

Radical bromination of 1,1- and 1,2-diphenylethylenes in 1,2-dichloroethane†

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ABSTRACT: The radical bromination of 1,1- and 1,2-diphenylethylenes in 1,2-dichloroethane was investigated on the basis of kinetic and product distribution data. Whereas the ionic process followed a third-order rate law (second order in Br₂), the radical bromination was second order in Br₂ and zero order in olefin in the reagent concentration range examined. Significant inverse kinetic isotope effects were found for the bromination of 3,4'-bis(trifluoromethyl)-1,1-diphenylethylene and *cis*-1,2-diphenylethylene under these conditions. At variance with the ionic bromination, which gave mixtures of *meso*- and *d,l*-dibromides only the *meso*-dibromides were obtained both from the *cis*- and *trans*-1,2-diphenylethylenes. The kinetic and product distribution data for the radical process are discussed in terms of a mechanism in which caged radical intermediates are formed. © 1998 John Wiley & Sons, Ltd.

KEYWORDS: radical bromination; diphenylethylenes; 1,2-dichloroethane; caged radical intermediates

INTRODUCTION

At variance with ionic bromination, which has been extensively investigated¹ for a long time, less attention has been paid to radical bromination in the liquid phase and the few published kinetic data are based on extremely different equations.² The diversity of reactions and difficulty of interpretation arise from the easy reversibility of many radical reaction steps involving bromo compounds. The following pertinent facts however, have recently been emphasized:³ (a) addition to a double bond competes with substitution at the allylic positions and the selectivity is controlled by the Br₂ concentration; (b) β-bromoalkyl radicals reversibly generate bromine atoms and alkenes;⁴ (c) alkyl radicals react with Br₂ at almost diffusion-controlled rates;⁵ and (d) radical bromination gives practically only the *anti* addition product.^{4b,d}

In this paper, we report kinetic and product distribution data for the radical bromination of arylalkenes, namely 1,1- and 1,2-diphenylethylenes, in a moderately polar aprotic solvent. We also relate the data to the kinetic and reaction products for ionic brominations in the same solvent.

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

RESULTS

Alkenes **1** (L = H or D) were prepared by conventional Grignard methods followed by dehydration of the resulting alcohols. *Cis*- and *trans*-1,2-diphenylethylenes, **2** and **3**, were synthesized by Wittig reactions under two-phase conditions.⁶ These alkenes were subjected to bromination with Bu₄⁺Br₃⁻ in 1,2-dichloroethane in the presence of an excess of Bu₄⁺Br⁻, a reaction that is known to give *anti* addition products.⁷ The *meso*-dibromides **5a–e** were obtained from the *trans*-alkenes **3**, whereas the *cis*-alkenes **2** gave pure *d,l*-isomers **6a–e**. Alkenes **1a** and **b** gave dibromides **4a** and **b**.

The ionic bromination rates of the alkenes **2a–e** and **3a–e** with Br₂ were measured in 1,2-dichloroethane (DCE) at 25 °C, using a conventional spectrophotometer, by monitoring the disappearance of the halogen. All the reactions followed the usual third-order rate law of Eqn (1), whose integrated form for excess alkene concentrations (pseudo-second-order conditions, $k_{pseudo-2} = k_3 [Al]$; Al = alkene) is given by Eqn (2) ($C = [Br_2]$) and for identical reagent concentrations by Eqn (3) ($C = [Br_2]$).

$$-d[Br_2]/dt = k_3[Al][Br_2]^2 \quad (1)$$

$$1/C - 1/C_0 = k_{pseudo-2}t \quad (2)$$

$$1/C^2 - 1/C_0^2 = 2k_3t \quad (3)$$

The k_3 values spanning six powers of ten are reported in Table 1, which also includes the relative product distribution data.

Table 1. Third-order rate constants, kinetic isotope effects and product distribution for the ionic bromination of 1,1-diphenylethylenes and 1,2-diphenylethylenes in DCE at 25 °C

Alkene	k_3 ($M^{-2} s^{-1}$)	k_H/k_D	5:6
1a	$8.0 (\pm 0.1) \times 10^4$	$0.75 (\pm 0.05)$	
1b	$52 (\pm 2)$	$0.70 (\pm 0.05)$	
2a	$2.8 (\pm 0.1) \times 10^2$	$0.75 (\pm 0.05)$	55:45 ^a
2b	$11.5 (\pm 0.5)$		56:44
2c	$3.7 (\pm 0.1)$		58:42
2d	$9.0 (\pm 0.1) \times 10^{-2}$		75:25
2e	$9.4 (\pm 0.15) \times 10^{-3}$		>95.5 ^a
3a	$50 (\pm 2)$		72:28 ^a
3b	$1.8 (\pm 0.1)$		71:29
3d	$1.7 (\pm 0.1) \times 10^{-2}$		87:13
3e	$2.6 (\pm 0.02) \times 10^{-3}$		>95.5 ^a

Table 2. Second-order rate constants, and kinetic isotope effects for the radical bromination of 1,1-diphenylethylenes and 1,2-diphenylethylenes in DCE at 25 °C

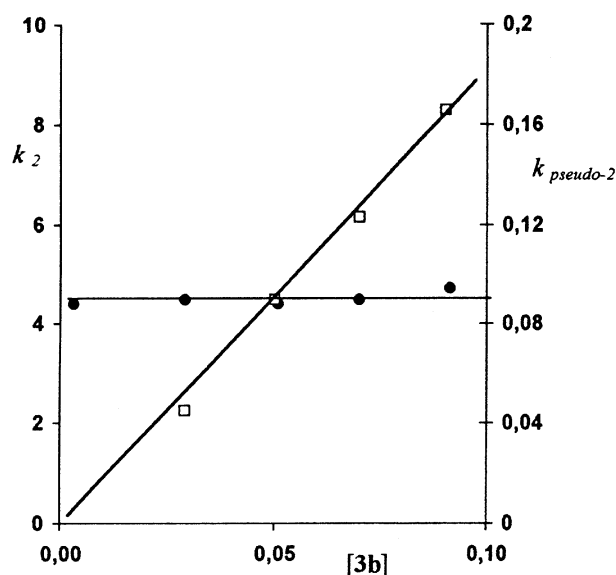
Alkene	k_2 ($M^{-1} s^{-1}$)	k_H/k_D
1a	$1.2 (\pm 0.1) \times 10^3$	
1b	$72 (\pm 2)$	$0.70 (\pm 0.05)$
2a	$6.2 (\pm 0.5)$	$0.75 (\pm 0.05)$
2b	$4.4 (\pm 0.5)$	
2c	$4.0 (\pm 0.2)$	
2d	$2.6 (\pm 0.2)$	
2e	$1.6 (\pm 0.1)$	
3a	$6.0 (\pm 0.5)$	
3b	$4.5 (\pm 0.5)$	
3d	$2.3 (\pm 0.2)$	
3e	$1.8 (\pm 0.1)$	

Reproducible brominations, following the second-order rate law of Eqn (4) whose integrated form is given by Eqn (5), occurred instead when DCE solutions of alkenes **1b** (5×10^{-2} – 2×10^{-3} M), **2a–e** (2.5×10^{-2} – 2.5×10^{-3} M) and **3a–e** (9×10^{-2} – 2.5×10^{-3} M), L = H or D, were mixed with Br₂ solutions (2.5×10^{-3} M) in a stopped-flow apparatus equipped with a diode-array detector and irradiated with a spherical W lamp (10 V, 3 A, 10 W) at 25 °C. The k_2 values for 1,1- and 1,2-diphenylethylenes are reported in Table 2. In Fig. 1 the observed second-order kinetic constants (k_2 and $k_{pseudo-2}$) are plotted against [3b] for the two processes [Eqns (1) and (4)]. Similar plots can be obtained with all the other alkenes. In agreement with Eqn (4) k_2 is of independent [A1].

$$-d[Br_2]/dt = k_2[Br_2]^2 \quad (4)$$

$$1/C - 1/C_0 = k_2 t \quad (5)$$

Moreover, at variance with the third-order process, virtually the same values of the rate constants k_2 were found for the bromination of both the *cis*- and *trans*-isomers of each pair of 1,2-diphenylethylenes. Under these conditions, only dibromides **4** and *meso*-dibromides

**Figure 1.** Plots of the observed second-order kinetic constants, k_2 (●) and $k_{pseudo-2}$ (□) vs [3b] for the bromine addition following Eqns (4) and (1), respectively.

5, without any *d,l*-isomer **6**, were formed from **1a** and **b** and from both **2a–e** and **3a–e**, respectively. A complete *cis* → *trans* isomerization of the unreacted alkene was observed when the reactions were carried out with a twofold excess of **2a–e**. Furthermore, under these conditions, the bromination of *trans*-1,2-dichloroethene gave a *trans* → *cis* isomerization, pointing to the involvement of a radical process. It is indeed known⁸ that *trans*-1,2-dichloroethene reacts with Br₂ only under radical conditions to give double bond isomerization without dibromide formation.

A rate law of the type in Eqn (6) was observed for alkene **1a**, consistent with the occurrence of two parallel ionic and radical reactions. The rate constants of the two processes, k_2 [$1.2 (\pm 0.1) \times 10^3 M^{-1} s^{-1}$] and k_3 [$7.6 (\pm 0.1) \times 10^4 M^{-2} s^{-1}$], were calculated from the slope and intercept, respectively, of a plot ($r = 0.997$) of k_{obsd} vs [A1] [Eqn (6)].

$$-d[Br_2]/dt = (k_3[A1] + k_2)[Br_2]^2 \quad (6)$$

The k_3 value so calculated was in good agreement with that [$8.0 (\pm 0.1) \times 10^4 M^{-2} s^{-1}$] measured directly [Eqn (1)] when the reactions were carried out in the absence of irradiation using the single-channel stopped-flow apparatus (Table 1).

Meaningful inverse kinetic isotope effects (KIEs), virtually identical with those for the third-order process,⁹ were found for the second-order bromination of **1b**, $k_H/k_D = 0.70 \pm 0.05$, and **2a**, $k_H/k_D = 0.75 \pm 0.05$. Furthermore, a satisfactory log–log correlation ($r = 0.995$) showing a slope (0.125 ± 0.01) markedly smaller than unity was obtained when the kinetic constants k_2 for the bromination of *trans*-1,2-diphenylethylenes, **3a–e** were plotted against the k_3 values. A

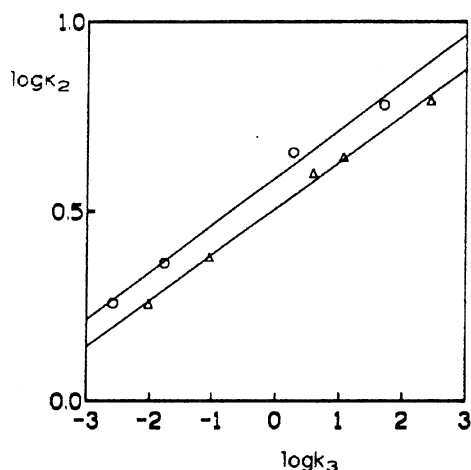


Figure 2. Comparison of the rate constants for the radical (k_2) and the ionic bromination (k_3) of *cis*- (Δ) and *trans*-1,2-diphenylethenes (\circ).

similar plot (slope 0.127 ± 0.01 , $r = 0.990$) was obtained for *cis*-alkenes **2a–e** (Fig. 2).

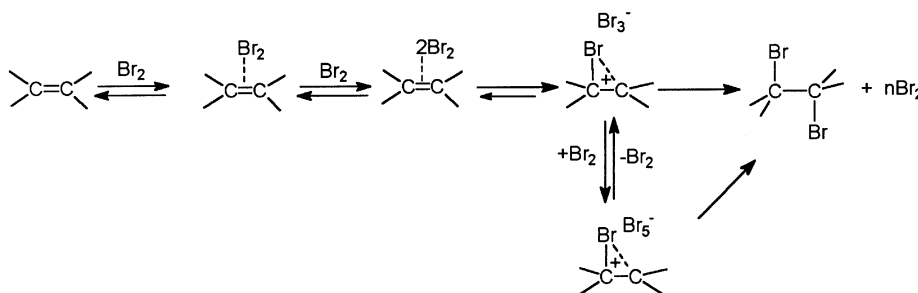
DISCUSSION

In the light of the most recent investigations,¹ the mechanism for the ionic bromination by molecular bromine of alkenes in aprotic solvents, sketched in Scheme 1 involves the formation of bromonium (or bromocarbenium)–tribromide ion pairs by ionization of the alkene– Br_2 π complexes formed in pre-equilibrium steps.^{1m} The symmetrically or asymmetrically bridged or unbridged nature of the cationic moiety of these intermediates strictly depends upon the ability of the substituents on the double bond to stabilize a positive charge on the carbon atoms. In particular, as regards the nature of the intermediates, it has been shown^{1g} by a product study that in the bromination of 1,2-diphenylethenes in DCE, not only the ratios between the isomeric dibromides, but also the reversibility of the ionization of the alkene– Br_2 π complexes to ion pairs depend on the bridged or open nature of the cationic moiety. Whereas electron-donating substituents favouring open β -bromocarbenium ion intermediates give stereoconvergent mixtures of *meso*- and *d,l*-dibromides

from both *cis*- and *trans*-alkenes and depress the reversibility, electron-withdrawing groups, such as CF_3 , favouring fully bridged bromonium ions give stereoselective and stereospecific reactions and make ion pair return very prominent. Furthermore, it has been also demonstrated that in aprotic solvents, at relatively high bromine concentrations, the counteranion can be in the form of pentabromide (and possibly higher polybromide species),¹⁰ and the nature of the anionic moiety can affect the product-determining step.¹¹

Although bromine addition in these solvents generally follows the third-order (second order in bromine) rate law of Eqn (1), it has been recently found¹² that at low temperatures and high bromine concentrations, which favour the transformation of the tribromide counteranion into pentabromide ion through a very fast equilibration, the bromination of deactivated alkenes can obey an overall fourth-order (third-order in bromine) rate law. This behaviour has been interpreted¹² as a kinetic evidence for rate determination during the nucleophilic step of bromination.

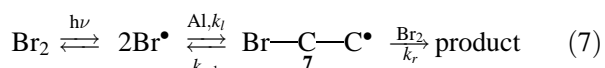
However, as far as we know, second-order brominations (zero order in alkene) of the type found in this work have been never reported. The independence of the bromination rate on the alkene concentration can be due in principle to two reasons, namely the activated complex for the rate-limiting step does not contain alkene, or the reaction follows Michaelis–Menten kinetics when the alkene concentration is sufficiently high to be under saturation conditions. The measured isotope effects and the dependence of k_2 on the substituents of the phenyl rings in the reactions of **2** and **3** are in agreement, however, with the presence of the alkene in the activated complex and point to a saturation effect. Michaelis–Menten kinetics imply the fast, reversible formation of a complex between the alkene and the brominating species prior to the rate-limiting step. Even if this could be due, at least in principle, to the formation of a highly stable alkene– Br_2 π -complex which captures virtually all of the Br_2 present in solution, the UV–visible spectrum registered immediately after mixing of Br_2 and alkene, when the reactions follow the second-order rate law, which is essentially that of free Br_2 , definitely rules out the possibility that Br_2 is completely transformed into one of the π -complexes reported in Scheme 1. Therefore,



Scheme 1.

on the basis of these data and taking into account the *trans* → *cis* isomerization observed in the bromination of *trans*-1,2-dichloroethene under the conditions in which the reactions of **1**, **2** and **3** follow the second-order rate law, the most probable origin of the independence of the rate constant on alkene concentration points to a radical process occurring through a pre-equilibrium step. In agreement with a radical process is also the negligible substituent effect on k_2 , shown by the markedly smaller than unity slope of the log–log correlation found when the kinetic constants k_2 for bromination of **2** and **3** are compared with the kinetic constants k_3 related to the ionic reaction.¹³

The ordinary radical mechanism¹⁴ [Eqn (7)], however, requires a different rate law.



When the reaction of the radical intermediate **7** with Br_2 is assumed to be rate limiting:

$$v = k_r [\text{Br}-\text{C}-\text{C}^\bullet] [\text{Br}_2] \quad (8)$$

an approximate value for $[\text{Br}-\text{C}-\text{C}^\bullet]$ can be obtained from Eqn (10) applying the steady-state approximation:

$$d[\text{Br}-\text{C}-\text{C}^\bullet]/dt = 0 = k_1 [\text{A1}] [\text{Br}^\bullet] - (k_{-1} + k_r) [\text{Br}-\text{C}-\text{C}^\bullet] \quad (9)$$

$$[\text{Br}-\text{C}-\text{C}^\bullet] = k_1 [\text{A1}] [\text{Br}^\bullet] / (k_{-1} + k_r) \quad (10)$$

Furthermore, $[\text{Br}^\bullet]$ can be expressed as function of $[\text{Br}^\bullet]_{\text{tot}}$ by

$$[\text{Br}^\bullet] = [\text{Br}^\bullet]_{\text{tot}} - [\text{Br}-\text{C}-\text{C}^\bullet] \quad (11)$$

From Eqns (11) and (10) the equation

$$[\text{Br}-\text{C}-\text{C}^\bullet] = k_1 [\text{A1}] [\text{Br}^\bullet]_{\text{tot}} / (k_{-1} + k_r + k_1 [\text{A1}]) \quad (12)$$

is obtained and, since $[\text{Br}^\bullet]$ is given by

$$[\text{Br}^\bullet] = k_{h\nu} [\text{Br}_2]^{1/2} \quad (13)$$

a rate law of the form

$$v = \frac{k_{h\nu} k_r [\text{A1}] [\text{Br}_2]^{3/2}}{\frac{k_{-1} + k_r}{k_1} + [\text{A1}]} \quad (14)$$

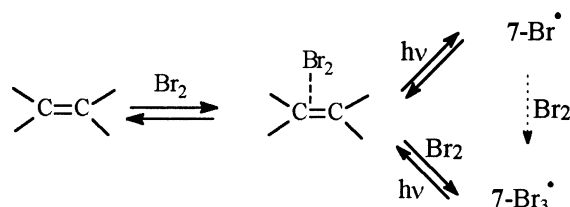
similar to that reported for the radical iodine addition to pentene isomers,¹⁴ can be obtained. Even if, when $[\text{A1}] \gg (k_{-1} + k_r) / k_1$, a simple expression:

$$v = k_{h\nu} k_r [\text{Br}_2]^{3/2} \quad (15)$$

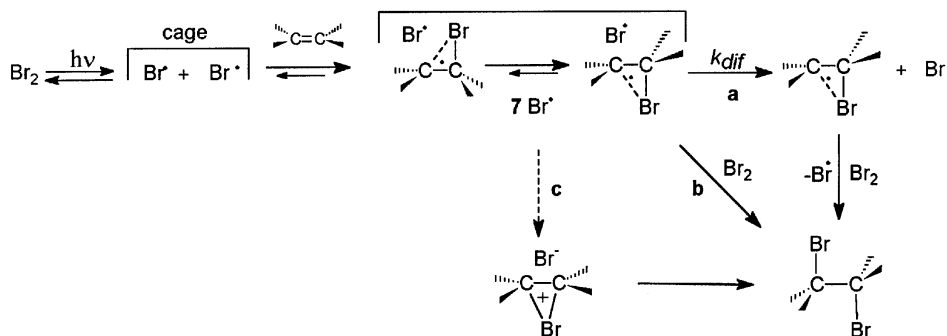
independent of the alkene concentration can be written, a 3/2 dependence of the rate on bromine concentration, at variance with the experimental results, should be found.

It is possible, however, that in DCE irradiation by the spectrophotometer produces a very low concentration of $\text{Br}^\bullet\text{Br}^\bullet$ (or $\text{Br}^\bullet\text{Br}_3^\bullet$)¹⁵ radical pairs in a cage of solvent molecules, which may be very rapidly captured by the alkene to give caged Br^\bullet (or Br_3^\bullet) benzyl radical pair intermediates (**7**- Br^\bullet in Scheme 2 or **7**- Br_3^\bullet in Scheme 3).

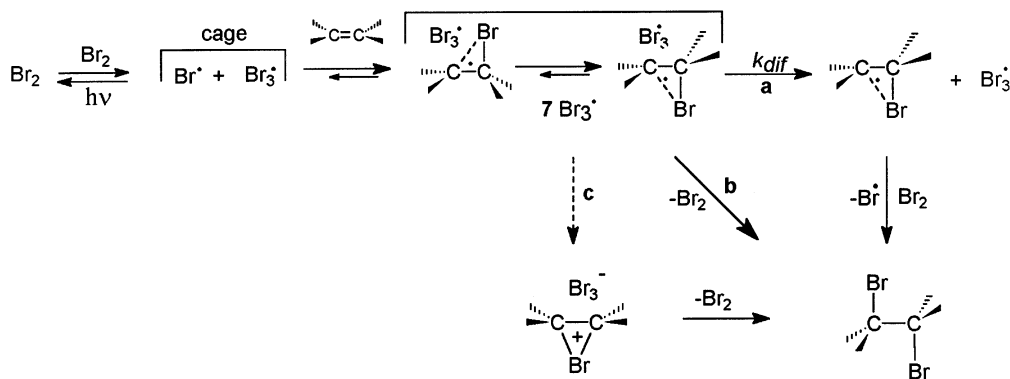
The same intermediates **7** could be formed also through the homolytic $\text{Br}-\text{Br}$ cleavage occurring at the stage of a 1:1 or 1:2 π -complex. It is generally accepted,¹⁶ indeed, that the first step in chlorination is always the formation of a Cl_2-Al complex which then breaks down by either homolytic or heterolytic dissociation of the $\text{Cl}-\text{Cl}$ bond. The involvement of complexes in the reaction has been assumed also for radical bromination^{17,18} and iodination.¹⁴ However, unambiguous experimental evidence, showing that complex formation precedes the formation of radical, has been never reported.



The nature of the β -bromo-substituted radicals has been the subject of extensive discussion¹⁹ and the kinetic and stereochemical data have been interpreted in terms of either bridged structures^{19a-d} (symmetric or asymmetric),



Scheme 2.

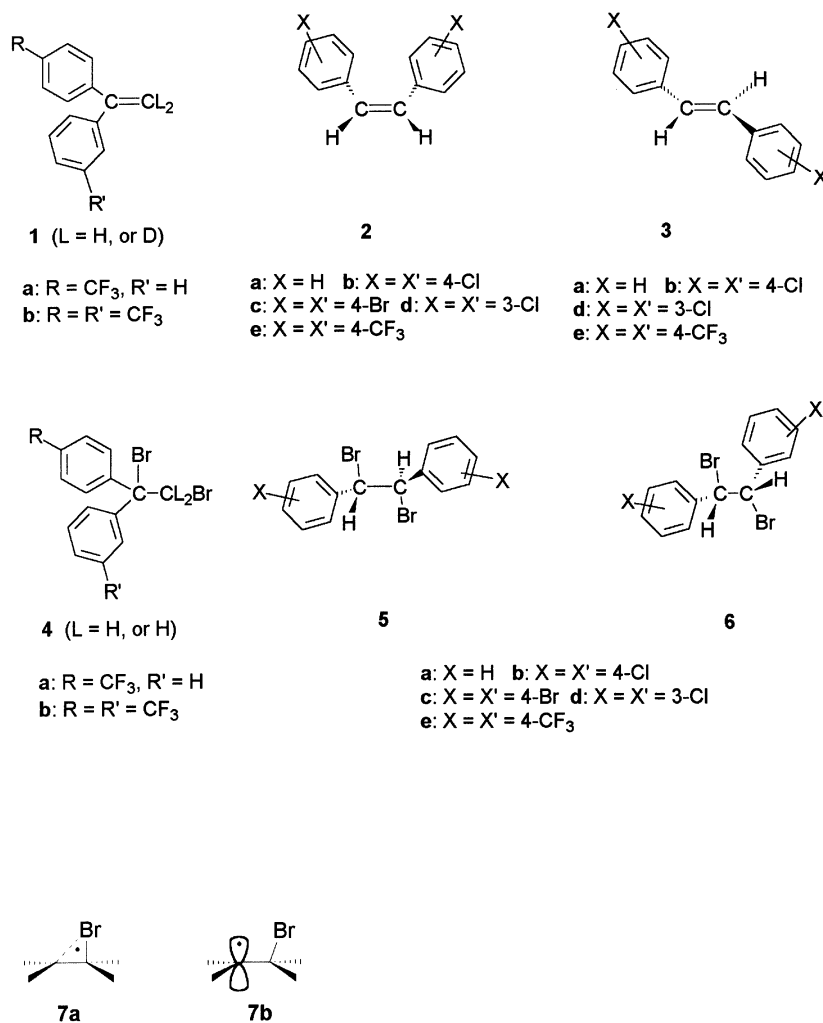


Scheme 3.

7a, or open radicals, **7b**, existing in a preferred conformation allowing for hyperconjugative stabilization by halogen.^{19e}

The stereoconvergent formation of *meso*-dibromides from alkenes **2** and **3** found in this work certainly indicates that on the intermediate **7** the *syn* attack is prevented by some interaction, such as the overlapping

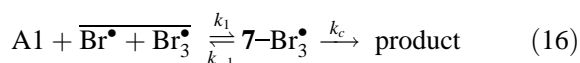
between the bromine atom and the adjacent radical centre (bridging) or the repulsive interaction between the bromine atom and the attacking radical. Furthermore, if bridged intermediates are involved, these data show that the interaction between the bromine atom and the adjacent radical centre should be small, at least in comparison with the $\text{Br}\cdots\text{C}^+$ interaction, since



the intermediates arising from all the *cis*-alkenes, independently of the substituents, are able to equilibrate to the more stable *trans* forms before the collapse to dibromides or return to alkenes, as shown by the presence of *meso*-dibromides and *trans*-alkenes in the reactions of the *cis*-isomers.

Finally, the complete *cis* → *trans* isomerization of the double bond of stilbenes observed, exclusively in the presence of Br₂, when the reactions were carried out with an excess of the *cis*-alkene points to a reversible formation of these β-bromobenzyl radicals. This is reasonable evidence for the caged nature of **7** and the relative difficulty for these intermediates to escape out of the cage and also for a subsequent rate-limiting dibromide formation.

The observed second-order dependence on halogen concentration and the saturation effect, resulting in kinetics of Michaelis–Menten type, can therefore be interpreted either on the basis of Scheme 2 (path **a**), or on the basis of Scheme 3 (path **b**). The *trans* intermediate 7–Br₃[•], formed directly in the case of **3**, or after rotation around the C—C[•] bond in the case of **2**, can undergo recombination (path **b**, Scheme 3) within the cage of solvent, in competition with internal return and diffusion (path **a**). Alternatively, the analogous intermediate 7–Br[•] can react with Br₂ (path **a** or **b**), leading, as shown in Scheme 2 to dibromo derivative **5** by an *anti* stereospecific attack on the benzylic carbon. Pathway **b** in Scheme 3 can be described by the equation



If every step preceding the collapse of 7–Br₃[•] is very fast, Eqn (17) can be written:

$$v = k_c[7-Br_3^{\bullet}] \quad (17)$$

and, again with the steady-state approximation, the approximate value for [7–Br₃[•]] can be obtained:

$$d[7-Br_3^{\bullet}]/dt = 0 \\ = k_1[Al][Br^{\bullet} + Br_3^{\bullet}]_{\text{free}} - (k_{-1} + k_c)[7-Br_3^{\bullet}] \quad (18)$$

$$[7-Br_3^{\bullet}] = k_1[Al][Br^{\bullet} + Br_3^{\bullet}]_{\text{free}} / (k_{-1} + k_c) \quad (19)$$

Furthermore, [Br[•] + Br₃[•]]_{free} can be expressed as function of [Br[•] + Br₃[•]]_{tot}:

$$[Br^{\bullet} + Br_3^{\bullet}]_{\text{free}} = [Br^{\bullet} + Br_3^{\bullet}]_{\text{tot}} - [7-Br_3^{\bullet}] \quad (20)$$

From Eqns (20) and (19), we obtain

$$[7-Br_3^{\bullet}] = k_1[Al][Br^{\bullet} + Br_3^{\bullet}]_{\text{tot}} / (k_{-1} + k_c + k_1[Al]) \quad (21)$$

and taking into account that

$$[Br^{\bullet} + Br_3^{\bullet}]_{\text{tot}} = k_{hv}[Br_2]^2 \quad (22)$$

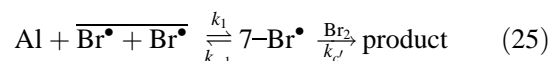
we can obtain the final expression of the rate [Eqn (23)], which is practically the Michaelis–Menten equation:

$$v = \frac{k_{hv}k_c[Al][Br_2]^2}{\left(\frac{k_{-1} + k_c}{k_1}\right) + [Al]} \quad (23)$$

When [Al] ≫ (k₋₁ + k_c)/k₁, a simpler expression [Eqn (24)] can be written, corresponding to Eqn (4), where k₂ = k_{hv}k_c:

$$v = k_{hv}k_c[Br_2]^2 \quad (24)$$

On the other hand, if the radical process follows path **a** or **b** of Scheme 2 Eqn (25) can be written:



If the reaction of the intermediate 7–Br[•], or after diffusion of **7**, with Br₂ is rate limiting,

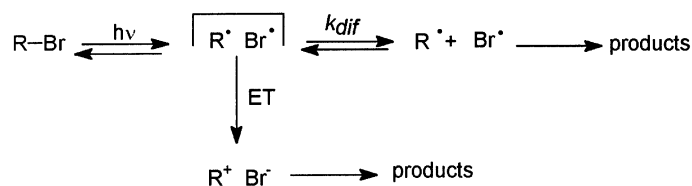
$$v = k_c'[7-Br^{\bullet}][Br_2]$$

Again, the application of the steady-state approximation, taking into account that [Br[•] + Br₃[•]]_{tot} = k_{hv}[Br₂], gives an equation analogous to Eqn (24), with k_c' instead of k_c:

$$v = k_{hv}k_c'[Br_2]^2 \quad (26)$$

It is noteworthy that the inverse KIEs measured for the bromination of **1b** and **2a** under radical conditions, 0.70 ± 0.05 and 0.75 ± 0.05, respectively, virtually identical with those found for the ionic process, are in agreement with a secondary isotope effect and indicate considerable rehybridization in the rate-limiting transition state from sp² towards sp³.²⁰ This behaviour can be consistent either with the radical recombination between the Br₃[•] and benzyl radicals **7**, probably having hybridization between sp² and sp³, or with the reaction of the benzylic radicals **7** with Br₂, to give in both cases the corresponding dibromides sp³ hybridized at the benzylic carbons.

Although both the pathways can account for the kinetic and product distribution data, they imply some different assumptions. Path **b** of Scheme 3 presupposes that diffusion of the radicals through the layer of solvent molecules should be a process slower than the rate-



Scheme 4.

limiting step, i.e. the collapse of 7-Br_3^\bullet an assumption which is unnecessary if the reaction follows Scheme 2 path **a**. In this case, however, the reaction of the alkene with the caged Br^\bullet , or the kinetically equivalent homolytic $\text{Br}\text{-Br}$ cleavage occurring at the stage of the 1:1 π -complex, should be a kinetically more important process than the reaction of the alkene with the Br^\bullet free radical formed during the course of the bromination.

Finally, it is noteworthy that taking into account the mechanism already proposed for the photochemical solvolysis of alkyl²¹ and vinyl²² halides (Scheme 4), the possibility that ionic intermediates can be formed even in the radical bromination of alkenes from caged radical pairs, 7-Br_3^\bullet or 7-Br^\bullet , through an electron transfer process, in competition with dissociation, cannot be excluded (Scheme 3 or 2, path **c**). The radical pairs produced in the photobromination of alkanes differ from those arising from bromination of alkenes only in the way in which they are generated, homolytic cleavage of the carbon halogen bond in the former case and radical addition to the double bond in the latter. Furthermore, if the reaction follows Scheme 3 the greater polarizability of Br_3^\bullet with respect to Br^\bullet could facilitate the electron transfer (ET) process. This, even if it requires an activation energy [the ET process could be at least partly driven by light itself (photoinduced electron transfer)], is able to compete with the radical recombination (Scheme 3 path **b**) when, as in our case, sufficiently stable radicals are involved and a proper mutual orientation of the reactants in the solvent cage is required for the occurrence of the reaction.²⁴ The ET can take place over a fairly long distance and has lower orientation requirements.²⁴

In conclusion, even if it is not possible on the basis of these results to establish unambiguously the exact mechanism of the radical bromination of diphenylethylenes in DCE, they give several important pieces of information. The radical bromination of these alkenes in DCE involves the reversible formation of caged radical pair intermediates whose collapse to products is the rate-limiting step. Furthermore, concerning the nature of β -bromobenzyl radical intermediates, important indications arise from the product distribution data. Finally, the results obtained in this work can be very useful from a practical point of view. They show not only that the radical bromination of aryl-substituted alkenes in aprotic solvents is a reproducible process, but also that this can be easily distinguished from the ionic process on the basis of the kinetic (zero order in alkene) and product distribution data.

EXPERIMENTAL

Melting points were determined on a Kofler apparatus and are uncorrected. ¹H NMR spectra were registered in CDCl_3 with a Bruker AC 200 instrument containing TMS

as the internal reference. Kinetic measurements were performed with a Cary 2200 spectrophotometer or with a Durrum D-110 stopped-flow instrument for the ionic reactions, and with a stopped-flow apparatus equipped with a parallel diode-array detector and irradiated with a spherical tungsten lamp (10 V, 3A, 10 W) for the radical reactions. HPLC analyses were carried out with an apparatus equipped with a diode-array detector using a 25 cm Spherisorb S5CN column, with hexane-THF (99:1, v/v) as the eluent, at a flow rate of 1 ml min^{-1} . Bromine (1 ml sealed ampoules, Carlo Erba, >99.5%) and DCE (Fluka, >99.5%) were used as supplied.

Alkenes **1a**, **1b** (L = H or L = D) and **2a** (L = D) were prepared as reported.⁹ *Cis*- and *trans*-stilbenes **2a-e** and **3a-e** were synthesized by the Wittig reaction as reported previously.⁶ Commercial *cis*-stilbene (Aldrich), *trans*-1,2-dichloroethene (Aldrich) and *cis*-1,2-dichloroethene (Aldrich) were distilled before use. All alkenes were finally checked by HPLC and/or NMR and were found to be >99% pure. Dibromides **4**, **5** and **6** were obtained from alkenes **1a** and **b**, **2a-e** and **3a-e**, respectively, by bromination with $\text{Bu}_4\text{N}^+\text{Br}_3^-$ in DCE following the reported procedure.^{7b}

Bromination procedure

Kinetic measurements and product analysis. Solutions of Br_2 in DCE, prepared shortly before use, were protected from daylight and adjusted to twice the desired initial concentrations in the kinetic runs. Aliquots of these solutions, pre-thermostated at $25 \pm 0.05^\circ\text{C}$, were mixed with equal volumes of pre-thermostated solutions of alkenes **1** or **2** or **3** of suitable concentrations. The ionic brominations of **1b**, **2a-d** and **3b** and **d** were carried out with a conventional spectrophotometer, those of **1a** with a Durrum stopped-flow apparatus. The following alkene and Br_2 concentrations, path lengths and monitored wavelengths were used. **1a** (L = H or D), alkene 5×10^{-3} – 5×10^{-4} M, Br_2 5×10^{-3} – 5×10^{-4} M, 2 cm, 480 and 410 nm; **1b** (L = H or D), alkene 5 – 2×10^{-2} M, Br_2 2.5 – 1×10^{-3} M, 1 cm, 410 nm; **2a** (L = H or D); alkene 2×10^{-2} – 2×10^{-3} M, Br_2 2×10^{-3} M, 1 cm, 410 nm; **2b**, alkene 4 – 2×10^{-2} M, Br_2 2×10^{-3} M, 1 cm, 410 nm; **2a**, alkene 1.5×10^{-1} – 2.5×10^{-2} M, Br_2 2.5×10^{-3} M, 1 cm, 410 nm; **2d**, alkene 5 – 2.5×10^{-1} M, Br_2 2.5×10^{-1} M, 0.1 cm, 410 nm; **3b**, alkene 9 – 2.5×10^{-2} M, Br_2 2.5×10^{-3} M, 1 cm, 410 nm; **3d**, alkene 5 – 2.5×10^{-1} M, Br_2 2.5×10^{-2} M, 0.1 cm, 410 nm.

The radical brominations of **1a** and **b**, **2a-e** and **3a, b, d** and **e** were carried out under irradiation with a spherical tungsten lamp (10 V, 3A, 10 W) in a stopped-flow apparatus equipped with a parallel diode-array detector, in a 1 cm pathlength cell. The following alkene and Br_2 concentrations were used: **1a** (L = H or D), alkene 5×10^{-2} – 5×10^{-4} M; Br_2 5×10^{-3} – 5×10^{-4} M; **1b**

(L=H or D), alkene $5 - 2 \times 10^{-3}$ M, Br_2 $2.5 - 1 \times 10^{-3}$ M; **2a** (L=H or D), alkene $1 \times 10^{-2} - 2.5 \times 10^{-3}$ M, Br_2 $2.5 - 1 \times 10^{-3}$ M; **2b**, alkene $2.5 \times 10^{-1} - 2.5 \times 10^{-2}$ M, Br_2 2.5×10^{-3} M; **2c**, alkene $2.5 \times 10^{-2} - 2.5 \times 10^{-3}$ M, Br_2 2.5×10^{-3} M; **2d**, alkene $2.5 \times 10^{-2} - 2.5 \times 10^{-3}$ M, Br_2 2.5×10^{-3} M; **2e**, alkene $2.5 \times 10^{-1} - 2.5 \times 10^{-2}$ M, Br_2 2.5×10^{-3} M; **3a**, alkene $1 \times 10^{-1} - 2.5 \times 10^{-3}$ M, Br_2 $2.5 - 1 \times 10^{-3}$ M; **3b**, alkene $9 \times 10^{-2} - 2.5 \times 10^{-3}$ M; Br_2 2.5×10^{-3} M; **3d**, alkene $8 \times 10^{-2} - 2.5 \times 10^{-3}$ M, Br_2 2.5×10^{-3} M; **3e**, alkene $2.5 \times 10^{-2} - 2.5 \times 10^{-3}$ M, Br_2 2.5×10^{-3} M. The absorbance–time data were fitted to the appropriate third-order, pseudo-second-order or second-order rate equation. All reactions were carried out at least in triplicate. The kinetic constants are reported in Tables 1 and 2.

At the end of the reactions, after evaporation of the solvent, all the reaction mixtures were analyzed by NMR and HPLC. The products formed were quantified using appropriate calibration graphs.

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