromide salts, which in low polarity nonprotic solvents bind Br_2 as a highly stable Br_3^- ion,[11] or when preformed Br_3^- salts are used as brominating agents, the bromination has been shown[7] to proceed through rate- and product-determining nucleophilic attack by Br^- on the 1:1 olefin−Br_2 π complex (Scheme 1, path c). The possibility that Br_3^- acting as an electrophile yields a bromonium ion plus $2Br^-$ has been also recently excluded,[13] in favor of a nucleophilic role of Br^- on the olefin−Br_2 π-complex, on the basis of kinetic isotope effects measured in the electrophilic bromination of cyclohexenes in acetic acid in the presence of bromide.

This mechanism not involving ionic intermediates agrees with the anti stereospecificity found in the reaction of the unsubstituted *cis*- and *trans*-stilbene,[14] and of the substituted stilbenes bearing electron-withdrawing or moderately electron-donating groups on the phenyl rings, and with the slope of the log−log plot between the rates of bromination with Br_3^- and with Br_2, showing that far less positive charge is generated on the carbon atoms during the Br_3^- addition.

The kinetic isotope effects (KIEs) measured for the reaction of **1c**, **5a**, and **5b** with TBAT, k_H/k_D 0.85, 0.80, and 0.85, respectively, although in agreement with a secondary effect, differ significantly from those found[15] (0.75, 0.97, and 0.70) for the reaction with Br_2. In the Br_2 addition, however, the inverse KIEs (0.70−0.75) were related[15] to the reversible formation of the at least weakly bridged bromonium-tribromide ion pair intermediates (Scheme 3). In this case, indeed, both the ionization and the nucleophilic step are partially rate determining and the hybridization changes occurring in the two transition states (TS) A and B, closely related to the structure of the intermediate (having probably a hybridization between sp^2 and sp^3), determine the KIE. So the rehybridization from sp^2 to partially sp^3, occurring in the TS (A), modifies k_i, and the rehybridization from partially sp^3 to sp^3, occurring in TS (B), affects k_N. Furthermore, return of the intermediate implies hybridization change from partially $sp^3 \rightarrow sp^2$ and affects k_{-i} giving a KIE >1. However, this KIE should be very low if the TS is close to the intermediate, and moreover, being the k_{-i} at the denominator in the expression of k_{obs}, it further contributes to an observed KIE < 1.

On the other hand, when the reaction occurs through the irreversible formation of bromocarbenium tribromide ion pairs, as in the bromination of **5a**, the rate-determining step is the ionization of the CTC and only its TS can affect the KIE (Scheme 4). Taking into account the structure of the intermediate, in which the carbon bearing the L substituents should be practically sp^3, the related TS (C) should have a hybridization at this carbon *ca.* sp^3, in particular if the TS is late. So an inverse α-effect, due to the rehybridization from sp^2 to *ca.* sp^3, and a β-effect arising from hyperconjugation of the C−L bonds with the empty orbital of the carbenium ion can be observed, and the compensation of the two opposite effects, probably of comparable magnitude, can give the apparent lack of secondary KIE.

In the Br_3^- addition, since the hyperconjugative β-effect cannot occur, the carbocationic character of the intermediate being very weak, the observed KIEs (around 0.85 significantly greater than 0.7) suggest far less rehybridization at the olefinic carbons in the related TS with respect to that occurring in the Br_2 addition. This supports a mechanism of the type reported in Scheme 1 (path c) with a nucleophilic role for the Br^- and almost pentacoordinated carbon atoms in the rate-limiting transition state. Indeed a small α-KIE has been used as a criterion for nucleophilic assistance in substitution reactions, and moreover, the α-KIEs observed in the S_N2 reactions are around 1.[16]

Finally, the positive value of the activation enthalpy found for the Br_3^- reaction of stilbene **2c**, $\Delta H^{\ddagger} = 9.25$ kcal mol^{-1}, at variance with the small negative one, $\Delta H^{\ddagger} = -0.6$ kcal mol^{-1}, found for the third-order addition of molecular Br_2, is in agreement with this mechanism. Indeed, between the two 1:1 complexes of Br_2 involved in the the mechanism sketched in Scheme 2, Br_3^- and olefin−Br_2 π-complex, the former is much more stable than the latter, so that this step is expected to be endothermic and raise the overall activation energy.

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(13) Slebocka-Tilk, H.; Zheng, C. Y.; Brown, R. S. *J. Am. Chem. Soc.* **1993**, *115*, 1347.

(14) Fieser, L. F. *J. Chem. Ed.* **1954**, *31*, 291.

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(16) Maskill, H. *The Physical Basis of Organic Chemistry*; Oxford University Press: New York, 1990; pp 386−393.

Furthermore, the lack of anti stereospecificity observed in the Br_3^- addition to **1a** and **2a** and the positive deviations from the linear correlations in the Hammett plots found for these olefins indicate a change in the mechanism or the involvement of a competitive reaction pathway when two methoxy groups are present on the phenyl rings. Taking into account the electron-donating nature of the substituents, able to stabilize the ionic intermediates, in agreement with the kinetic and product distribution data, we hypothesize that the first formed π-complex evolves to products not only through a direct Br^- attack (Scheme 2, path c), but also through an uncatalyzed ionization, giving a bromocarbenium−bromide ion pair (Scheme 2, path b). Although a second-order process of this type has never been reported in chlorinated solvents, but only in the protic ones in which the Br^- formation is favored by hydrogen bonding to the solvent, in this case the stability of the carbocationic moiety could make the formation of the ion pair with Br^- as counteranion possible. The second-order kinetic constants, k_2 and $k_{Br_3^-}$, calculated on the basis of eq 8 for the bromination of **2a** with TBAT in DCE and chloroform are in agreement with the different nature of the two processes. Indeed, while k_2 decreases on going from the more polar DCE to the less polar chloroform, in agreement with the ionic mechanism involving the formation of a bromocarbenium−bromide ion pair, $k_{Br_3^-}$ shows an inverse trend, suggesting that the electrophilic solvation by hydrogen bonding to bromide ions, exerted by chloroform in a transition state having more charge delocalization than the initial state, is the main factor.

It is noteworthy that the kinetic constants obtained from eq 8 are in agreement with the product distribution data. If we assume indeed that practically the same dibromide ratios arise from the collapse of a bromocarbenium−bromide or bromocarbenium−tribromide ion pair, in other words that the product ratios depend primarily on the cationic moiety, it is possible to calculate the *d,l* to meso ratios for the reactions carried out in the presence of Br^- on the basis of k_2 and $k_{Br_3^-}$ values and of the $[Br^-]$ considering that the ionic process gives an 85:15 meso:*d,l* ratios in both solvent while the TBAT addition is completely anti stereospecific. The calculated *d,l*:meso ratios on the basis of the derived eq 11, respectively 92:8 and 87:13 in DCE and chloroform, are in good agreement with those experimentally found and reported in Table 2.

$$\frac{[d,l]}{[\text{meso}]} = \frac{0.15k_2}{0.85k_2 + k_{Br_3^-}K_f[Br^-]} \qquad (11)$$

Finally, in relation to the third-order bromination process, the reaction of **2a** with Br_2 shows an apparent negative activation energy, $E_a = -6.5$ kcal mol^{-1}, that is consistent with the involvement of exothermic preequilibrium steps followed by the rate-determining ionization.[16] Furthermore, the large and negative entropy factor, $\Delta S^\ddagger = -50$ eu, in agreement with a termolecular transition state, is essentially independent of the nature of the cationic moiety of the intermediate. Very similar values have been found for the bromination of **2a** and **2c** in DCE. On the other hand, the structural effects on the rate are reflected in the $\Delta H^\ddagger$ value, which is in fact more negative in the presence of the electron-donating methoxy groups, in agreement with the involvement of more stable π-complex and/or with a more stable transition state for the ionization step. Furthermore, on going from DCE to chloroform, $\Delta S^\ddagger$ remains practically unchanged, showing that the formation of a bromocarbenium−tribromide ion pair proceeds without electrophilic assistance by the solvent, while $\Delta H^\ddagger$ becomes less negative in accordance with the effect of solvent polarity on the formation of the ionic intermediate.

It is noteworthy that, at variance with the third-order bromination, the second-order (first in Br_2) process shows a positive activation energy. In particular, the $\Delta S^\ddagger$ value found for the bromination of **2a** in DCE is less negative than that obtained for the third-order bromination, but becomes more unfavorable in chloroform, where probably the Br^- formation involves hydrogen bonding to the solvent. Moreover, the $\Delta H^\ddagger$ value, even if always positive, is larger in the more polar DCE, where the stabilization of the counteranion by hydrogen bond cannot take place.

Although the positive activation energy found for the k_2 process gives no indication about the involvement of a π-complex, there is little doubt that a 1:1 π-complex is involved as an essential intermediate, too. Since in this case the 1:1 π-complex directly ionizes to a bromocarbenium−bromide ion pair without the involvement of the complex of 1:2 stoichiometry, the energy of the species undergoing the ionization is not further decreased by association with a second Br_2, so the rate-determining step may now be to a higher energy level with respect to the reagents. A lower stability of the bromocarbenium−bromide ion pair with respect to the bromocarbenium−tribromide one further contributes to the positive value of the activation energy.

In conclusion the results of the present investigation not only confirm the nucleophilic role of the Br^- ion in the bromination, with TBAT, of stilbenes in halogenated solvents but also show that with activated olefins, like methoxystilbenes, even in aprotic solvents, the unassisted ionization of the first-formed 1:1 π-complex to a bromocarbenium−bromide ion pair compete both with the formation of a bromocarbenium tribromide ion pair, in the Br_2 addition, and with the nucleophilic attack by Br^-, in the reaction of TBAT. In other words, these results reveal the possibility of an electrophilic mechanism of the Br_3^- species, already reported[2b] for the bromination in protic solvents of highly reactive olefins in the presence of Br^-, and show for the first time that, even in aprotic solvents, the second-order (first order in Br_2) bromination process can compete with the third-order one.

Experimental Section

Melting points were determined on a Kofler apparatus and are uncorrected. ^1H NMR spectra were registered in $CDCl_3$, with a 200 MHz instrument, containing TMS as the internal reference. HPLC analyses were carried out with an apparatus equipped with a diode array detector using a Spherisorb S5CN column, 25 cm, with hexane−THF (99:1 v/v) as the eluent, at a flow rate of 1 mL/min. Kinetic measurements were performed with a conventional spectrophotometer or with a stopped-flow apparatus equipped with a parallel diode-array detector.

Bromine (1 mL sealed ampules, C. Erba >99.5%), tetrabutylammonium tribromide (TBAT), tetrabutylammonium bromide (TBAB), 1,2-dichloroethane (Fluka >99.5%), and chloroform (Fluka > 99.5%) were used as supplied.

Olefins. *cis*- and *trans*-stilbenes **1a−g** and **2a−g** were synthesized by the Wittig reaction as previously reported.[17] 4,3′-Bis(trifluoromethyl)-1,1-diphenylethylene(L = H) was prepared by reacting methylmagnesium bromide with 4,3′-bis-

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[17] Bellucci, G.; Chiappe, C.; Lo Moro G. *Tetrahedron Lett.* **1996**, *37*, 4225.

(trifluoromethyl)benzophenone, followed by dehydration with *p*-toluenesulfonic acid in refluxing benzene. 1,1-Diphenylethylene (L = D) and 4,3′-bis(trifluoromethyl)-1,1-diphenylethylene (L = D) were obtained with the same procedure using (methyl-d_3)magnesium iodide. ^{1}H NMR analysis indicated the presence of *ca.* 2% of H at the vinylic position. Olefin **1a** (L = D) was prepared by reduction of the 1,2-diphenylacetylene with $LiAlD_4$.[18] ^{1}H NMR analysis indicated the presence of *ca.* 10% of H at the vinylic positions. Commercial 1,1-diphenylethylene (Aldrich, 97%) and *cis*-stilbene (Aldrich >97%) were distilled before use. All olefins were finally checked by HPLC and NMR and were found to be >99% pure.

Bromination Procedure: Product Distribution. 1,2-Dichloroethane or chloroform solutions of Br_2 (1 mL, 10^{-2} M) or TBAT (1 mL, 10^{-2} M) were rapidly mixed with 1 mL of 10^{-2} M solutions of olefins **1a** or **2a** in the same solvent, and the reaction mixtures were stored in the dark at 25 °C. At preset times samples were withdrawn and stopped by washing with saturated aqueous $NaHSO_3$, and the mixtures were analyzed by HPLC and NMR. The **3**:**4** ratios were determined using appropriate calibration curves. All the reactions were carried out in triplicate. The ratios reported in Tables 1 and 2 were reproducible within ±2%. The stability of dibromides **3a** and **4a** in the presence of the halogen and TBAT was checked by exposing all dibromides to Br_2 and TBAT under conditions identical with those employed in the bromination reactions, following by HPLC analysis.

3d: mp 119−121 °C; ^{1}H NMR δ 5.35 (s, 2H, CH_2Br), 7.30−7.45 (AA'BB' system, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Cl_2Br_2$: C, 41.12; H, 2.46. Found: C, 41.03; H, 2.45.

3e: mp 161−163 °C; ^{1}H NMR δ 5.25 (s, 2H, CH_2Br), 7.00−7.30 (m, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Br_4$: C, 33.78; H, 2.02. Found: C, 33.80; H, 2.05.

3f: mp 100−101 °C; ^{1}H NMR δ 5.33 (s, 2H, CH_2Br), 7.30−7.50 (m, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Cl_2Br_2$: C, 41.12; H, 2.46. Found: C, 41.15; H, 2.50.

3g: mp 210−211 °C (lit.[5e] mp 210−211 °C).

4d: mp 236−238 °C; ^{1}H NMR δ 5.41 (s, 2H, CH_2Br), 7.10−7.20 (AA′BB′ system, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Cl_2Br_2$: C, 41.12; H, 2.46. Found: C, 41.20; H, 2.37.

4e: mp 256−258 °C; ^{1}H NMR δ 5.32 (s, 2H, CH_2Br), 7.00−7.30 (m, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Br_4$: C, 33.78; H, 2.02. Found: C, 33.67; H, 2.05.

4f: mp 208−210 °C; ^{1}H NMR δ 5.37 (s, 2H, CH_2Br), 7.30−7.45 (m, 10H, aromatic protons). Anal. Calcd for $C_{14}H_{10}Cl_2Br_2$: C, 41.12; H, 2.46. Found: C, 41.18; H, 2.35.

4g: mp 237−238 °C (lit.[5e] mp 237−238 °C).

Kinetic Measurements and Product Analysis. 1,2-Dichloroethane or chloroform Br_2 solutions, prepared shortly before use, were protected from daylight and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquotes of these prethermostated solutions were mixed with equal volumes of prethermostated solutions of olefins **1a** or **2a** of suitable concentrations. The following olefin and Br_2 concentrations (molar), pathlength (centimeters), and monitored wavelengths (nanometers) were used. **1a**: 5×10^{-3}−5×10^{-4} and 5×10^{-3}−5×10^{-4}, 2, 480, and 410. **2a**: (5−2.5) × 10^{-1} and 2.5×10^{-2}, 0.1, 410. The brominations with TBAT of **1b**−**g**, **2b**−**g,** and **3a**−**c** were carried in the conventional spectrophotometer using the following olefin and TBAT concentrations (molar): olefins 10^{-2}−10^{-1} M, TBAT 10^{-2}−10^{-1} M. The absorbance/time data were fitted to the appropriate second-order or pseudo-first-order rate law.

The rate constants for the bromination of **1a** and **2a** with Br_2 in the presence of TBAB were measured both in DCE and chloroform at three different temperatures, 10 ± 0.05, 25 ± 0.05, and 40 ± 0.05 °C, using the following reagent concentrations: olefin 10^{-2} M, Br_2 10^{-3} M, and TBAB between 1×10^{-2} and 10^{-1}. The temperature inside the reaction mixtures was periodically measured as precise as possible by inserting a termocouple into the cell. The kinetic constants k_2 and $k_{Br_3^-}$ were obtained by plots of $k_{obsd}(1 + K[Br^-])$ against the added $[Br^-]$. All reactions were carried our at least in triplicate. The kinetic constants and the activation parameters are reported in Tables 1 and 3.

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Supporting Information Available: Tables of kinetic constants measured in each experiment and some kinetic and Arrhenius plots (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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