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Formation of Pentabromide Ions from Bromine and Bromide in Moderate-Polarity Aprotic Solvents and Their Possible Involvement in the Product-Determining Step of Olefin Bromination

Giuseppe Bellucci,[*,†] **Roberto Bianchini,**[†] **Cinzia Chiappe,**[†] **and Roberto Ambrosetti**[*,‡]

Contribution from the Istituto di Chimica Organica, Facoltà di Farmacia, via Bonanno 33, I-56100 Pisa, Italy, and Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R., via Risorgimento 35, I-56100 Pisa, Italy. *Received March 10, 1988*

Abstract: The electronic spectra of 1,2-dichloroethane solutions containing $Bu_4N^+Br^-$ and excess bromine showed around the UV minimum of Br_2 (320 nm) an absorption that was higher than that attributable to the presence of tribromide ions and that increased with increasing bromine concentration. Measurements taken at 15, 25, and 48 °C in the 250–600-nm range on 2.6×10^{-4} to 3.6×10^{-1} M Br_2 and 1.1×10^{-4} to 5.6×10^{-4} M $Bu_4N^+Br^-$ solutions yielded, by a simultaneous nonlinear least-squares fitting, reliable values of the molar extinction coefficients and of the formation constant of a $Bu_4N^+Br_5^-$ species from $Bu_4N^+Br_3^-$ and Br_2: $\epsilon = 5.38\ (0.24) \times 10^4\ M^{-1}\ cm^{-1}$ at 310 nm; $\Delta H = -3.54\ (0.43)$ kcal mol^{-1}; $\Delta S = -6.60\ (1.37)$ cal mol^{-1} K^{-1}; $K_f = 17.7\ (0.6)$ at 15 °C, 14.3 (0.7) at 25 °C and 9.3 (0.5) M^{-1} at 48 °C. The data suggest that a significant amount of the bromonium–tribromide ion pairs formed as the intermediate in the slow step of the olefin bromination in moderate-polarity aprotic solvents is actually present as bromonium–pentabromide ion pairs, especially when the bromination is carried out in the presence of relatively high Br_2 concentrations, and that the collapse of the latter ion pairs should be responsible for changes in the distribution of dibromo adducts.

While exhaustive information can be found in the literature about the formation, structure, and spectral and thermodynamic data of the tribromide anion,[1] higher polybromide ions have received much less investigation. Experimental solubility data suggest the presence of polybromide ions other than Br_3^-,[2] and the pentabromide anion Br_5^- has been postulated to be present in solutions containing Br_2 and Br^- ions.[3-5] Values of $K_5 = [Br_5^-]/([Br^-]\ [Br_2]^2)$ ranging between 20 and 40 M^{-2} at 25 °C have been reported for this Br_5^- ion in water,[6] but no data are available concerning its formation in low-polarity aprotic solvents.

Information of this type would, on the other hand, be important for a more thorough comprehension of the mechanism of one of the apparently simplest standard textbook organic reactions such as olefin bromination. Extensive experimental evidence supports the formation of ion pair intermediates in the slow step of this reaction.[7] Much speculation has been presented concerning the structure of the cationic moieties of these ion pairs, which are alternatively viewed as strongly or weakly bridged bromonium ions or open bromocarbonium ions, depending on the structure of the substrate or of the dibromide products. Much less attention has been paid to the nature of the counteranion. This is implicitly considered to be a bromide ion in protic solvents, where the overall reaction is first order in Br_2,[8] and a tribromide ion in low-polarity aprotic solvents, where the reaction is second order in the halogen.[9] Kinetics can, however, give information only about the number of halogen molecules involved in the rate-determining step, while larger bromine aggregates could well take part in the product-determining step if the ion pair intermediates, once formed, are subjected to fast bromide–polybromide equilibration in the presence of Br_2.

This possibility cannot be tested directly, since, under the bromination conditions, the involved ion pairs are very short-lived, usually undetectable intermediates. Indirect information can, however, be obtained from the knowledge of the formation constant of polybromide ions paired to unreactive organic cations in low-polarity aprotic solvents of the type most commonly employed in Br_2 addition reactions. For this purpose we undertook a UV–vis spectrophotometric investigation of the tribromide–pentabromide equilibrium, choosing the tetrabutylammonium ion as the cationic moiety and 1,2-dichloroethane as the solvent. The formation constant of the Br_3^- ion in this system had already been evaluated to be $\geq 2 \times 10^7\ M^{-1}$.[10] Studies of the present type have probably been discouraged so far by the extensive overlap of the electronic absorptions of the involved polybromide ions. A specially designed least-squares fitting procedure has now allowed us to treat simultaneously data taken over a large spectral range at different concentrations and temperatures. Only in this way information pertaining to each species at equilbrium could be extracted reliably, thus obtaining as fitting parameters the electronic spectrum of the Br_5^- ion and the thermodynamic parameters for its formation from Br_3^- and Br_2.

Results

Spectral Data. Bromide ion is known to be completely transformed into tribromide when an equimolar amount of Br_2 is added to solutions of tetrabutylammonium bromide (TBAB) in 1,2-dichloroethane.[9d] The resulting electronic spectrum exhibits an intense band with $\lambda_{max} = 273$ nm and $\epsilon = 5 \times 10^4\ M^{-1}\ cm^{-1}$. Ion pair dissociation phenomena, if present at all, have no effect on this spectrum, since identical λ_{max} and band shape were found after dilution from 10^{-4} to 10^{-7} M. However, the spectra of 1,2-dichloroethane solutions obtained from TBAB and excess Br_2 showed around the UV minimum of Br_2 (320 nm, $\epsilon = 6.5$) absorptions that were higher than those attributable to the presence of tetrabutylammonium tribromide (TBAT) and that increased with increasing Br_2 concentration. Figure 1 shows the changes

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[†] Istituto di Chimica Organica.

[‡] Istituto di Chimica Quantistica ed Energetica Molecolare del C.N.R.

(1) *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Bromine, Supplement Volume A; Springer-Verlag: Berlin 1985; pp 502–519.

(2) Popov, A. I. *Halogen Chem.* **1967**, *1*, 225–264.

(3) Scaife, D. B.; Tyrrell, H. J. V. *J. Chem. Soc.* **1958**, 386–392.

(4) Dubois, J. E.; Garnier, F. *Bull. Soc. Chim. Fr.* **1965**, 1715–1718.

(5) Hecquet, B.; Landais, J. *C. R. Séances Acad. Sci.* **1972**, *C274*, 1353–1356.

(6) See ref 1, pp 520–521.

(7) For extensive recent reviews of olefin bromination, see: (a) Schmid, G. H.; Garratt, D. G. *The Chemistry of Double Bonded Functional Groups*; Patai, S., Ed.; Wiley: New York, 1977; Suppl. A, Part 2, p 725. (b) V'yunov, K. A.; Ginak, A. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1981**, *50*, 151–163. (c) De la Mare, P. B. D.; Bolton, R. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982; Chapter 5, pp 136–197.

(8) See ref 7c, notes 6–13.

(9) (a) See ref 7c, note 19a. (b) Modro, A.; Schmid, G. H.; Yates, K. *J. Org. Chem.* **1977**, *42*, 3673–3676. (c) Bellucci, G.; Bianchini, R.; Ambrosetti, R. *J. Am. Chem. Soc.* **1985**, *107*, 2464–2471. (d) Bellucci, G.; Bianchini, R.; Ambrosetti, R.; Ingrosso, G. *J. Org. Chem.* **1985**, *50*, 3313–3318. (e) Bellucci, G.; Bianchini, R.; Vecchiani, S. *J. Org. Chem.* **1986**, *51*, 4224–4232. (f) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515–522.

(10) Bellucci, G.; Berti, G.; Bianchini, R.; Ingrosso, G.; Ambrosetti, R. *J. Am. Chem. Soc.* **1980**, *102*, 7480–7486.

0002-7863/89/1511-0199$01.50/0

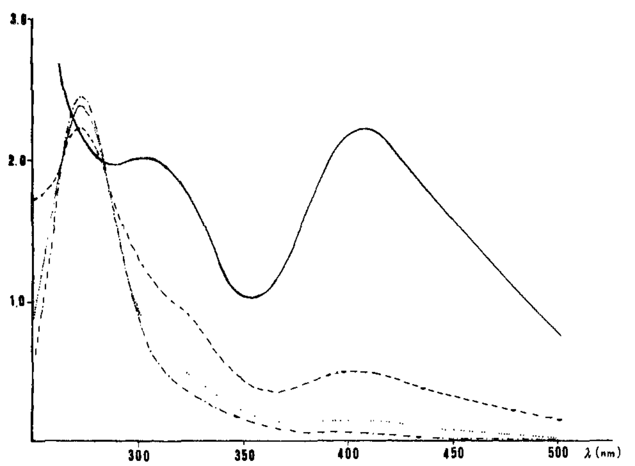

Figure 1. UV–vis spectra of 1,2-dichloroethane solutions of tetrabutylammonium bromide (5×10^{-4} M) containing 1×10^{-3} (·–·), 5×10^{-3} (···), 2×10^{-2} (–––), and 1×10^{-1} M (—) Br_2 at 25 °C.

occurring in the 250–500-nm range on progressive addition of Br_2 to a 5×10^{-4} M solution of TBAB in 1,2-dichloroethane at 25 °C. Besides large absorptions due to the excess halogen at 410 nm and below 300 nm, as well as to tribromide in the latter range, a new band centered around 300–310 nm was clearly observed at sufficiently high Br_2 concentration, where a decrease in the contribution of tribromide is also recognizable.

At given TBAB and Br_2 concentrations the new absorption decreased markedly but reversibly with increasing temperature. All these data indicated the exothermic formation of a new polybromide species, with a UV spectrum shifted bathochromically relative to that of the tribromide ion and hypsochromically relative to that of Br_2. The most probable candidate was, of course, tetrabutylammonium pentabromide (TBAP), formed according to equilibrium 1:

$$Bu_4N^+Br_3^- + Br_2 \overset{K}{\rightleftarrows} Bu_4N^+Br_5^- \qquad (1)$$

In order to check the stoichiometry and to determine the thermodynamic parameters relative to this equilibrium, a series of spectra were taken at 15, 25, and 48 °C in the 250–600-nm wavelength range at analytical concentrations of Br_2 and TBAB ranging respectively between 2.6×10^{-4} and 3.6×10^{-1} M and between 1.1×10^{-4} and 5.6×10^{-4} M.

The overlap of the absorptions of the three species involved in equilibrium 1 prevented a conventional treatment of these measurements. The following new computational procedure was therefore devised.

Computational Procedures. Spectrophotometric measurements were fitted by nonlinear least-squares (NLLSQ) techniques[11] to a model described by the successive formation of a 1:1 (TBAT) and a 1:2 (TBAP) bromide–bromine complex.

Each "experimental datum" consisted of a set of six measures on the same solution: concentrations of bromide and bromine, temperature, wavelength, optical path, and transmittance. More than 700 such data were collected and all were included in an overall fitting.

Fitting parameters were the formation enthalpy ΔH and entropy ΔS of pentabromide ion from tribromide and bromine and the molar extinction coefficient of pentabromide at each measured wavelength. Preliminary fittings were conducted on the three subsets of data taken at 15, 25, and 48 °C in order to obtain values of the formation constant at each temperature.

The fitting program allowed inclusion of the molar extinction coefficients of each species (bromine, bromide, tribromide, pentabromide) at each wavelength as fitting parameters. The absorbances measured in the presence of a large excess of TBAB were expected to exhibit little, if any, temperature dependence, since essentially all available Br_2 is then converted to TBAT at any temperature, and furthermore the known thermal expansivity of 1,2-dichloroethane can only yield a quite negligible effect of temperature on the concentrations. On the contrary, we measured a slight temperature dependence of the spectra, which can only be due to a temperature dependence of the molar extinction coefficients of TBAT. As a consequence we included as fitting parameters, for both TBAT and TBAP, a linear (l) and a quadratic (q) temperature coefficient, defined by the equation

$$\epsilon_t = \epsilon_{25}[1 - l(t - 25) + q(t - 25)^2]$$

This brought the overall number of parameters to 255, although it was not necessary to refine more than 50 of them in any fitting. The best fit was found when l was around 0.003 for both TBAT and TBAP at the respective absorption maxima, where l also had its maximum. The best-fit value of q was essentially zero at all wavelengths.

The inclusion of this correction reduced the residuals of the fitting. However, it had little effect on the value of K, and the spectrum of TBAP retained essentially the same shape and intensity. As a consequence, for the sake of simplicity, we will quote, both in the text and in the tables, only results obtained when no temperature coefficient of the molar extinction parameters was included.

The very high formation constant of TBAT allowed us to neglect, to a good approximation, its dissociation at all bromine concentrations used, thus allowing us to deal with a single equilibrium (tribromide–pentabromide). However, we devised a computational scheme able to take into account both equilibria at once, since this allowed both checking the validity of the above assumption and extending measurements to different solvents, in which tribromide could be less stable than in 1,2-dichloroethane.

Although the available data allowed us to refine simultaneously the spectra of both TBAT and TBAP, the resulting best-fit spectrum of TBAT was not significantly different from the one obtained directly from measurements taken in the presence of excess TBAB. Therefore, again for the sake of simplicity, we will constantly make reference to the directly measured TBAT spectrum, which in turn essentially duplicates the known one.[9d]

The fitting program evaluates at each temperature t the formation constant K (for pentabromide) from formation enthalpy ΔH and entropy ΔS:

$$K = \exp(-\Delta H/(RT) + \Delta S/R)$$

Then the equilibrium concentrations are evaluated as follows. Let us define

$$a = [Br_2]$$

$$b = [Bu_4N^+Br^-]$$

$$c = [Bu_4N^+Br_3^-]$$

$$d = [Bu_4N^+Br_5^-]$$

where the concentrations are initially put equal to the total stoichiometric amounts of the various species (thus, for instance, c and d are always set equal to zero initially). If we introduce the variables x and y as the concentrations of bromine disappearing respectively for the equilibrium formation of tribromide and pentabromide, then the equilibrium conditions are

$$K_3 = (c + x - y)/[(a - x - y)(b - x)] \qquad (2)$$

$$K_5 = (d + y)/[(a - x - y)(c + x - y)] \qquad (3)$$

Equations 2 and 3 define a fourth-degree equation set (second degree in both x and y). Of the many strategies tried for reducing the degree of the set, we chose a simple one that worked for any combination of initial concentrations and gave relatively rapid convergence. It consisted of omitting in the fully developed denominator the second-degree terms containing the products xx, yy, or xy, thus yielding an easily solved first-degree set. The computed x and y values were used for correcting a, b, c, and d (thus giving the corrected a as $a - x - y$ etc.). In this way, c and d assume nonzero values. The corrected values were used for

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(11) (a) Hamilton, W. C. *Statistics in Physical Science*; Ronald Press: New York, 1965. (b) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96.

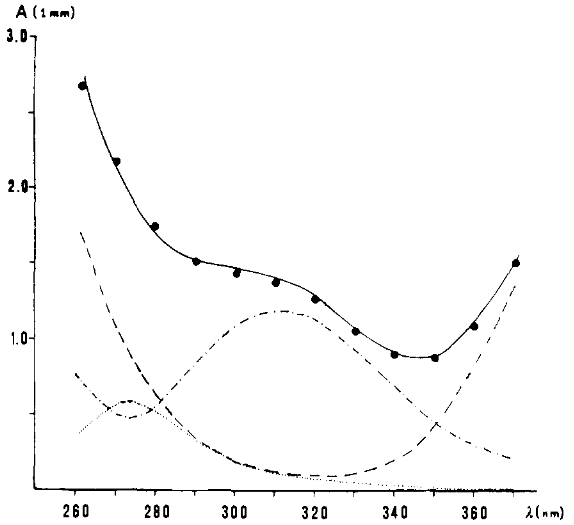

Figure 2. Experimental (●) and calculated (—) UV spectrum of a 3.3 × 10^{-4} M tetrabutylammonium bromide and 1.4 × 10^{-1} M Br_2 solution in 1,2-dichloroethane at 25 °C. The calculated spectrum is the sum of the calculated single spectra of the three species present at equilibrium: Br_2 (– – –), tribromide (···), and pentabromide (·–·).

reevaluating the coefficients of eq 2 and 3, which were solved iteratively until convergence was attained.

Having obtained the equilibrium concentrations, the program computes from them the absorbances at each wavelength. The absorbances are then converted to transmittance and subtracted from the measured ones in order to obtain the residuals, which are then minimized according to standard NLLSQ procedures.[11] The reason for obtaining the residuals as transmittance, instead of absorbance, differences stems from the fact that the transmittance spectrophotometric error is essentially independent of the transmittance measured: this makes a constant-weight scheme, such as the one used by us, entirely correct, under the reasonable hypothesis that this is the main source of error.

Figure 2 shows a typical experimental and calculated spectrum obtained at respective TBAB and Br_2 analytical concentrations of 3.3 × 10^{-4} and 1.4 × 10^{-1} M in 1,2-dichloroethane at 25 °C in the 260–370-nm range. The dissection of the spectrum into those of the three species present at equilibrium is also shown. TBAP has its λ_{max} around 312 nm. The molar extinction coefficients at several wavelengths, obtained as fitting parameters in the simultaneous NLLSQ fitting of the whole experimental data, are reported with their standard deviations in Table I. The variance of the fit was 6.2 × 10^{-4} (squared transmittance units).

The values obtained for the formation enthalpy and entropy of TBAP from TBAT and Br_2 (eq 1) are $\Delta H = -3.54$ (0.43) kcal mol^{-1} and $\Delta S = -6.60$ (1.37) cal mol^{-1} K^{-1}. The correlation coefficient between ΔH and ΔS was 0.996. This high value is typical of this type of determination, since it depends essentially on the temperature interval of the measurements, and does not affect adversely the definition of the formation constant in the investigated temperature range. The correlation coefficient between either ΔH or ΔS and any molar extinction coefficient never exceeded 0.55; it was still lower between any couple of extinction coefficients.

From such data, the formation constant K and its standard deviation can be estimated at any temperature of interest in the measured range. In particular, we obtain $K = 17.7$ (0.6) at 15 °C, 14.3 (0.7) at 25 °C, and 9.3 (0.5) M^{-1} at 48 °C. As an effect of the large correlation between formation enthalpy and entropy, the given K value can only be obtained when taking all significant figures reported above.

Discussion

The present results conclusively show that a pentabromide species is formed, besides the tribromide, when bromide and excess bromine are dissolved in an aprotic solvent of moderate polarity such as 1,2-dichloroethane. As expected, the formation of Br_5^- from Br_3^- and Br_2 is exothermic and involves an entropy decrease. Since very similar average values (around 30 M^{-1} or M^{-2}, respectively) can be obtained from the available literature for K_3 and K_5 (defined by equilibria 4 and 5) in aqueous solution[1,6] and since $K = K_5/K_3$, a rough value near unity can be evaluated for the formation constant K of equilibrium 6 under these conditions.

Table I. Extinction Parameters Employed for Fitting Spectrophotometric Data Taken on Solutions of TBAB in 1,2-Dichloroethane Containing Excess Br_2 at 15, 25, and 48 °C[a]

	molar ext coeff, cm^{-1} M^{-1}		
wavelength, nm	bromine	tribromide	pentabromide
250	256	11000	69340 (11000)
260	130.5	31200	32590 (10000)
270	78.0	48670	18230 (9600)
280	45.0	44880	23100 (5500)
290	25.0	28710	36650 (3100)
300	13.3	15940	49540 (2500)
310	8.9	9565	53850 (2400)
320	6.5	6750	51640 (2200)
330	7.7	5005	42400 (1700)
340	14.3	3575	31150 (1400)
350	31.0	2440	20100 (1300)
360	60	1540	13350 (1200)
370	99	1150	9010 (1300)
380	145	940	6480 (1400)
390	182	800	5280 (1500)
400	205	680	3400 (1500)
410	211	535	2400 (1400)
420	204	400	1400 (1200)

[a] Standard deviations are parenthesized following the value of the corresponding parameter. Parameters not accompanied by a standard deviation were kept fixed in the fitting. The highest correlation coefficient between the reported parameters is 0.55.

$$Br^- + Br_2 \overset{K_3}{\rightleftharpoons} Br_3^- \qquad (4)$$

$$Br^- + 2Br_2 \overset{K_5}{\rightleftharpoons} Br_5^- \qquad (5)$$

$$Br_3^- + Br_2 \overset{K}{\rightleftharpoons} Br_5^- \qquad (6)$$

This value is 1 order of magnitude lower than that found for equilibrium 1 in 1,2-dichloroethane. The available data indicate that the formation constant for equilibrium 4 is not substantially affected by the nature of the cation.[1] If this is valid also for equilibrium 6, it can be concluded that the stability of the pentabromide ion relative to tribromide is considerably higher in 1,2-dichloroethane than in water. This is not surprising, since in a solvent incapable of electrophilic solvation the larger Br_5^- ion is expected to be more stabilized than the Br_3^- one by internal charge delocalization. A similar but much more marked trend was found for K_3, which increases by several orders of magnitude on passing from water to organic low-polarity aprotic solvents.[9d]

According to equilibrium 6, in the presence of an excess of Br_2 the ratio of the concentrations of Br_5^- and Br_3^- depends only on the concentration of the halogen (eq 7). The presently determined

$$[Br_5^-]/[Br_3^-] = K[Br_2] \qquad (7)$$

K value shows that a Br_2 concentration as low as 10^{-2} M gives a 13:87 ratio of penta- to tribromide at 25 °C. This ratio raises to 59:41 at 10^{-1} M Br_2 and to 93:7 at 1 M Br_2. If a similar K value applies also to the formation of Br_5^- from Br_3^- in the intermediates arising during olefin bromination in low-polarity aprotic solvents like 1,2-dichloroethane, it can be inferred that, while at $[Br_2] < 10^{-2}$ M most of these ion pairs are in the tribromide form, at $[Br_2] \geq 10^{-1}$ M most of them are in the pentabromide form, and intermediate situations are found in the 10^{-1}–10^{-2} M Br_2 concentration range.

Different intermediates are therefore likely to be involved in the product-determining step of olefin bromination depending on the Br_2 concentration during the course of the addition. Dropwise addition of Br_2 to a solution of the olefin should produce a low halogen concentration during most of the reaction and therefore

Table II. Composition of the 1,2-Dichloroethane Solutions Used in Spectrophotometric Measurements

anal. concn, M		computed equilib comp at 25 °C	
$[Br^-]$	$[Br_2]$	% Br_5^{-} [a]	$[Br_5^-]/[Br_3^-]$
1.52×10^{-4}	2.6×10^{-4}	0.15	0.0015
4.94×10^{-4}	2.1×10^{-3}	2.2	0.022
5.60×10^{-4}	2.9×10^{-3}	3.2	0.033
4.48×10^{-4}	5.8×10^{-3}	7.9	0.076
2.21×10^{-4}	1.2×10^{-2}	14.4	0.17
2.61×10^{-4}	2.0×10^{-2}	22.0	0.28
2.94×10^{-4}	3.0×10^{-2}	29.7	0.42
1.37×10^{-4}	5.3×10^{-2}	43.0	0.75
2.21×10^{-4}	9.1×10^{-2}	56.5	1.3
3.32×10^{-4}	0.14	66.6	2.0
2.29×10^{-4}	0.18	72.0	2.6
1.97×10^{-4}	0.23	76.7	3.2
1.71×10^{-4}	0.27	79.4	3.9
1.64×10^{-4}	0.28	80.0	4.0
1.14×10^{-4}	0.36	83.7	5.1

[a] $100 \times [Br_5^-]/([Br_5^-] + [Br_3^-])$.

involve mainly tribromide type ion pair intermediates. An inverse addition, on the other hand, may produce either tribromide or pentabromide as counteranions, depending on the employed Br_2 concentration. This may be one of the reasons for the variations in the distribution of bromination products with the mode of addition and the concentration of Br_2 occasionally reported[12-14] for conjugated olefins, when both syn and anti addition or 1,2 and 1,4 addition are possible. In fact, ion pair intermediates differing in the anionic moieties may well have different modes of collapse to products. Furthermore, a different charge localization in the anion could affect the charge distribution of the cation of the ion pairs, which may change from a bridged bromonium to an open bromocarbonium ion, thus affecting the syn/anti or the 1,2/1,4 addition ratio. Work is in progress in order to check these hypotheses.

Experimental Section

1,2-Dichloroethane and bromine (both C. Erba RPE >99.5%) were treated as previously reported.[10] Commercial tetrabutylammonium bromide (EGA ca. 99%) was purified by crystallization from ethyl acetate/toluene and stored under dry argon.

Stock 1,2-dichloroethane solutions of Br_2 and TBAB were prepared by weighing appropriate amounts of solute and solvent and stored in the dark no longer than 2 h. The concentrations of the Br_2 solutions were also determined spectrophotometrically.[10] These solutions were then checked during storage by registering the UV absorption in the 280–350-nm range, around the UV minimum of Br_2, and discarded when higher than expected absorptions were found, indicating the spurious presence of trihalide ions.[9c]

Working-strength solutions were prepared by mixing solvent and stock solution aliquots withdrawn from precision microburets. The total amount was checked by weighing. The composition of these solutions is reported in Table II, which also includes the computed ratios of pentabromide to tribromide concentrations (a complete list of the available data may be obtained as Supplementary Material). These solutions were measured in 0.1–2-cm cells, as required, in a Pye-Unicam SP8-400 UV–vis spectrophotometer in the 250–600-nm range, although only data in the 250–420-nm range were used for the computations, since at higher wavelengths no significant contribution for pentabromide could be found. Spectra were taken at 15, 25, and 48 °C (±0.05 °C). The stability of the solutions was checked occasionally by remeasuring the spectra after 1–2 h. Attention was paid throughout to avoid contamination of the solutions from atmospheric humidity.

Computations were carried out either by a BASIC program for a Commodore home computer or by a FORTRAN program for a powerful minicomputer (Gould 32/87); however, some combinations of initial concentrations and formation constants yielded serious numerical precision problems, which were only avoided by using 14-figure precision, not available in Commodore BASIC. A further reason for preferring the Gould minicomputer was the time required by the fitting (a day or two on the home computer). Convergence was attained normally in 4–5 iterations, although occasionally up to 10 were required.

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Supplementary Material Available: A table containing all the measured data (temperature, optical path, concentration, and absorbance) used in the determination of the thermodynamic and spectral parameters relative to equilibrium 1, a listing of the FORTRAN 77 (Gould version) fitting program, a listing of the data in the format required by the fitting program, and a listing of the resulting output (102 pages). Ordering information is given on any current masthead page. Further details on the computational procedures are available directly from the authors (inquiries to R.A.) to any non-profit organization.

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(12) Wilson, M. A.; Woodgate, P. D. *J. Chem. Soc., Perkin Trans. 2* **1976**, 141–147.

(13) Heublein, G. *J. Prakt. Chem.* **1966**, *31*, 84–91.

(14) Heasley, G. E.; McCall Bundy, J.; Heasley, V. L.; Arnold, S.; Gipe, A.; McKee, D.; Orr, R.; Rodgers, S. L.; Shellhamer, D. F. *J. Org. Chem.* **1978**, *43*, 2793–2799.