Acknowledgment. Thanks are due to S. E. Sugamori and G. Charette for technical assistance. G.F.B. would like to express his special gratitude to the Fonds der Chemischen Industrie for a grant. We also thank the Natural Sciences and Engineering Research Council of Canada and the SFB 247 der Chemischen Institute, Heidelberg, for financial support.

Registry No. 1, 3225-37-4; 2, 53905-02-5; 3, 138435-10-6; 4, 932-97-8; 5, 937-37-1; 6, 99230-11-2; 7, 118949-77-2; 8, 144084-88-8; 9, 99967-24-5; 10, 144084-89-9; 12, 2122-46-5; 13a, 144084-90-2; 14, 144084-91-3; 15, 19329-94-3; Freon-113, 76-13-1; O_2, 7782-44-7; MeOH, 67-56-1; cyclohexane, 110-82-7.

Stereoselectivity and Reversibility of Electrophilic Bromine Addition to Stilbenes in Chloroform: Influence of the Bromide–Tribromide–Pentabromide Equilibrium in the Counteranion of the Ionic Intermediates

Roberto Bianchini* and Cinzia Chiappe

Dipartimento Chimica Bioorganica, via Bonanno 33, Pisa 56126, Italy

Received July 20, 1992

Two equilibria were found in chloroform solutions of $Bu_4N^+Br^-$ and Br_2, leading to tribromide and pentabromide salts. The electronic spectra and formation constants of both ($K_3 = 2.77$ (0.13) $\times 10^4$ M^{-1} and $K_5 = 3.51$ (0.35) $\times 10^6$ M^{-2} at 25 °C) were computed from spectrophotometric data. The stability of the Br_3^- species in chloroform resulted to be at least 3 orders of magnitude lower than in 1,2-dichloroethane. A change from prevalent formation of *d,l*-1,2-dibromo-1,2-diphenylethane to prevalent formation of meso dibromide, accompanied by a cis–trans isomerization of the unreacted olefin, has been observed in the bromination of *cis*-stilbene with decreasing reagent concentrations, when the bromide–tribromide–pentabromide equilibrium in the counteranions of the ion pairs intermediates is shifted in favor of the Br^- form. The results show that these intermediates are reversibly formed even when the anion is Br^-.

The electrophilic addition of bromine to alkenes is one of the most investigated reactions. It is well known[1] that its apparently simple mechanism is stepwise in nature and proceeds through the formation of bromonium or bromocarbonium bromide,[2] or tribromide,[3] intermediates, subsequently collapsing to addition products. A new important feature recently reported for this reaction pertains to the reversibility of the formation of the ionic intermediates.[4] In methanol and ethanol this reversibility has been admitted only for highly congested bromonium ions.[5] In contrast, in 1,2-dichloroethane a relevant internal return has been shown with uncongested olefins, too, and this requires that nucleophilic attack in the product forming step is slow.[4e] One explanation for the difference between the two types of solvents assumes[6] that in halogenated hydrocarbons the product-forming step is slow since the counter tribromide ion is not a highly nucleophilic species, so that the effective nucleophile must be provided by dissociation of the very stable Br_3^-, a process which is not necessarily fast.[7] In order to check this rationalization, an investigation of the olefin bromination in a solvent in which the stability of the Br_3^- ion is reduced appeared promising.

Here we are reporting on a study of the equilibria involving Br^-, Br_3^-, and Br_5^- anions in a low polarity aprotic solvent, chloroform, and on their influence on the product distribution of the electrophilic addition of Br_2 to *cis*- and *trans*-stilbene. We demonstrate that reversibility of theionic intermediate formation can occur even when a significant amount of Br^- is present as counteranion, at sufficiently low bromine concentration.

Results

The Br^-–Br_3^-–Br_5^- Equilibrium. The UV-vis spectra of solutions of tetrabutylammonium bromide (TBAB) and Br_2 in ethanol-free chloroform[8] were taken, at the concentrations reported in the Experimental Section, in the 250–500-nm range. An absorption band with $\lambda_{max} = 272$ nm was apparent in solutions containing a slight Br_2 over Br^- excess (curve a of Figure 1). When a large Br_2 excess was used, a new absorption band appeared, besides the 272-nm one, in the 290–330-nm interval (curves b, c, and d of Figure 1). These phenomena were considered as evidence for the formation of Br_3^- and Br_5^- anions from Br^- and Br_2, as already observed in 1,2-dichloroethane,[9] according to eqs 1 and 2.

$$Br^- + Br_2 \overset{K_3}{\rightleftharpoons} Br_3^- \tag{1}$$

$$Br^- + 2Br_2 \overset{K_5}{\rightleftharpoons} Br_5^- \tag{2}$$

---

(1) See, for instance: (a) Schmid, G. H. *The Chemistry of Double-Bonded Functional groups*, Suppl. A.; Patai, S., Ed. Wiley: New York, 1989; Vol. 2, Part 1, p 699. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev. (Engl. transl.)* **1981**, *50*, 151. (c) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; pp 136–137.

(2) (a) Garnier, F.; Donnay, R. H.; Dubois, J.-E. *J. Chem. Soc., Chem. Commun.* **1971**, 829. (b) Modro, A.; Schimd, G. H.; Yates, K. *J. Org. Chem.* **1979**, *44*, 4221.

(3) (a) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464. (b) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

(4) (a) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515. (b) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515. (c) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988**, *110*, 546. (d) Bennet, A. J.; Brown, R. S.; Slebocka-Tilk, H.; Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1990**, *112*, 6310. (e) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012.

(5) (a) Ruasse, M.-F.; Motallebi, S.; Galland, B.; Lomas, J. S. *J. Org. Chem.* **1990**, *55*, 2298. (b) Ruasse, M.-F.; Motallebi, S.; Galland, B. *J. Am. Chem. Soc.* **1991**, *113*, 3440.

(6) Ruasse, M.-F.; Motallebi, S. *J. Phys. Org. Chem.* **1991**, *4*, 527.

(7) Ruasse, M.-F. *Acc. Chem. Res.* **1990**, *23*, 87, footnote 23.

(8) See Experimental Section.

(9) Bellucci, G.; Bianchini, R.; Chiappe, C.; Ambrosetti, R. *J. Am. Chem. Soc.* **1989**, *111*, 199.

0022-3263/92/1957-6474$03.00/0 © 1992 American Chemical Society

Table I. Downfield Shift ($\Delta\delta$) of the Proton of Chloroform Added to Solutions of TBAB, TBAT, and TBAP in Acetonitrile-d_3 at 25 °C

run	[TBAB],[a] M	[Br_2],[a] M	[$CHCl_3$], M	[Br_2]$_{free}$,[b] M	δ,[c] Hz	$\Delta\delta$,[d] Hz
1			0.711		1128.1588	
2	0.240		0.711		1198.0948	69.936
3	0.240	0.245	0.711	5×10^{-3}	1129.0948	1.694
4	0.240	0.741	0.711	>0.23	1125.2670	−2.892
5		0.541	0.711	0.541	1123.8218	−4.337
6			0.071		1129.8218	
7	0.024		0.071		1140.1578	10.587
8	0.024	0.025	0.071	1×10^{-3}	1129.7938	0.223
9	0.024	0.502	0.071	0.5	1128.0228	−1.548

[a] Total concentrations. [b] Calculated on the basis of a quantitative formation of TBAT and TBAP from TBAB and Br_2. [c] Central signal of CH_3CN-d_2 impurity at 1.9400 ppm taken as reference. [d] Calculated with respect to δ of $CHCl_3$ in sol. 1 in runs 2–5 and to δ of $CHCl_3$ in sol. 6 in runs 7–9.

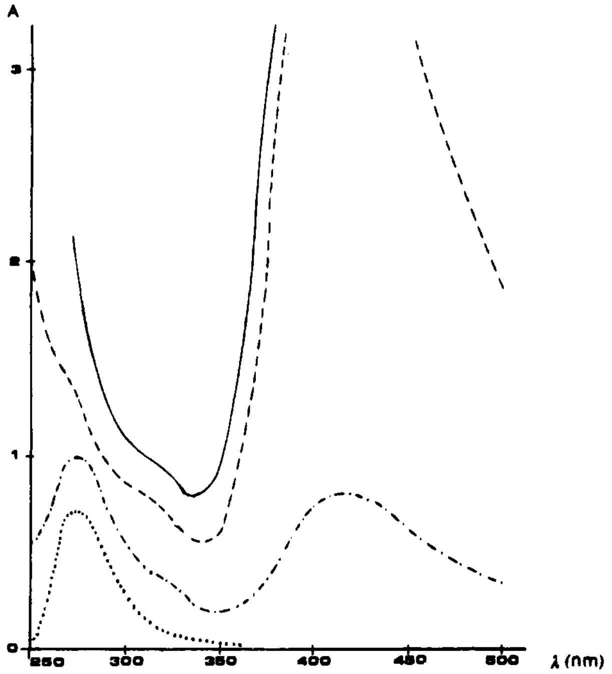


Figure 1. UV-vis spectra (0.1-cm optical path) of chloroform solutions of tetra-*n*-butylammonium bromide (1.0×10^{-4} M) containing the following: (a) 2.1×10^{-4} (···); (b) 2×10^{-2} (–·–); (c) 1.0×10^{-1} (– – –); and (d) 2.1×10^{-1} (—) M Br_2 at 25 °C.

The progressive dilution of a 1×10^{-4} M Br_2 and TBAB solution led to 272-nm absorptions that did not obey the Lambert–Beer law, suggesting an appreciable dissociation of Br_3^- to Br_2 and Br^-. At the lowest examined Br_2 and TBAB concentration, 3.5×10^{-5} M, the reduction of the absorptivity at the 272-nm Br_3^- maximum reached 50%. On this basis the K_3 of eq 1 could be roughly estimated to be around 3×10^4 M^{-1}.

In order to obtain accurate values of both K_3 and K_5 and of their molar absorptivities all the spectrophotometric measurements were included in a fitting based on a nonlinear least-squares (NLLSQ) procedure[10] using a previously described program.[9] The molar absorptivities obtained in the 250–420-nm interval were very similar to those found for the tetrabutylammonium tribromide and pentabromide, respectively, in 1,2-dichloroethane. The values obtained for the Br_3^- and Br_5^- formation constants were, respectively, $K_3 = 2.77(0.13) \times 10^4$ M^{-1} and $K_5 = 3.51(0.35) \times 10^5$ M^{-2}. Their correlation coefficient was +0.612. Correlation coefficients between K_3 or K_5 and any molar absorptivity never exceeded ±0.380, and those between any couple of molar absorptivities were even lower. The goodness of the overall fitting was shown by the s° = 0.051 absorbance units, an acceptably low variance value.[11] The calculated absorption spectra of the Br_3^- and Br_5^- species are given as supplementary material.

The ability of chloroform to form hydrogen bonds to halide ions is known.[12] Hydrogen bonding between a number of chlorinated solvents and the bromide ion of TBAB has been tackled by an NMR approach.[13] In Table I are reported accurate NMR measurements on the shift (δ) of the proton signal of chloroform in the presence of tetra-*n*-butylammonium bromide, tribromide, pentabromide, and free bromine in acetonitrile-d_3. In all runs a 3:1 ratio between chloroform and the anion was used. Two series of spectra, 1–5 and 6–9, at concentrations differing by a factor of 10, were recorded. Run 2 exhibited the highest observed shift, pointing to a hydrogen bond between the bromide ion and the proton of chloroform. This effect was still present in run 7, where 10-fold lower TBAB and chloroform concentrations were used. Very small shifts were observed in runs 3 and 8, where all bromine is in the form of Br_3^- ion, showing that very little, if any, hydrogen bond to chloroform is present from this charge-diffused ion. When larger Br_2 amounts were added, a small negative shift was instead observed, both in the presence (runs 4 and 9) and absence of added bromide (run 5), indicative of some type of interaction between Br_2 and $CHCl_3$. In conclusion, in both the 1–4 and 6–9 series, a similar trend appeared, confirming the capability of the Br^- anion, but not of the higher polibromide ions, to form hydrogen bonds with chloroform.

Bromination Rates. The same third-order kinetic law, first order in olefin and second order in Br_2, found in 1,2-dichloroethane, was observed for the bromination of *cis*- and *trans*-stilbene in chloroform at 25 °C. The reactions were followed spectrophotometrically at different wavelengths under third-order and pseudo-second-order conditions. The rate constants obtained, k_3 = 17.4 (0.6) for the cis olefin and k_3 = 7.43 (0.43) M^{-2} s^{-1} for the trans isomer, were 15- and 7-fold lower than those found for 1 and 2, respectively, in 1,2-dichloroethane. This is attributable to the bulk solvent polarity effect on the formation of the ionic intermediates.[13]

Product Distributions. Table II reports the ratio of *meso*- to *d,l*-1,2-dibromo-1,2-diphenylethane (3 and 4) obtained from the reaction of *cis*- and *trans*-stilbene (1 and 2) with molecular Br_2 at different concentrations in $CHCl_3$ at 25 °C. The products were determined by the HPLC technique. The distribution of the counteranion of the ionic intermediates between bromide and polibromide

---

(10) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96.

(11) Ambrosetti, R.; Bellucci, G.; Bianchini, R. *J. Phys. Chem.* **1986**, *90*, 6263.

(12) Ahmed, W. *J. Chem. Educ.* **1979**, *56*, 795.

(13) Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, G. *J. Org. Chem.* **1985**, *50*, 3313.

Table II. Product Distribution in the Bromination of *cis*- and *trans*-Stilbene and Calculated Equilibria among Bromide, Tribromide, and Pentabromide Anions in $CHCl_3$ at 25 °C

run	[Br2], M	[1], M	[2], M	3/4	2/(3 + 4)	$[Br_5^-]/[Br_3^-]$[a]	$[Br_3^-]/[Br^-]$[b]
1	1.5	5.0×10^{-1}		21:79		1.9×10^{1}	4.2×10^{4}
2	1.0	5.0×10^{-1}		20:80		1.3×10^{1}	2.8×10^{4}
3	5.0×10^{-1}	5.0×10^{-1}		23:77		6.3	1.4×10^{4}
4	2.5×10^{-1}	5.0×10^{-1}		30:70		3.1	7.1×10^{3}
5	1.0×10^{-1}	2.0×10^{-1}		35:65		1.2	2.9×10^{3}
6	2.5×10^{-2}	5.0×10^{-2}		39:61		3.0×10^{-1}	7.3×10^{2}
7	1.0×10^{-2}	2.0×10^{-2}		42:58		1.0×10^{-1}	3.5×10^{2}
8	2.5×10^{-3}	5.0×10^{-3}		50:50	0.02	3.2×10^{-2}	6.9×10^{1}
9	1.0×10^{-3}	2.0×10^{-3}		56:44	0.06	1.3×10^{-2}	2.8×10^{1}
10[c]	5.0×10^{-4}	1.0×10^{-3}		60:40	0.22	6.3×10^{-3}	1.4×10^{1}
11[c]	2.5×10^{-4}	5.0×10^{-4}		65:35	0.30	3.2×10^{-3}	6.9
12[c]	1.5×10^{-4}	7.5×10^{-4}		72:28	0.55	1.9×10^{-3}	4.1
13[c]	1.5×10^{-4}	3.0×10^{-4}		75:25	0.48	1.9×10^{-3}	4.1
14	5.0×10^{-1}		5.0×10^{-1}	75:25		6.9	1.4×10^{4}
15	1.0×10^{-1}		2.0×10^{-1}	78:22		1.3	2.9×10^{3}
16	2.5×10^{-2}		5.0×10^{-2}	80:20		3.0×10^{-1}	7.3×10^{2}
17	1.0×10^{-2}		2.0×10^{-2}	78:22		1.0×10^{-1}	3.5×10^{2}
18	2.5×10^{-3}		5.0×10^{-3}	80:20		3.2×10^{-2}	6.9×10^{1}
19[c]	1.0×10^{-3}		2.0×10^{-3}	83:17		1.3×10^{-2}	2.8×10^{1}
20[c]	5.0×10^{-4}		5.0×10^{-4}	91:9		6.3×10^{-3}	1.4×10^{1}

[a] Calculated on the basis of the $k_5/k_3 - 12.66\ M^{-1}$ value. [b] Calculated on the basis of $K_3 = 2.77 \times 10^4\ M^{-1}$ value (eq 1). [c] Reaction carried out at uncomplete conversion. The product ratios did not change during the course of the reaction.

species, calculated on the basis of the above obtained K_3 and K_5 values, is also shown in Table II. With the cis olefin 1 the 3/4 ratio increased with decreasing reagent concentrations and was pratically reversed at 1 M and 1×10^{-4} M Br_2. Furthermore, at sufficiently low reagent concentrations, *trans*-stilbene (2) was found besides the unreacted cis olefin 1 when the latter was used in excess. The formation of 2 during the bromination of 1 could not, however, affect the dibromide ratio, since 1 was always in excess over 2 and the former reacts with Br_2 at a two to three times higher rate. No isomerization to *cis*-1,2-dichloroethylene, indicative of an eventual presence of free radicals, was detected when the reactions were carried out in the presence of *trans*-1,2-dichloroethylene.[14] No *trans*-stilbene was formed when *cis*-stilbene was left in $CHCl_3$ both in the absence and in presence of gaseous HBr, that could have been generated during the bromination by adventitious side reactions. The dibromides 3 and 4 were found to be stable when left in chloroform in the presence of Br_2 under the reaction conditions. The dibromide distribution, and the formation of the trans olefin from *cis*-stilbene, were thus shown to depend neither on radical processes nor on a Br_2- or HBr-promoted product interconversion. In contrast with the behavior of *cis*-stilbene no relevant changes were found in the 3/4 ratio for the bromination of the trans isomer.

Discussion

Chloroform appears to be an appropriate solvent to compare the influence of the three different counteranions Br^-, Br_3^-, and Br_5^- on the bromination reaction path, and specifically on the reversibility of the bromonium ion formation.

Previous reports quoted higher K_3 values, 9×10^4,[15] 1.2×10^5,[16] and $1 \times 10^6\ M^{-1}$,[17] for the tribromide formation (eq 1) in this solvent, where Br_5^- formation had never been observed before. The reliability of the presently obtained K_3 and K_5 values lies on the large number of spectrophotometric data and on the low s^o value of their fitting. These values are at least 3 orders of magnitude lower with respect to the formation constants of TBAT and TBAP in the more polar 1,2-dichloroethane.[9] The hydrogen bond of the proton of chloroform to the bromide ion,[13] confirmed by the present NMR data, appears to be responsible for these differences. The TBAB–TBAT–TBAP equilibrium constants K_3 and K_5 have been used to obtain an evaluation of the distribution of the counteranions of the ionic intermediates formed during the bromination of stilbenes between Br^-, Br_3^-, and Br_5^- (Table II). This is allowable, even if the cation in this case is a bromonium ion, because the cation seems to have only a minor effect on the bromide polibromide equilibrium of the counteranion. For instance, in acetic acid K_3 changes only by a factor of 1.7 on passing from lithium bromide[18] to sodium or hydrogen bromide as sources of bromide ion.[19] More importantly, we showed that the K_5/K_3 value computed for the pentabromide formation from tribromide and bromine remains substantially constant (17.7 and 22.4 M^{-1}, respectively) on passing from tetrabutylammonium[9] to the adamantylideneadamantane–bromonium[20] countercation in 1,2-dichloroethane. We therefore believe that the figures reported in the last two columns of Table II provide acceptable evaluations of the anionic equilibria along the bromination pathway.

At a first glance, the data of Table II for the bromination of *cis*-stilbene show a trend similar to that found for the same reactions in 1,2-dichloroethane[4e,21] consisting of an increasing formation of the meso adduct 3 accompanied by the obtainment of the trans olefin 2, with decreasing reagent concentrations. This trend is in the same direction as the change from pentabromide to tribromide and to bromide as counteranions of the ionic intermediates. These results can be rationalized on the basis of the reaction sequence shown in Scheme I. Partially bridged cationic intermediates are suggested by the around 80%

---

(14) Walling, C.; Rieger, A. L.; Tanner, D. D. *J. Am. Chem. Soc.* **1963**, *85*, 3129.

(15) Dunn, G. E.; Blackburn, B. J. *Can. J. Chem.* **1974**, *52*, 2552.

(16) Le Goaller, R.; Hendel, H.; Labbe, P.; Pierre, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1694.

(17) Labbe, R.; Le Goaller, R.; Handel, H.; Pierre, J. L. *Electrochim. Acta* **1982**, *27*(2), 257.

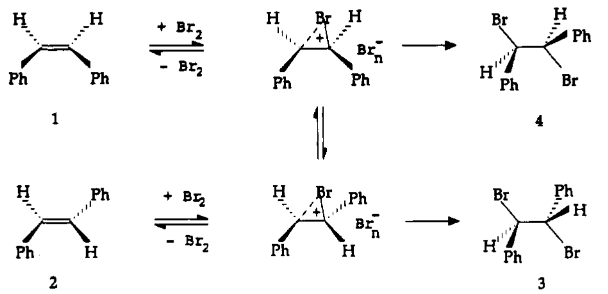
(18) Rolston, J. H.; Yates, K. *J. Am. Chem. Soc.* **1969**, *91*, 1483.

(19) Nakagawa, T. W.; Andrews, L. J.; Keefer, R. M. *J. Phys. Chem.* **1957**, *61*, 1007.

(20) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Ambrosetti, R.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1989**, *111*, 2640.

(21) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F. *J. Org. Chem.* **1990**, *55*, 4094.

Scheme I



anti stereoselective formation of dibromides **3** and **4**, respectively, from *trans*-stilbene and from *cis*-stilbene at the highest concentrations. On the other hand, some loss of stereochemical constraints can be inferred by (a) the lack of stereospecificity in both reactions and (b) the dependence of the **3**/**4** ratio in the bromination of the cis olefin **1** on the reagent concentrations.

The reaction of run 2 of Table II is completely nonstereoselective, but runs 8–13 show a progressively increasing formation of meso dibromide, accompanied by an increasing cis–trans isomerization of the excess olefin. Since this cis–trans isomerization cannot be attributed to adventitious free-radical or acid-catalyzed processes, it can only be rationalized by a release of Br_2, through an attack of Br_n^- at Br^+, from a *trans*-bromonium ion-like intermediate that is formed by isomerization of the less stable cis form and is also mainly responsible for the formation of the meso dibromide **3**. At $[Br_2] = 1.5 \times 10^{-4}$ M (runs 12 and 13) the amount of formed **2** is about half of the total dibromide amount. An increasing anti stereoselectivity, without cis–trans olefin isomerization, is instead found with raising Br_2 concentration (runs 7–1) when the counteranion equilibrium are progressively shifted toward Br_3^- and Br_5^- species. The lack of trans olefin formation in these runs suggests that in this concentration range the cis–trans isomerization of the cationic intermediate is less important or that the polibromide anions are less stable to abstract Br^+ from the intermediate.

In the apolar chloroform solvent the intermediates are surely formed as intimate ion pairs, and a reciprocal counterion stabilization is provided by electrostatic interactions. When the anion is a charge-diffused polibromide, electrostatic stabilization of the cation is likely lower and this should reduce the lifetime of the intermediates and therefore the possibility of its cis–trans isomerization before collapse to products or reversal to olefin. Moreover, if the configuration of the Br_5^- ion is not linear as that of Br_3^-,[3b] but is L-shaped as found for the pentaiodide anion,[22] it could easily locate a Br^- ready for anti-attack without translocation of the counteranion, a process requiring a temporary separation of the two electrostatically bound ions. A progressive change from intimate to solvent-separated ion pairs, and perhaps to free ion,[23] may occur in the region of lowest Br_2 concentration, since the concentration of the intermediates should be reduced, too. This could allow for a longer lifetime, and therefore for a more extensive cis–trans isomerization of the first-formed *cis*-bromonium intermediate, leading to the progressive increase of meso dibromide **3** and trans olefin **2** observed in runs 9–13. A factor that can may favor ion-pair separation in reactions carried out at very low bromine concentration is that the counteranion is essentially Br^- and this is hydrogen bonded to chloroform, as the NMR measurements show. It must be stressed that the extent of reversal of the intermediate to trans olefin and Br_2, measured by the **2**/(**3** + **4**) ratio of Table II, does increase with increasing amount of counteranion present as Br^-. This shows that even with uncrowded olefins nucleophilic attack by this anion at the bromonium carbons can be slow enough to allow for a competitive attack at Br^+,[4e] in contrast with the tentative rationalization of the different reversal in protic and aprotic solvents mentioned in the introduction.[6,7] On the other hand, the meso dibromide **3** is always the main product of the bromination of *trans*-stilbene, and this is consistent with the intermediacy of a partially bridged *trans*-bromonium ion-like intermediate, which is attacked mainly in an anti fashion. Finally, it can be noted that, although the brominations of **1** and **2** tend to become stereoconvergent with decreasing reagent concentrations, they do not become completely stereospecific as found in 1,2-dichloroethane.[21] This is probably due to the fact that, on account of the much slower rates in chloroform, these reactions cannot be practically carried out at low enough reagent concentrations.

Experimental Section

Materials. Best quality commercial bromine (C. Erba RPE >99.5%) was kept in 1-mL sealed ampules which were opened immediately before use. Tetrabutylammonium bromide (EGA ≃ 99%) was crystallized twice from ethyl acetate/toluene and stored under dry argon. Commercial *cis*-stilbene (Aldrich, >97%) and *trans*-stilbene (Schuchardt >99%) were purified as previously reported.[4b] Good quality commercial chloroform (C. Erba RPE >99%) was purified using a reported procedure[24] modified as follows: chloroform was washed with sulfuric acid until the acid phase remained colorless, and then with water, saturated aqueous sodium hydrogen carbonate, and water. The organic phase was left over $MgSO_4$ and finally distilled under argon at reduced pressure, boiling point never exceeding 30 °C. A central fraction was collected and immediately used. The overall purification procedure was carried out in the dark, and any exposure of the purified chloroform, as well as bromine and stilbenes or TBAB solutions, to daylight was carefully avoided.

Equilibrium Measurements. Appropriate quantities of Br_2 and TBAB were weighed in known volumes of chloroform to prepare stock solutions, which were stored no longer than 1 h. These solutions were discarded when higher than expected absorptions occurred in the 280–350-nm range. Suitable aliquots of the Br_2 and TBAB chloroform solutions were withdrawn from precision microburettes, and the UV–vis spectra of the resulting mixtures were recorded at 25 ± 0.1 °C in the 250–500-nm range on a Cary 2200 spectrophotometer. Only measurements that resulted reproducible within a 0.5–1 h interval time and were obtained from solutions containing the same analytical Br_2 and TBAB concentrations from different chloroform stocks were accepted. Absorbances at selected wavelengths of solutions containing bromine and TBAB were also measured by using a Durrum stopped-flow kinetic spectrophotometer. The registered absorbance values fully matched those measured on the standard spectrophotometer, and no kinetic event apparently occurred. Computations were performed by fitting the spectrophotometric measurements by a NLLSQ technique[9] to a model describing the formation of each possible A_mB_n complex (A stands for TBAB, B for Br_2 in the present case), the *m*,*n* pair having been limited to the 1,1 and 1,2 values in the present approach.[20]

---

(22) (a) Broekema, J.; Havinga, E. E.; Wieberg, E. H. *Acta Crystallogr.* **1957**, *10*, 596. (b) Hach, R. J.; Rundle, R. E. *J. Am. Chem. Soc.* **1951**, *50*, 1953.

(23) Bromonium tribromide ion pair dissociation is surely occurring in 1,2-dichloroethane, as shown by the remarkable conductivity measured for solutions of adamantylideneadamantane–bromonium tribromide.[20] That some ion pair dissociation occurs even in chloroform is indicated by the low, but detectable, conductivity of tetrabutylammonium bromide solutions in this solvent ($\Lambda^m = 0.55$ S cm^2 mol^{-1} in the 10^{-2}–10^{-3} M concentration range). This dissociation may be favored in bromination carried out at very low Br_2 concentration by the fact that the Br^- counteranion is hydrogen bonded to chloroform as shown by the present NMR measurements.

(24) Morgan, S. O.; Lowry, H. H. *J. Phys. Chem.* **1930**, *34*, 2385.

6478 *J. Org. Chem.* **1992**, *57*, 6478–6487

NMR Spectra. Purified chloroform was added in appropriate amounts as such, or containing TBAB and/or Br_2, to acetonitrile-d_3 solvent (Aldrich, 99.5 atom % D). Spectra were run on a Bruker AC 200 instrument, the reproducibility of chloroform chemical shift being ±0.022 Hz.

Kinetic Measurements. Solutions of Br_2 and *cis*- or *trans*-stilbene in chloroform were prepared shortly before use, protected from the light, and mixed in appropriate amounts. The bromine disappearance was followed at 380, 410, and 480 nm on a Cary 2200 spectrophotometer. The absorbance/time data were fitted to the third-order or pseudo-second-order rate equation.

Bromination Procedure and Product Analyses. Chloroform solutions of *cis*- and *trans*-stilbenes **1** and **2** were mixed with bromine solutions in various ratios, the reagent concentrations after mixing being reported in Table II. The reaction mixtures were allowed to react in the dark at 25 °C for times ranging between 1 h and 2 days. The solutions were directly analyzed by HPLC (Waters 600 E, equipped with diode array detector), the yields being calculated by addition of *erythro*-1,2-dibromo-1-phenylpropane as standard[21] using a 25-cm Hypersil 70 C18 column, with methanol/water 72:28 v/v as the eluent at a flow rate of 1.2 mL/min. For each run reported in Table II *trans*-1,2-dichloroethylene was added at concentrations equal to that of **1**. No isomerization to the cis isomer was ever observed by HPLC analysis. The stability of dibromides **3** and **4** in $CHCl_3$ in the presence of Br_2 was also checked by exposing chloroform solutions of each dibromide to bromine concentrations varying in the range reported in Table II. Both pure dibromides were quantitatively recovered even after several days. The dibromide distributions reported in Table II are the averages of at least triplicate runs and were reproducible to ±3%, whereas the **2**:(**3** + **4**) ratios were reproducible to ±15% of the quoted values.

Acknowledgment. This work was granted from CNR and MURST of Italy. We thank prof. Giuseppe Bellucci for the helpful discussion and valuable comments on the manuscript.

Registry No. **1**, 645-49-8; **2**, 103-30-0; $Bu_4N^+Br^-$, 1643-19-2; $Bu_4N^+Br_3^-$, 38932-80-8; $Bu_4N^+Br_5^-$, 117040-00-3.

Supplementary Material Available: Tables containing the Br_2 and TBAB concentrations of the chloroform solutions used in the spectrophotometric measurements (Table A), all the measured data (wavelength, concentrations, absorbances, optical path) used in the determination of the equilibrium constants and spectral parameters relative to species involved in eqs 1 and 2 (Table B), and the calculated extinction parameters of TBAT and TBAP in chloroform in the 250–420-nm range (Table C) (10 pages). This material is contained in many 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.

Reaction of Organic Sulfides with Singlet Oxygen. A Theoretical Study Including Electron Correlation

Frank Jensen

Department of Chemistry, Odense University, DK-5230 Odense M., Denmark

Received August 10, 1992

The reaction of H_2S and $(CH_3)_2S$ with $^1O_2$ has been reinvestigated with ab initio methods including electron correlation. While only a peroxy sulfoxide is an intermediate at the Hartree–Fock level of theory, a second intermediate, a thiadioxirane, is found at the MP2 level. The computational results suggest that these two intermediates are almost isoenergetic in the gas phase, but the peroxy sulfoxide may be slightly favored in solution. MP2/6-31G* vibrational frequencies are calculated for both species, and it is possible that a previously observed intermediate may be the thiadioxirane. The transition structures for the formation of the peroxy sulfoxide and for interconversion between the two intermediates have also been located. The peroxy sulfoxide formation is calculated to be entropy controlled, in agreement with experimental data. Interconversion between the two intermediates is calculated to have an activation energy close to 20 kcal/mol, inconsistent with the previously accepted reaction mechanism.

Introduction

The photooxidation of organic sulfides is probably one of the mechanistically most complex reactions of singlet oxygen studied so far.[1,2] The overall reaction is oxidation of the sulfide to sulfoxide and sulfone, and the former is usually the major product. The limiting quantum yield is two; i.e., each molecule of singlet oxygen results in 2 mol of sulfoxide.[3,4] Early studies showed that a reactive intermediate could act as an oxidizing species toward trapping agents such as diphenyl sulfide and diphenyl sulfoxide.[3-6] A peroxy sulfoxide structure ("persulfoxide") was tenatively assigned to this intermediate. Later it was found by competitive trapping studies that different kinetic schemes were observed in protic and aprotic solvents. In protic solvents a single intermediate is sufficient for explaining the kinetic data, while a scheme involving two different intermediates were suggested for aprotic solvents.[4,6] Trapping studies indicate that an oxygen-transfer agent acts as an electrophile toward phenyl sulfides,[7,8] while the intermediate that can be intercepted by phenyl sulfoxides is nucleophilic.[5] The structures of the inter-

---

(1) (a) Schench, G. O.; Krausch, C. H. *Angew. Chem.* **1962**, *74*, 510. (b) Ando, W. In *Singlet Oxygen*; CRC Press: Boca Raton, 1984; Vol III, Part 2, p 1.

(2) For other related work see: (a) Miyke, A.; Tomoeda, M. *J. Chem. Soc., Chem. Commun.* **1970**, 240. (b) Adam, W.; Liu, J. C. *J. Chem. Soc., Chem. Commun.* **1972**, 73. (c) Corey, E. J.; Quannes, C. *Tetrahedron Lett.* **1976**, 4263. (d) Burgess, E. M.; Zoller, U.; Burger, R. L., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 1128. (e) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1987**, *109*, 1478. (f) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *J. Am. Chem. Soc.* **1988**, *110*, 494. (g) Clennan, E. L.; Chen, X. *J. Am. Chem. Soc.* **1989**, *111*, 5787.

(3) Foote, C. S.; Peters, J. W. *J. Am. Chem. Soc.* **1971**, *93*, 3795.

(4) (a) Gu, C.-L.; Foote, C. S.; Kacher, M. L. *J. Am. Chem. Soc.* **1981**, *103*, 5949. (b) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717.

(5) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5947.

(6) (a) Clennan, E. L.; Wang, D.-X.; Yang, K.; Hodgson, D. J.; Oki, A. R. *J. Am. Chem. Soc.* **1992**, *114*, 3021. (b) Sheu, C.; Foote, C. S.; Gu, C.-L. *J. Am. Chem. Soc.* **1992**, *114*, 3015.

(7) Watanabe, Y.; Kuriki, N.; Ishiguro, K.; Sawaki, Y. *J. Am. Chem. Soc.* **1991**, *113*, 2677.

(8) (a) Kasher, M. L.; Foote, C. S. *Photochem. Photobiol.* **1979**, *29*, 765. (b) Monroa, B. M. *Photochem. Photobiol.* **1979**, *29*, 761. (c) Ando, W.; Kabe, Y.; Miyazaki, H. *Photochem. Photobiol.* **1980**, *31*, 191.

0022-3263/92/1957-6478$03.00/0