

The Solution Behavior of the Adamantylideneadamantane-Bromine System: Existence of Equilibrium Mixtures of Bromonium-Polybromide Salts and a Strong 1:1 Molecular Charge-Transfer Complex

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Abstract: An investigation of the adamantylideneadamantane-Br₂ system using stopped-flow spectrokinetic and conventional UV-vis spectrophotometric techniques has shown that in 1,2-dichloroethane solution an equilibrium is instantaneously established with 2:1, 1:1, 1:2, and 1:3 olefin-Br₂ aggregates having extensively overlapping electronic spectra. The stoichiometry and the maximum molar extinction coefficient of the 1:1 complex have been preliminarily established with the Scott method from spectral data obtained at sufficiently high [olefin]:[Br₂] ratios. The stoichiometries, the formation constants, and the electronic spectra of all four species at equilibrium have been determined by a new, expressly devised computational method based on nonlinear least-squares procedures. The following values of the formation constants from adamantylideneadamantane and Br₂ have been obtained in 1,2-dichloroethane at 25 °C: $K_{21} = 1.11 \times 10^3$ (18) M⁻²; $K_{11} = 2.89 \times 10^2$ (4.0) M⁻¹; $K_{12} = 3.23 \times 10^5$ (4.5 × 10³) M⁻²; $K_{13} = 7.23 \times 10^6$ (2.6 × 10⁵) M⁻³. Conductivity measurements on 1,2-dichloroethane solutions containing the four olefin-Br₂ species in variable amounts have confirmed that the 1:1 species is a molecular charge-transfer complex, while the other three are ionic in nature. The 1:2 and the 1:3 species have been respectively identified as the bromonium tribromide and the bromonium pentabromide salts. A comparison of the present results with previous ones has shown the existence of very marked structural effects on the formation constants of the olefin-Br₂ charge-transfer complexes which are involved in olefin bromination. The implications of this finding in the interpretation of the reactivity of olefins in bromination is discussed.

Although charge-transfer complexes (CTCs) between olefins and bromine have been known for a long time¹⁻⁸ and have been supposed to be involved in the mechanism of the olefin bromination,⁹ quantitative data of the structural effects on their formation constants are still lacking. Information of this type has become crucial for a more complete understanding of structure-reactivity relationships in the ionic addition of bromine to olefins, after the conclusive demonstration that bromine-olefin CTCs are essential intermediates of this reaction.¹⁰ The main difficulty for these studies stems from the high reactivity of the olefin-bromine CTCs, which even in solvents of moderate polarity evolve into ion pairs (bromonium-bromide^{11,12} or -polybromide,^{10,13-15} depending on the solvent and halogen concentration) and finally into dibromo adducts too fast to be investigated with conventional spectrophotometric and, for the most reactive olefins, even with stopped-flow spectrokinetic techniques.¹⁶

A promising approach to prolong the lifetime of these complexes seemed to us to study sterically crowded olefins, where steric hindrance retards the final addition step by hampering rear-side nucleophilic attack of the counteranion at the bromonium carbons of the intermediate ion pairs so that the reversibility of bromonium ion formation^{17,18} may allow the establishment of CTC-ion pair equilibria. In this paper we are reporting the results of a study of the adamantylideneadamantane-Br₂ system, which previous investigations^{19,20} had shown to form a stable, isolable bromonium-tribromide salt unable to further evolve to a vicinal dibromide. In the following, we demonstrate that adamantylideneadamantane and Br₂ form in solution a stable 1:1 CTC that is in rapid equilibrium with a number of other species. Moreover, the large value of its formation constant as compared with that of a disubstituted olefin such as cyclohexene demonstrates that the K_f values for olefin-Br₂ CTCs are dependent on the olefin

structure, a finding that has important consequences for the mechanism of electrophilic bromination of olefins.

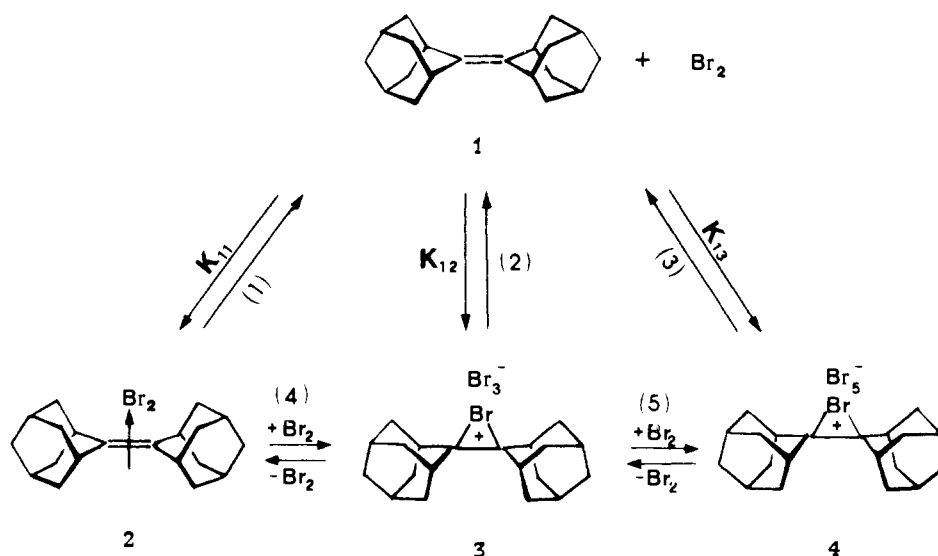
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Scheme I



Results

(a) **Spectral Data.** No kinetics could be observed, but an equilibrium between the reactants and new UV-absorbing species (monitored at 272 nm (Br_3^-)¹⁵) was instantaneously^{20b} attained when 3×10^{-5} M adamantylideneadamantane (1) and 3×10^{-4} M Br_2 solutions in 1,2-dichloroethane were mixed 1:1 in a stopped-flow apparatus at 25 °C. Since the equilibrium mixtures obtained from 1 and Br_2 in any ratio were perfectly stable for at least $1/2$ h, they could be investigated by a combination of conventional spectrophotometric and conductimetric techniques.

Spectral data were collected in the 250–600 nm wavelength range at 3.9×10^{-4} – 1×10^{-2} M Br_2 and 1×10^{-3} – 6.1×10^{-2} M 1 (see Table II). Higher concentrations could not be attained owing to the limited solubility of 1 and to the precipitation of the bromonium-tribromide salt. All spectra exhibited a maximum around 272 nm, near the λ_{max} for the Br_3^- ion,¹⁵ as expected for the reported formation of the bromonium-tribromide salt 3.^{20a} Solutions obtained either by dissolving 1 and Br_2 in a 1:2 molar ratio or by redissolving the precipitated salt 3 had identical spectra. However, the observed dependence of the 272-nm absorption on the reagent concentrations when these solutions were progressively diluted was absolutely inconsistent with the sole presence of equilibrium 2 of Scheme I, and it clearly pointed to the formation of other species absorbing in the same spectral range. The most reliable candidate was a 1:1 CTC (2) formed through equilibrium

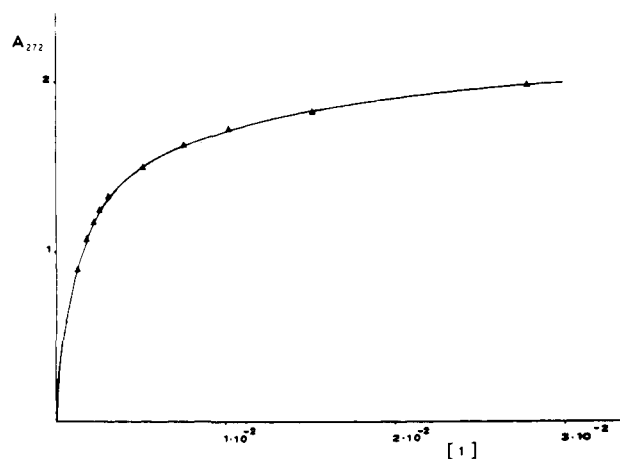


Figure 1. Absorbance at 272 nm (0.1-cm optical path) of 1,2-dichloroethane solutions of Br_2 and adamantylideneadamantane at 25 °C (runs 15–17 and 34–40 of Table II) against the olefin concentration.

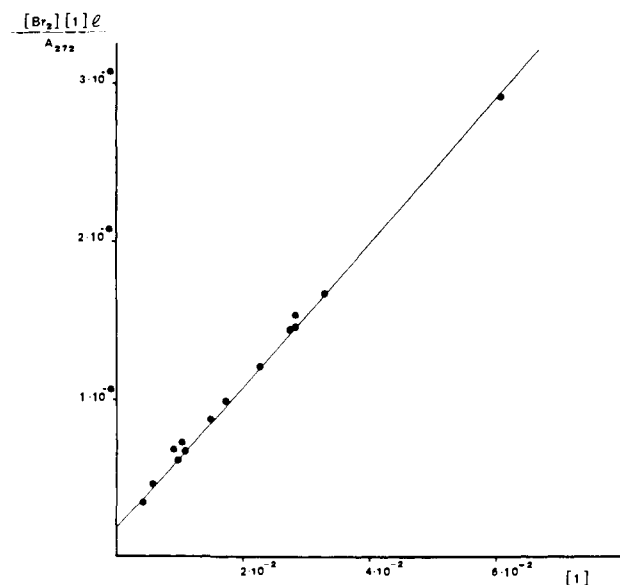


Figure 2. Scott plot (eq 6) of the absorbances at 272 nm (25 °C, 0.1-cm optical path) and the reagent concentrations for 1,2-dichloroethane solutions of adamantylideneadamantane and Br_2 in ratios ranging between 10 and 60 (runs 9–22 of Table II).

(16) The obtaining of colored solutions and, in a few cases, of colored, saltlike solids has been reported for aryl substituted ethylenes-bromine systems and has been attributed to the formation of stable bromocarbenium ions associated with tribromide anions. (Wizinger, R.; Fontaine, J. *Ber. Dtsch. Chem. Ges.* **1927**, *60*, 1377–1389. Pfeiffer, P.; Wizinger, R. *Justus Liebigs Ann. Chem.* **1928**, *461*, 132–154. Pfeiffer, P.; Schneider, P. *J. Prakt. Chem.* **1931**, *129*, 129–144.) The spectrophotometric observation of several colored complexes has been reported for solutions of tetrakis(*p*-methoxyphenyl)-ethylene and Br_2 , and a formation constant of $(6.8 \pm 0.5) \times 10^2 \text{ M}^{-1}$ has been calculated for a blue 1:1 complex, whose nature, however, was not conclusively established. It can also be pointed out that these compounds were not simple olefins but contained several possible sites of Br_2 complexation, i.e. the aromatic rings and dimethylamino or methoxy substituents, beside the olefin double bond.

(17) Brown, R. S.; Gedye, R.; Slebocka-Tilk, H.; Buschek, J. M.; Kopecky, K. R. *J. Am. Chem. Soc.* **1984**, *106*, 4515–4521.

(18) (a) Bellucci, G.; Chiappe, C.; Marioni, F. *J. Am. Chem. Soc.* **1987**, *109*, 515–522. (b) Bellucci, G.; Bianchini, R.; Chiappe, C.; Marioni, F.; Spagna, R. *J. Am. Chem. Soc.* **1988**, *110*, 546–552.

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(20) (a) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508. (b) In the earlier study^{20b} it was reported that separate solutions comprised of adamantylideneadamantane + 2Br_2 or bromonium-tribromide salt 3 in 1,2-dichloroethane attained some equilibrium position after prolonged time, in contrast to the instantaneous equilibrium attained here. We attribute the previous observation^{20a} to adventitious solution impurities (e.g. water) that in prolonged contact with the reaction components influenced the absorbances.

1. In order to favor the formation of this species at the expense of the bromonium-tribromide salt 3, the olefin concentration was

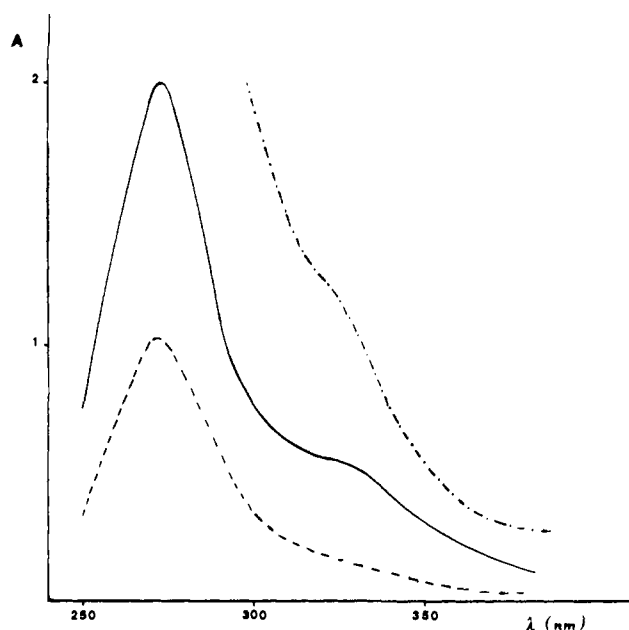


Figure 3. UV spectra at 25 °C (0.1-cm optical path) of 1,2-dichloroethane solutions containing adamantylideneadamantane and Br_2 at the following analytical concentrations: 2.06×10^{-3} M **1**, 9.83×10^{-4} M Br_2 (---); 6.07×10^{-2} M **1**, 9.70×10^{-4} M Br_2 (—); and 9.93×10^{-4} M **1**, 9.19×10^{-3} M Br_2 (-·-).

increased at constant $[\text{Br}_2]$. Spectra with a maximum around 272 nm were also obtained under these conditions.

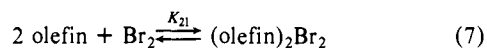
The curve reported in Figure 1 was obtained when the 272-nm absorbance of these solutions was plotted against the adamantylideneadamantane concentration. This curve showed that, around 10^{-3} M analytical concentration of Br_2 , complete complexation of the halogen was approached above 3×10^{-2} M adamantylideneadamantane. Assuming, as a first approximation, that only a 1:1 complex was present under the latter conditions, a molar extinction coefficient of $\epsilon_{272} \approx 2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ was evaluated for this complex.

A very satisfactory fit was obtained (Figure 2) when the 272-nm absorbances, A , of solutions with $10 \leq [\text{I}]:[\text{Br}_2] \leq 60$ were introduced into the Scott equation for 1:1 complexes, eq 6,^{10,21} where

$$[\text{Br}_2][\text{OI}]/A = 1/(K\epsilon) + (1/\epsilon)[\text{OI}] \quad (6)$$

$[\text{Br}_2]$ and $[\text{OI}]$ are analytical concentrations, $[\text{OI}] \gg [\text{Br}_2]$, l is the optical path, and K and ϵ are respectively the formation constant and the molar extinction coefficient of the 1:1 complex.²²

This result provided a clear confirmation of the formation of a surprisingly stable 1:1 complex between adamantylideneadamantane and Br_2 (Scheme I, eq 1). However, the parameters obtained for this complex from the slope and intercept of the linear plot shown in Figure 2, $K_{11} = 2.4 \times 10^2 \text{ M}^{-1}$ and $\epsilon_{272} = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, were considered only preliminary estimates, since they had been obtained under the arbitrary assumption of a complete absence of salt **3**, which, as will be shown below, gives a non negligible contribution even at $[\text{I}]:[\text{Br}_2] > 10$. Furthermore, a careful examination of the entire UV spectrum revealed that an increasing excess of olefin produced a shoulder around 320 nm (Figure 3), pointing to the formation of small but detectable amounts of species containing more than one olefin molecule, the simplest of which was obviously a 2:1 complex (eq 7).



Moreover, a similar shoulder around 320 nm appeared in the spectrum of solutions containing a large excess of Br_2 (Figure 3). The latter finding could be accounted for on the basis of the

formation of a bromonium-pentabromide salt (**4**) through equilibrium 3 of Scheme I. The formation constant of $\text{Bu}_4\text{N}^+\text{Br}_5^-$ from $\text{Bu}_4\text{N}^+\text{Br}_3^-$ and Br_2 in 1,2-dichloroethane, $K = 14.3$ (0.7) M^{-1} at 25 °C, and its spectral parameters, $\lambda_{\text{max}} = 310 \text{ nm}$ and $\epsilon_{\text{max}} = 5.38 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$, had been determined previously.¹⁵

All these data clearly showed that several different species of different stoichiometry, having extensively overlapping electronic spectra, are involved at equilibrium in 1,2-dichloroethane solutions of adamantylideneadamantane and Br_2 (Scheme I). A conventional treatment of all the spectral measurements to obtain the pertinent equilibrium constants was therefore unfeasible, and a nonlinear least-squares (NLLSQ) computational procedure, of the type used in a similar but simpler case,¹⁵ was needed.

(b) Computational Procedures. Spectrophotometric measurements were fitted by NLLSQ techniques²³ to a model describing the formation of each possible A_mB_n complex (A stands for adamantylideneadamantane, B for bromine), the (m,n) pair having the values (2,2), (2,1), (1,1), (1,2), and (1,3).

Each "experimental datum" consisted of a set of five measures on the same solution, that is, concentrations of olefin and bromine, wavelength, optical path, and absorbance. About 900 such data were collected and all were included in an overall fitting.

Fitting parameters were the formation constants K_{mn} of the A_mB_n complexes from olefin and bromine and the molar extinction coefficients of such complexes at each measured wavelength.

The general lines of the fitting procedure were similar to the ones followed for the determination of the stability of $\text{Bu}_4\text{N}^+\text{Br}_5^-$.¹⁵ However, the evaluation of the equilibrium concentrations was more complex, due to the number of complexes involved, and required a new approach.

To do that, first we write down the equations obtained from conservation of mass from both olefin and bromine:

$$[\text{A}]_t = [\text{A}] + \sum_{m,n} (m[\text{A}_m\text{B}_n]) \quad (8)$$

$$[\text{B}]_t = [\text{B}] + \sum_{m,n} (n[\text{A}_m\text{B}_n]) \quad (9)$$

where the t subscript stands for the total analytical concentration. The concentrations of the complexes in eq 8 and 9 can be described as a function of $[\text{A}]$ and $[\text{B}]$:

$$[\text{A}_m\text{B}_n] = K_{mn} [\text{A}]^m [\text{B}]^n \quad (10)$$

Since both eq 8 and 9 thus become second degree in $[\text{A}]$ and third degree in $[\text{B}]$, the equation set $\{(8),(9)\}$ has a number of solutions. Although they were in fact obtained in explicit analytical form by means of a symbolic language (MUSIMP), the resulting expressions are far too complicated to be of any use. However, chemical intuition suggests that a unique equilibrium exists: in other words, a unique pair of real, positive $[\text{A}]$ and $[\text{B}]$ values satisfies the set. Furthermore, the unique solution is certainly bound by $0 < [\text{A}] < [\text{A}]_t$ and $0 < [\text{B}] < [\text{B}]_t$. Such bounds define an open rectangular region in the $([\text{A}], [\text{B}])$ plane. Both (8) and (9) can be solved, either numerically or analytically, with respect to $[\text{A}]$ by formally considering $[\text{B}]$ as an independent variable, thus obtaining a pair of functions, (11) and (12), which can be

$$[\text{A}] = f([\text{B}]) \quad (11)$$

$$[\text{A}] = g([\text{B}]) \quad (12)$$

plotted, given a set of K_{mn} values, within the defined rectangle. The uniqueness of the equilibrium condition insures the existence of a unique crossing point of the f and g curves. The coordinates of the crossing point are the equilibrium concentrations $[\text{A}]_e$ and $[\text{B}]_e$. From these and the K_{mn} values, all other concentrations can be obtained from equation 10. Figure 4 shows the functions f and g computed for a solution of adamantylideneadamantane (**A**) and Br_2 (**B**) (run 3 of Table II). The set of values for K_{21} , K_{11} , K_{12} , and K_{13} used for the calculations is given below in the text.

The numerical evaluation of the crossing point was carried out by a Newton-Raphson (iterative power-series expansion) procedure on the $\{(8),(9)\}$ set.²⁴ However, the procedure failed to

(21) Scott, R. L. *Recl. Trav. Chim. Pays-Bas* **1956**, *75*, 787-789.

(22) The contribution to the 272-nm absorbance by free Br_2 present at equilibrium can be safely neglected, the molar extinction coefficient of Br_2 at this wavelength being about 250 times lower relative to that of the 1:1 CTC.

(23) (a) Hamilton, W. C. *Statistics in Physical Sciences*; Ronald Press: New York, 1965. (b) Wentworth, W. E. *J. Chem. Educ.* **1965**, *42*, 96-103.

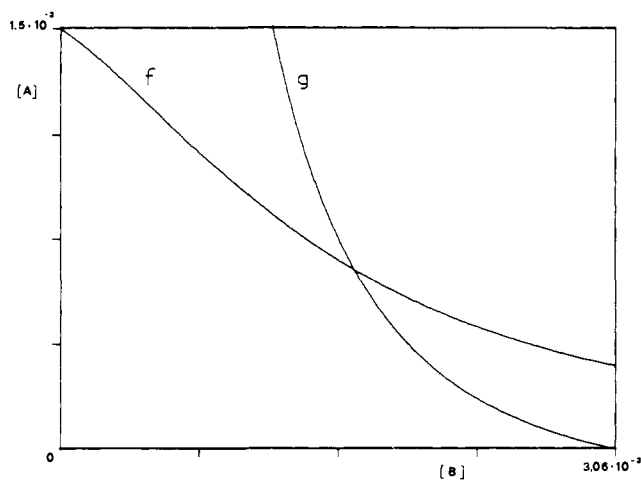


Figure 4. Plot of the f and g functions (eq 11 and 12) for a solution of adamantylideneadamantane (A) and Br_2 (B) (run 3 of Table II). The crossing point corresponds to equilibrium values of olefin and Br_2 .

converge unless a reasonable initial guess for the solution was supplied. Such a guess was obtained by repeated bisection of the $(0, [B]_i)$ interval, so as to isolate a reduced interval of $[B]$ values containing the crossing point. The corresponding interval of $[A]$ values stems from eq 11 and 12. In practice, 5 bisections, reducing the interval of $[B]$ values to 2–5 times that of the $(0, [B]_i)$ one, were always sufficient to insure convergence of the Newton–Raphson procedure, which in turn required 3–7 iterations to achieve final convergence.

The remaining steps of the fitting procedure were essentially the same as those already described.¹⁵ Most fittings were done with a FORTRAN version of the program running on a personal computer using MS-DOS.²⁵

When the data employed in the Scott plot of Figure 2 (runs 9–22 in Table II) were used in a NLLSQ fitting including equilibria 1, 2, and 7, with the preliminary values of K_{11} and ϵ for the CTC 2 and the spectrum of $\text{Bu}_4\text{N}^+\text{Br}_3^-$ for salt 3 as refinable starting parameters and arbitrary guesses for K_{21} and K_{12} , a very satisfactory fitting was obtained (root mean square deviation of 3×10^{-2} absorbance units), with the following values for the formation constants: $K_{21} = 7.70 \times 10^2$ (18) M^{-2} , $K_{11} = 2.65 \times 10^2$ (5.5) M^{-1} , and $K_{12} = 1.05 \times 10^5$ (1.2×10^4) M^{-2} .

On the other hand, attempts at fitting the entire set of spectral data obtained in 1,2-dichloroethane at 25 °C on the basis of equilibria 1 and 2 alone, using the above starting parameters, gave only moderately satisfactory results. The main deviations were found, as expected, for solutions containing large excesses of 1 or Br_2 , where the $(\text{olefin})_2\text{Br}_2$ species or the pentabromide salt 4 were also present, respectively. A very good fitting of the same whole set of data (root mean square deviation of 3×10^{-2} absorbance units) was obtained when equilibria 1, 2, 3, and 7 were included. The spectra of $(\text{olefin})_2\text{Br}_2$ and of salt 4 were respectively fixed at the values obtained in the above mentioned partial fitting and to that obtained for $\text{Bu}_4\text{N}^+\text{Br}_5^-$,¹⁵ and K_{21} , K_{11} , K_{12} , K_{13} , and the spectra of species 2 and 3 were allowed to vary freely. The following values were obtained: $K_{21} = 1.11 \times 10^3$ (18) M^{-2} , $K_{11} = 2.89 \times 10^2$ (4.0) M^{-1} , $K_{12} = 3.23 \times 10^5$ (4.5×10^3) M^{-2} , and $K_{13} = 7.23 \times 10^6$ (2.6×10^5) M^{-3} . The molar extinction coefficients at several wavelengths obtained in these fittings for all olefin- Br_2 aggregates found at equilibrium in 1,2-dichloroethane are reported in Table I.

It is noteworthy that the calculated spectrum of the bromonium-tribromide species 3 was very similar to that of $\text{Bu}_4\text{N}^+\text{Br}_3^-$,¹⁵ as expected for salts owing their absorption only to their common anion. This provided an indirect support for the reliability of the fitting. Also the excellent agreement of the K_{11} value with its

Table I. Extinction Parameters Employed for Fitting Spectrophotometric Data Taken in 1,2-Dichloroethane Solutions of Br_2 and Adamantylideneadamantane at 25 °C^a

wave-length, nm	molar extinction coefficients, $\text{M}^{-1} \text{cm}^{-1}$				
	Br_2^b	$(\text{olefin})_2\text{Br}_2^c$	2 ^d	3 ^d	4 ^b
250	256	21 107 (313)	5 527 (14)	12 026 (26)	69 340
260	130	29 853 (316)	11 759 (15)	31 365 (33)	32 590
270	78	36 788 (322)	17 748 (16)	45 722 (50)	18 320
272	66	35 794 (323)	18 224 (16)	45 780 (49)	20 000
280	45	30 235 (321)	16 199 (16)	40 257 (47)	23 100
290	25	22 152 (314)	10 141 (14)	26 941 (30)	36 650
300	13	19 449 (311)	5 820 (13)	16 024 (23)	49 540
310	8.9	17 160 (306)	4 086 (13)	10 227 (24)	53 850
320	6.5	19 612 (310)	3 431 (13)	7 641 (24)	51 640
330	7.7	18 975 (316)	2 938 (14)	5 926 (22)	42 400
340	14	15 846 (308)	2 460 (12)	4 309 (21)	31 150
350	31	11 323 (297)	1 928 (11)	2 986 (20)	20 100
360	60	7 490 (252)	1 438 (11)	1 949 (19)	13 350
370	99	5 361 (255)	1 044 (11)	1 382 (18)	9 010
380	145	3 887 (254)	789 (12)	1 129 (18)	6 480
390	182	2 704 (246)	638 (12)	909 (19)	5 280
400	205	1 981 (297)	497 (11)	788 (18)	3 400
410	211	1 419 (292)	324 (11)	707 (19)	2 400
420	204	1 025 (289)	281 (10)	484 (19)	1 400

^aStandard deviations are given in parentheses following the value of the corresponding parameters. Parameters not accompanied by a standard deviation were kept fixed in the fitting. ^bTaken from ref 15. ^cObtained in the NLLSQ fitting of data from runs 9–22 of Table II. ^dObtained in the NLLSQ fitting of data from runs 1–40 of Table II.

estimate deduced from the Scott plot was reassuring, if somewhat surprising, since the latter had been obtained from the spectra of solutions which, based on the above set of K values, contained also salt 3 and the $(\text{olefin})_2\text{Br}_2$ species at respective concentrations ranging between 12.3 and 3.3% and between 2 and 16.7% of the Br_2 analytical concentration.

A large variation in the K_{12} value was found in the two above fittings of comparable quality but including respectively only a limited subset of the entire set of data. This is not surprising, since at $[1]:[\text{Br}_2] \geq 10$ the concentrations of salt 3 were too low (and its concentration range too restricted) to provide enough information from the spectral data to define both K_{12} and the related spectrum of 3. A firm value of this constant and the pertinent spectrum could only be obtained, together with the values of all other formation constants, from fittings including all data obtained in the most extended range of concentrations of both reactants, when the concentrations of all various olefin- Br_2 aggregates increase continuously up to the highest experimentally attainable values (see Table II).

A typical experimental and calculated spectrum obtained at respective 1 and Br_2 analytical concentrations of 1.13×10^{-3} and 2.3×10^{-3} M in the 250–400-nm range is reported in Figure 5. The figure also shows the dissection of the spectrum into those of the main absorbing species present at equilibrium.

(c) **Conductimetric Data.** Conductivity measurements were carried out at 25 °C in about the same concentration range used for the spectrophotometric measurements (Table II). Solutions containing an excess of 1 exhibited a low conductivity that, at constant $[\text{Br}_2]$, increased slightly with increasing concentration of 1. On the other hand, at constant olefin concentration the conductivity rose markedly with increasing concentration of Br_2 .

The equilibrium concentrations of species 2, 3, and 4 and that of $(\text{olefin})_2\text{Br}_2$ were calculated for each examined solution with the set of K values obtained in the overall fitting of the spectrophotometric data and are reported in Table II. The conductimetric measurements obtained in the whole investigated concentration range of reactants did not correlate with either the concentrations of 2 or with the sum of those of 2, 3, and 4 (Figure 6). However, subsets of data, obtained at constant analytical concentration of one of the reactants and increasing concentration of the other or at increasing concentrations of both reagents at constant ratio, exhibited regularly rising conductivity trends. A steadily increasing curve was obtained (Figure 7) when the conductivity data were plotted against the concentrations of 3 or the sum of the concentrations of 3 and 4 when the latter was present in appreciable

(24) See for instance: Berezin, I. S.; Zhidkov, N. P. *Computing Methods*; Pergamon: Oxford, 1965; Vol. II; p 136.

(25) A copy of the MS-DOS diskette containing the program and the data is available to any nonprofit organization.

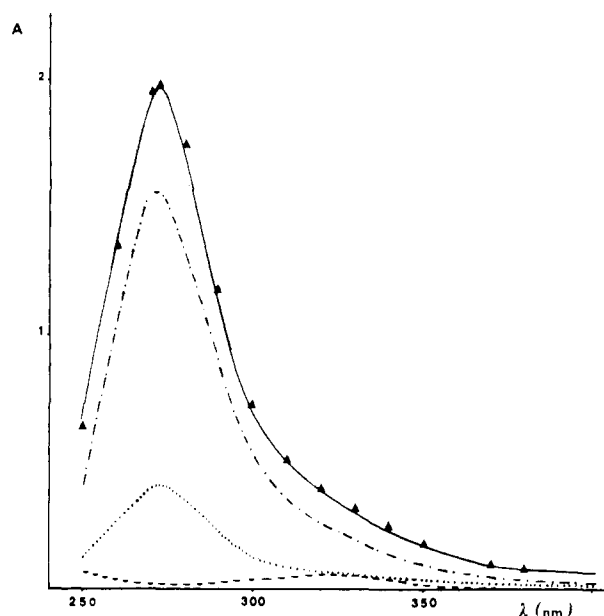


Figure 5. Experimental (—) and calculated (▲) UV spectrum at 25 °C (0.1-cm optical path) of a 1,2-dichloroethane solution of adamantylideneadamantane and Br_2 at respective 1.13×10^{-3} M and 2.30×10^{-3} M analytical concentrations. The calculated spectrum is the sum of the computed single spectra of all species present at equilibrium in run 2 of Table II. The contributing spectra of species 2 (···), 3 (-·-), and 4 (- -) are also shown. The absorbances of Br_2 and $(\text{Olefin})_2\text{Br}_2$ do not give significant contributions to the spectrum.

amounts, with the exception of the data obtained at $[\mathbf{1}]:[\text{Br}_2] > 2$, which exhibited marked deviations. A regular conductivity-concentration dependence similar to that shown in Figure 7 was also found for $\text{Bu}_4\text{N}^+\text{Br}^-$ and $\text{Bu}_4\text{N}^+\text{Br}_3^-$ salts in 1,2-dichloroethane, the curvature being probably due to ion-pairing phenomena. These results excluded an ionic structure for the 1:1 species, which is therefore to be identified as the molecular complex **2**, but are consistent with salt structures for species **3** and **4**. The molar conductance calculated for **3** from the curve of Figure 7 in the 1×10^{-4} – 5×10^{-4} M concentration range, $\Lambda^m = 25 \text{ S cm}^2 \text{ mol}^{-1}$, compared very well with that measured for $\text{Bu}_4\text{N}^+\text{Br}_3^-$ in the same concentration range, $\Lambda^m = 26 \text{ S cm}^2 \text{ mol}^{-1}$.

An examination of Figure 7 and Table II shows that solutions containing an excess of **1** exhibited extra conductivities which increased with increasing olefin excess. When plotted against the

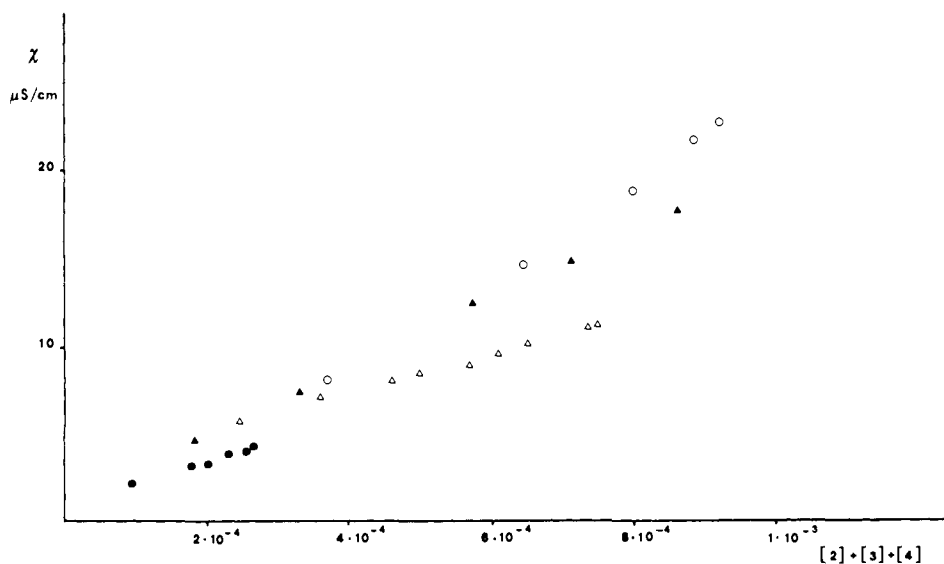
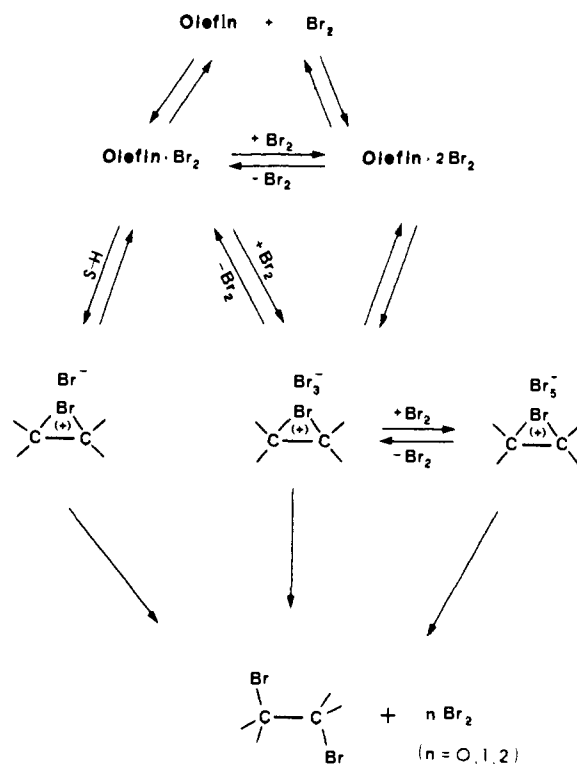
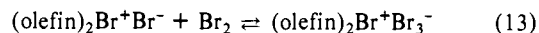


Figure 6. Conductivity at 25 °C of 1,2-dichloroethane solutions of adamantylideneadamantane and Br_2 against the sum of the equilibrium concentrations of species **2**, **3**, and **4**. The data are taken from runs 19–23 and 41 (●), runs 5–11 and 42–43 (Δ), runs 1–4 and 44 (▲), and runs 24–28 (○) of Table II.

Scheme II



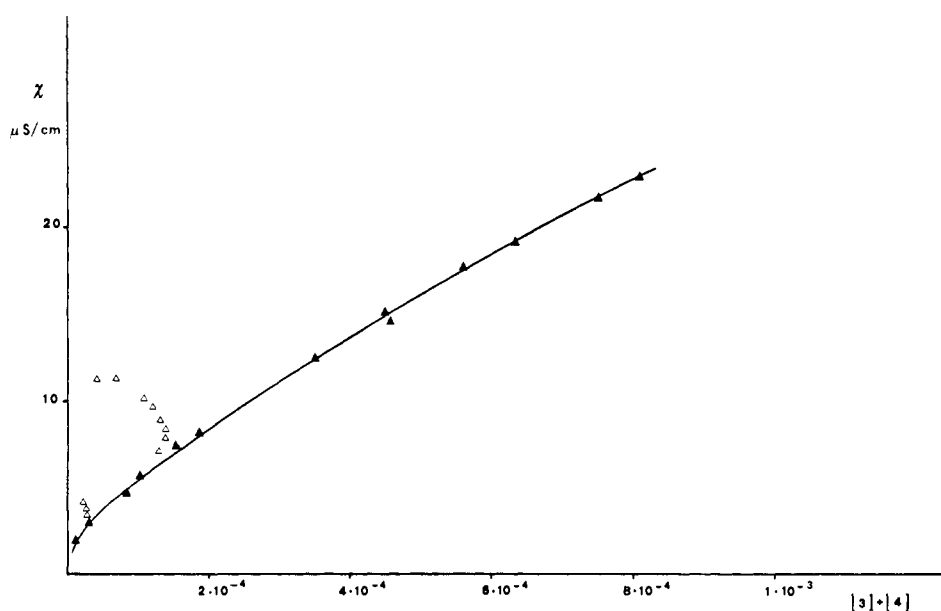
calculated concentrations of the 2:1 olefin- Br_2 complex, these extra conductivities defined a regularly increasing curve similar to that of Figure 7, pointing to an ionic nature also for this species. A possible structure could be of type $(\text{olefin})_2\text{Br}^+\text{Br}^-$. Since Br^- is known to be highly associated with Br_2 in 1,2-dichloroethane,^{13a} this hypothesis raised the possibility of an additional equilibrium, eq 13, leading to a 2:2 olefin- Br_2 aggregate, which was again



expected to exhibit the absorption of the Br_3^- ion around 270 nm. However, attempts at including equilibrium 13 into the fitting of the spectrophotometric data were frustrated by the fact that the data did not contain sufficient information, because of the overlap of the spectra of the involved species and because of the too low equilibrium concentrations attainable for species containing two olefin molecules even in olefin saturated solutions. No ad-

Table II. Analytical Concentrations of Br₂ and Adamantylideneadamantane and Equilibrium Concentrations of (Olefin)₂Br₂, 2, 3 and 4 in 1,2-Dichloroethane Solutions Used for Spectrophotometric and Conductimetric Measurements^a

run	[1] _i	[Br ₂] _i	[(olefin) ₂ Br ₂] _e	[2] _e	[3] _e	[4] _e
1*	7.56 × 10 ⁻⁴	1.50 × 10 ⁻³	2.41 × 10 ⁻⁷	1.36 × 10 ⁻⁴	1.58 × 10 ⁻⁴	3.67 × 10 ⁻⁶
2*	1.13 × 10 ⁻³	2.30 × 10 ⁻³	4.77 × 10 ⁻⁷	2.21 × 10 ⁻⁴	3.38 × 10 ⁻⁴	1.04 × 10 ⁻⁵
3*	1.50 × 10 ⁻³	3.06 × 10 ⁻³	7.37 × 10 ⁻⁷	2.99 × 10 ⁻⁴	5.41 × 10 ⁻⁴	1.96 × 10 ⁻⁵
4*	1.32 × 10 ⁻³	2.68 × 10 ⁻³	6.10 × 10 ⁻⁷	2.61 × 10 ⁻⁴	4.38 × 10 ⁻⁴	1.47 × 10 ⁻⁵
5*	2.07 × 10 ⁻³	9.83 × 10 ⁻⁴	1.55 × 10 ⁻⁶	2.37 × 10 ⁻⁴	1.28 × 10 ⁻⁴	1.39 × 10 ⁻⁶
6*	3.10 × 10 ⁻³	9.83 × 10 ⁻⁴	3.12 × 10 ⁻⁶	3.05 × 10 ⁻⁴	1.36 × 10 ⁻⁴	1.21 × 10 ⁻⁶
7*	4.13 × 10 ⁻³	9.83 × 10 ⁻⁴	5.01 × 10 ⁻⁶	3.58 × 10 ⁻⁴	1.37 × 10 ⁻⁴	1.05 × 10 ⁻⁶
8*	8.26 × 10 ⁻³	9.70 × 10 ⁻⁴	1.44 × 10 ⁻⁵	4.88 × 10 ⁻⁴	1.21 × 10 ⁻⁴	6.04 × 10 ⁻⁷
9*	1.10 × 10 ⁻²	9.70 × 10 ⁻⁴	2.16 × 10 ⁻⁵	5.43 × 10 ⁻⁴	1.11 × 10 ⁻⁴	4.52 × 10 ⁻⁷
10*	3.30 × 10 ⁻²	9.70 × 10 ⁻⁴	8.60 × 10 ⁻⁵	6.93 × 10 ⁻⁴	5.80 × 10 ⁻⁵	9.71 × 10 ⁻⁸
11*	6.07 × 10 ⁻²	9.70 × 10 ⁻⁴	1.62 × 10 ⁻⁴	7.03 × 10 ⁻⁴	3.20 × 10 ⁻⁵	2.93 × 10 ⁻⁸
12*	2.74 × 10 ⁻²	9.74 × 10 ⁻⁴	6.96 × 10 ⁻⁵	6.80 × 10 ⁻⁴	6.75 × 10 ⁻⁵	1.34 × 10 ⁻⁷
13*	2.24 × 10 ⁻²	9.74 × 10 ⁻⁴	5.47 × 10 ⁻⁵	6.57 × 10 ⁻⁴	7.77 × 10 ⁻⁵	1.84 × 10 ⁻⁷
14*	1.74 × 10 ⁻²	9.74 × 10 ⁻⁴	4.00 × 10 ⁻⁵	6.23 × 10 ⁻⁴	9.03 × 10 ⁻⁵	2.62 × 10 ⁻⁷
15*	2.78 × 10 ⁻²	1.03 × 10 ⁻³	7.45 × 10 ⁻⁵	7.19 × 10 ⁻⁴	7.45 × 10 ⁻⁵	1.55 × 10 ⁻⁷
16*	1.52 × 10 ⁻²	1.03 × 10 ⁻³	3.50 × 10 ⁻⁵	6.32 × 10 ⁻⁴	1.08 × 10 ⁻⁴	3.68 × 10 ⁻⁷
17*	1.01 × 10 ⁻²	1.03 × 10 ⁻³	2.01 × 10 ⁻⁵	5.55 × 10 ⁻⁴	1.27 × 10 ⁻⁴	5.82 × 10 ⁻⁷
18*	2.78 × 10 ⁻²	5.18 × 10 ⁻⁴	4.07 × 10 ⁻⁵	3.86 × 10 ⁻⁴	2.12 × 10 ⁻⁵	2.31 × 10 ⁻⁸
19*	4.13 × 10 ⁻³	3.86 × 10 ⁻⁴	2.61 × 10 ⁻⁶	1.72 × 10 ⁻⁴	2.93 × 10 ⁻⁵	9.98 × 10 ⁻⁸
20*	6.07 × 10 ⁻³	3.86 × 10 ⁻⁴	4.60 × 10 ⁻⁶	2.04 × 10 ⁻⁴	2.77 × 10 ⁻⁵	7.53 × 10 ⁻⁸
21*	8.82 × 10 ⁻³	3.86 × 10 ⁻⁴	7.70 × 10 ⁻⁶	2.33 × 10 ⁻⁴	2.48 × 10 ⁻⁵	5.26 × 10 ⁻⁸
22*	1.10 × 10 ⁻²	3.86 × 10 ⁻⁴	1.03 × 10 ⁻⁵	2.50 × 10 ⁻⁴	2.25 × 10 ⁻⁵	4.07 × 10 ⁻⁸
23*	3.10 × 10 ⁻³	3.86 × 10 ⁻⁴	1.67 × 10 ⁻⁶	1.49 × 10 ⁻⁴	2.93 × 10 ⁻⁵	1.16 × 10 ⁻⁷
24*	9.93 × 10 ⁻⁴	1.53 × 10 ⁻³	4.21 × 10 ⁻⁷	1.74 × 10 ⁻⁴	1.90 × 10 ⁻⁴	4.06 × 10 ⁻⁶
25*	9.93 × 10 ⁻⁴	3.06 × 10 ⁻³	2.64 × 10 ⁻⁷	1.96 × 10 ⁻⁴	4.30 × 10 ⁻⁴	1.87 × 10 ⁻⁵
26*	9.93 × 10 ⁻⁴	6.13 × 10 ⁻³	5.70 × 10 ⁻⁸	1.37 × 10 ⁻⁴	6.80 × 10 ⁻⁴	6.75 × 10 ⁻⁵
27*	9.93 × 10 ⁻⁴	4.60 × 10 ⁻³	1.23 × 10 ⁻⁷	1.70 × 10 ⁻⁴	5.92 × 10 ⁻⁴	4.14 × 10 ⁻⁵
28*	9.93 × 10 ⁻⁴	7.66 × 10 ⁻³	2.82 × 10 ⁻⁸	1.10 × 10 ⁻⁴	7.22 × 10 ⁻⁴	9.41 × 10 ⁻⁵
29*	9.93 × 10 ⁻⁴	9.19 × 10 ⁻³	1.52 × 10 ⁻⁸	9.09 × 10 ⁻⁵	7.38 × 10 ⁻⁴	1.20 × 10 ⁻⁴
30*	7.47 × 10 ⁻³	9.74 × 10 ⁻⁴	1.24 × 10 ⁻⁵	4.71 × 10 ⁻⁴	1.25 × 10 ⁻⁴	6.68 × 10 ⁻⁷
31*	7.03 × 10 ⁻³	9.74 × 10 ⁻⁴	1.13 × 10 ⁻⁵	4.59 × 10 ⁻⁴	1.27 × 10 ⁻⁴	7.04 × 10 ⁻⁷
32*	5.75 × 10 ⁻³	9.74 × 10 ⁻⁴	8.36 × 10 ⁻⁶	4.19 × 10 ⁻⁴	1.31 × 10 ⁻⁴	8.26 × 10 ⁻⁷
33*	3.19 × 10 ⁻³	9.74 × 10 ⁻⁴	3.27 × 10 ⁻⁶	3.08 × 10 ⁻⁴	1.34 × 10 ⁻⁴	1.17 × 10 ⁻⁶
34*	2.97 × 10 ⁻³	1.03 × 10 ⁻³	2.99 × 10 ⁻⁶	3.08 × 10 ⁻⁴	1.47 × 10 ⁻⁴	1.40 × 10 ⁻⁶
35*	2.38 × 10 ⁻³	1.03 × 10 ⁻³	2.04 × 10 ⁻⁶	2.69 × 10 ⁻⁴	1.43 × 10 ⁻⁴	1.51 × 10 ⁻⁶
36*	1.78 × 10 ⁻³	1.03 × 10 ⁻³	1.22 × 10 ⁻⁶	2.22 × 10 ⁻⁴	1.34 × 10 ⁻⁴	1.62 × 10 ⁻⁶
37*	1.19 × 10 ⁻³	1.03 × 10 ⁻³	5.76 × 10 ⁻⁷	1.65 × 10 ⁻⁴	1.16 × 10 ⁻⁴	1.65 × 10 ⁻⁶
38*	7.58 × 10 ⁻³	1.03 × 10 ⁻³	1.33 × 10 ⁻⁵	4.96 × 10 ⁻⁴	1.38 × 10 ⁻⁴	7.66 × 10 ⁻⁷
39*	5.05 × 10 ⁻³	1.03 × 10 ⁻³	7.14 × 10 ⁻⁶	4.12 × 10 ⁻⁴	1.47 × 10 ⁻⁴	1.05 × 10 ⁻⁶
40*	2.53 × 10 ⁻³	1.03 × 10 ⁻³	2.26 × 10 ⁻⁶	2.79 × 10 ⁻⁴	1.44 × 10 ⁻⁴	1.49 × 10 ⁻⁶
41*	1.03 × 10 ⁻³	3.86 × 10 ⁻⁴	2.63 × 10 ⁻⁷	7.27 × 10 ⁻⁵	2.18 × 10 ⁻⁵	1.30 × 10 ⁻⁷
42*	1.03 × 10 ⁻³	9.83 × 10 ⁻⁴	4.35 × 10 ⁻⁷	1.43 × 10 ⁻⁴	1.01 × 10 ⁻⁴	1.43 × 10 ⁻⁶
43*	6.20 × 10 ⁻³	9.83 × 10 ⁻⁴	9.47 × 10 ⁻⁶	4.37 × 10 ⁻⁴	1.32 × 10 ⁻⁴	7.90 × 10 ⁻⁷
44*	5.67 × 10 ⁻⁴	1.08 × 10 ⁻³	1.38 × 10 ⁻⁷	9.18 × 10 ⁻⁵	8.37 × 10 ⁻⁵	1.53 × 10 ⁻⁶

^aThe marks denote runs for which spectrophotometric (*) or conductimetric (°) measurements have been carried out.**Figure 7.** Plot of the conductivities at 25 °C of 1,2-dichloroethane solutions of adamantylideneadamantane and Br₂ against the sum of the equilibrium concentrations of 3 and 4. The data are taken from runs 1-4, 23-28, 41, 42, and 44 (▲) and from runs 5-11, 19-21, and 43 (△) of Table II.

ditional information could thus be gained concerning the mode of bonding of the two components in these weak complexes.

Discussion

A picture summarizing the various mechanistic pathways which have been proposed for the ionic bromination of olefins is given in Scheme II.²⁶ It includes a sequence of multiple equilibria involving 1:1 and 1:2 olefin-Br₂ molecular complexes and bromonium-bromide, -tribromide, and -pentabromide salts arising from a solvent-assisted, Br₂-assisted or unassisted ionization of the molecular complexes and from the tribromide-pentabromide equilibrium. Unfortunately, the experimental investigation of these complicated equilibrium stages is usually impossible with typical olefins, because they precede very fast product-forming steps. The presently reported one is the first case in which the suppression of the final step has allowed us to carry out a quantitative study of this type.

A bromonium-bromide salt was not expected to be formed in solutions of adamantylideneadamantane and Br₂ in 1,2-dichloroethane. Such species should be present in protic solvents, while in aprotic ones the corresponding tribromide (**3**) and pentabromide (**4**) salts were expected, because of the high association of Br₂ and Br⁻.^{13,15} The results obtained have confirmed this anticipation and have furthermore shown the existence of a surprisingly stable 1:1 CTC, **2**. Unfortunately, the formation of both CTC **2** and salt **3** was too fast to be followed even with a stopped-flow apparatus. It was therefore impossible to check experimentally if **3** is formed directly from **1** and Br₂ (eq 2 of Scheme I) or by a Br₂-assisted ionization of the first formed CTC **2** (eq 4). For this reason the formation constant of salt **3** was defined in the computational procedure by eq 10, with $m = 1$ and $n = 2$. However, on the basis of the proven involvement of CTCs on the reaction coordinate for the ionic bromination of cyclohexene in 1,2-dichloroethane,¹⁰ it seems very probable that **3** arises through **2**. The pertinent formation constant is $K'_{12} = [3]/([2][Br_2]) = K_{12}/K_{11} = 1.12 \times 10^3 \text{ M}^{-1}$.

No evidence could be found in the present work for the formation of nonionic 1:2 olefin-Br₂ complexes of the type shown in Scheme II. These had been observed at low temperature by spectroscopic^{5,7} and thermographic analysis⁴ and had also been postulated at room temperature on the basis of spectroscopic^{6b} and kinetic studies.¹⁰ A very weak ionic 2:1 olefin-Br₂ aggregate was observed instead when a large excess of **1** was present. Neither its structure nor its mode of formation (directly from **1** and Br₂ as in eq 7 or from the first formed 1:1 CTC and **1**) are clear. Its formation constant was defined by eq 10, with $m = 2$ and $n = 1$, but it can also be defined as $K'_{21} = [(olefin)_2Br_2]/([(olefin)-Br_2][olefin]) = K_{21}/K_{11} = 3.86 \text{ M}^{-1}$. This value is so low that, at 10⁻³ analytical concentration of Br₂, only 2 × 10⁻⁵ M (olefin)₂Br₂ is found at equilibrium, along with 5.5 × 10⁻⁴ M **2**, 1.3 × 10⁻⁴ M **3**, and 5.8 × 10⁻⁷ M **4**, even when a 10-fold excess of **1** was present. Since kinetic orders in olefin higher than unity have never been observed in bromination, 2:1 species of this type should not lie on the reaction coordinate and have not been included in Scheme II.

The bromonium-pentabromide salt **4** was found at equilibrium in appreciable amounts at sufficiently high Br₂ analytical concentrations. Although its formation constant was again defined in the computational procedure by eq 10, with $m = 1$ and $n = 3$, there is no doubt that **4** is formed from **3** and Br₂ (eq 5 of Scheme I). The pertinent formation constant is $K'_{13} = [4]/([3][Br_2]) = K_{13}/K_{12} = 22.4 \text{ M}^{-1}$, a value that, as expected, is not too different from that found¹⁵ for the formation of Bu₄N⁺Br₅⁻ from Bu₄N⁺Br₃⁻ and Br₂, 14.3 M⁻¹. This, besides providing a further support to the reliability of the adopted equilibrium model, confirmed the hypothesis of the involvement of bromonium-pentabromide ion pairs in olefin bromination at high Br₂ concentration.¹⁵

The most striking finding of the present study is the very large value of the formation constant of the 1:1 adamantylideneadamantane-Br₂ CTC, $K_{11} = 2.89 \times 10^2$ (4.0) M⁻¹. This value

is higher by (6 × 10²)-fold than that previously obtained under the same conditions for a disubstituted olefin, namely the 1:1 cyclohexene-Br₂ CTC.¹⁰ We admit that adamantylideneadamantane is a unique olefin, in that it is unable to give the usual bromination product. However it should not differ too much from normal tetrasubstituted olefins in the formation of a 1:1 CTC with Br₂. The main peculiarities are perhaps a longer donor-acceptor distance due to steric crowding around the double bond^{27a} and the lack of loss in rotational entropy, due to the rigid structure of adamantylideneadamantane, resulting in a less negative CTC formation entropy. The opposite effects of these two factors on the formation constant of **2** should tend to balance.

Thus, these results provide stringent evidence for the existence of very marked structural effects on olefin-Br₂ CTC formation, in contrast with previous assumptions to the contrary.^{27b} This has important implications in the interpretation of the reactivity of olefins in bromination. According to Scheme II, the experimentally obtained rate constants for bromination, k_{exp} , are a product of the rate constant for the slow step, k , and one or two equilibrium constants for CTC formation according to whether only 1:1 or both 1:1 and 1:2 CTCs are involved prior to bromonium ion formation. Although we have no information about 1:2 CTCs, we can infer from the above discussed comparison of K_{11} for different olefins that at least a large part of the increase in bromination rate resulting from increasing substitution on the double bond²⁸ must be due to an increase in the olefin-Br₂ CTC formation constant. A similar conclusion had been drawn in a study of the addition of ICl to alkenes,²⁹ showing that the effect of the alkene structure on the formation constant of 1:1 molecular complexes contributes at least 24% of the overall change in rate due to changes in the alkene structure. This contribution may well be larger in bromination, owing to the smaller steric effect associated with olefin-Br₂ relative to olefin-ICl CTC formation.

An important consequence of the above analysis is that ρ values obtained in linear free energy relationships for olefin bromination are sums of ρ_k and ρ_K terms, and that the latter are far from being negligible. This should warn that composite ρ values obtained simply by k_{exp} measurements for these multistep reactions can lead to misleading mechanistic conclusions.

Experimental Section

Adamantylideneadamantane (**1**) was obtained according to the procedure of Geluk,³⁰ the product being crystallized from acetonitrile and finally sublimed to yield colorless crystals, mp 184–186 °C (lit.³⁰ 184–187 °C). Adamantylideneadamantane bromonium ion tribromide (**2**) was prepared from **1** and Br₂ in dichloromethane and recrystallized from acetonitrile, as reported.^{20a} 1,2-Dichloroethane and bromine (both C. Erba RPE >99.5%) were treated as previously reported.³¹ Tetrabutylammonium tribromide for conductimetric measurements was prepared in situ from Br₂ and pure tetrabutylammonium bromide, the latter being obtained by crystallization of the commercial product (EGA, >99%) from ethyl acetate-toluene.

Stock 1,2-dichloroethane solutions of Br₂ and of **1** were prepared by weighing the reagents in accurately calibrated volumetric flasks. The Br₂ solutions, the concentrations of which were also determined spectrophotometrically,³¹ were stored in the dark for no longer than 2 h. They were checked periodically by registering the UV spectrum in the 280–350-nm range, around the UV minimum of Br₂, and discarded when absorptions higher than expected were found.

Working-strength solutions were prepared by mixing solvent and aliquots of the reagent stock solutions withdrawn with precision microburettes. Attention was paid throughout to avoid contamination from

(27) (a) Dubois (Dubois, J.-E.; Garnier, F. *Tetrahedron Lett.* **1965**, 3961–3968; *Tetrahedron Lett.* **1966**, 3047–3052; *Spectrochim. Acta* **1967**, *23a*, 2229–2288) has discussed the effects of olefin structure on the properties of olefin-Br₂ CTCs, notably the absorption frequencies (ν_{CTC}) and the spectroscopic parameters Γ which represent the dissociation energy of the excited state (O1⁺-Br₂⁻) of the CT complex. (b) For a discussion in support of the assumption that structural effects on olefin-halogen complex stabilities are negligible, see footnote 19 in: Ruasse, M.-F.; Dubois, J.-E. *J. Am. Chem. Soc.* **1984**, *106*, 3230–3234.

(28) See ref 9a and b.

(29) Schmid, G. H.; Gordon, J. W. *Can. J. Chem.* **1986**, *64*, 2171–2174.

(30) Geluk, H. W. *Synthesis* **1970**, 652–653.

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

(26) For recent discussions of these mechanisms see ref 10, 15, and 18.

atmospheric humidity. The analytical concentrations of **1** and Br₂ in these solutions are reported in Table II, which also includes the calculated equilibrium concentrations of all present species. The UV spectra were immediately measured at 25 ± 0.05 °C in 0.1-, 1-, or 4-cm cells, as required, in a Pye-Unicam SP8-400 UV-vis spectrophotometer in the 250–600-nm range. Occasional checks showed that identical spectra were obtained in several consecutive recordings. A complete list of the absorbances of the solutions used in the fittings is supplied as supplementary material.

Computations were carried out with a FORTRAN program for a fast minicomputer (GOULD 32/87) or a personal computer. Only data collected in the 250–420-nm wavelength range were used, since no additional useful information was contained above this range. The values of the standard deviations for the fitting parameters given in the text are those obtained directly from the fitting program. However, due to the strong nonlinearity of the fitting function,^{23a} a reliable estimate of the confidence interval of the parameters requires multiplying the standard deviations by at least a factor of 3.

The conductivities of the solutions listed in Table II were measured at 25 ± 0.05 °C with a Philips PW 9509 digital conductivity meter. The conductivity values are supplied as supplementary material.

Attempts at kinetic measurements were carried out at 25 ± 0.05 °C with a Durrum stopped-flow kinetic spectrophotometer.¹⁰ The lowest

reactant concentrations (3 × 10⁻⁵ M **1** and 3 × 10⁻⁴ M Br₂) leading to **2** and **3** in concentrations suitable to try to monitor the transformation of the former into the latter were chosen. Absorbance values consistent with those measured with the Pye-Unicam spectrophotometer were instantaneously attained, showing that the formation of both species was too fast for the stopped-flow time scale.^{20b}

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Registry No. **2**, 118761-15-2; **3**, 24315-87-5; **4**, 118725-12-5.

Supplementary Material Available: A table containing all the measured data (temperature, optical path, concentration, absorbance, and conductivity) used in the determination of the formation constants and spectral parameters relative to equilibria **1**, **2**, **3**, and **7** (1 page). Ordering information is given on our current masthead page. Further details on the computational procedure are available directly from the authors (inquiries to R.A.) to any nonprofit organization.

Concerted Acetyl Group Transfer between Substituted Phenolate Ion Nucleophiles: Variation of Transition-State Structure as a Function of Substituent

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Abstract: Second-order rate constants (k_{ARO}) have been measured for the concerted displacement of aryl oxide from aryl acetates in aqueous solution by substituted phenoxide ions. Values of k_{ARO} obey linear Brønsted correlations when either the leaving group or the attacking phenolate ion structures are varied. The Brønsted coefficients obey the equations $\beta_{\text{nuc}} = 0.20 \text{ p}K_{\text{lg}} - 0.68$ and $\beta_{\text{lg}} = 0.15 \text{ p}K_{\text{nuc}} - 1.73$ to a good degree of precision, and the variation indicates that the structure of the transition-state changes within the range of phenolate ions studied; this also provides confirmation that a concerted mechanism operates. The equations for β_{nuc} and β_{lg} predict the equation ($\log k_{\text{ii}} = 0.17 \text{ p}K_{\text{a}}^2 - 2.41 \text{ p}K_{\text{a}} + C$) for k_{ii} , the rate constant for the reaction of aryl oxide ion with acetates bearing identical aryl oxide leaving groups. The identity rate constants may be interpolated from the observed rate constants (k_{ARO}) and exhibit excellent fit to the above equation with the single disposable parameter, C , set at 6.5. This is the first report of curvature in a Brønsted plot of identity rate constants. Effective charge development and loss on leaving and attacking oxyanions is fully balanced in the transition state when entering and leaving nucleophiles have a $\text{p}K_{\text{a}}$ of 7.1. Tetrahedral or acylium ion-like transition-state structures are predicted for hypothetical phenols with $\text{p}K_{\text{a}}$'s of 11.7 and 2.0, respectively.

Recent observations of linear Brønsted correlations for attack of phenolate ion nucleophiles on phenyl esters and pyridines on *N*-acylpyridinium ions^{1,2} are consistent with single transition states for these reactions because the $\text{p}K_{\text{a}}$ values of the nucleophiles lie significantly above and below that predicted for the breakpoint for the putative stepwise process. In order to investigate these novel concerted mechanisms for acyl group transfer it will be necessary to study the state of the forming *and* breaking bonds in the transition state; such a study will give information as to the state of coupling^{3a} between the two major bond changes. Application of single uncalibrated β or ρ values is not appropriate to elucidate transition-state structures for reactions involving two or more major bond changes.^{3a}

Since the concerted carbonyl-transfer reaction between similar nucleophiles is essentially symmetrical, the transition state will lie close to the tightness diagonal^{3b,4,5a} illustrated in Figure 1 for

the transfer of the acetyl group between phenolate ion nucleophiles. The transition state for the reaction where nucleophile and leaving group are identical will fall *on* the tightness diagonal. Kreevoy and his collaborators^{4,5a} proposed a relationship (eq 1) between

(4) Albery, W. J.; Kreevoy, M. M. *Adv. Phys. Org. Chem.* **1978**, *16*, 87.

(5) (a) Kreevoy, M. M.; Lee, I. S. H. *J. Am. Chem. Soc.* **1984**, *106*, 2550.

(b) Reactions in solution require that any effect on the transition-state and ground-state energies results from bonding *and* solvation changes. These cannot be easily separated in the observed parameter; since it is false from many points of view to consider *only* changes in bonding, measures of "bond order" should relate to the *total* of bond and solvation changes. Effective charge changes derived from Brønsted β or Hammett ρ values from proper calibration procedures^{13d,19} are proportional to the change in charge resulting from both solvation and bonding changes. Paper mechanisms invariably omit solvent and treat all reactions as though they were occurring in the gas phase. We use the term "bond order" in this paper as a *combination* of binding and solvation changes which are proportional to changes in effective charge. (c) A transition state with a structure close to that of a tetrahedral intermediate is called a "tight" transition state and will have $\delta = +1$ because the phenolate attacking group *loses* one unit of negative charge (going from ground to transition state). A loose or "exploded"^{6,7} transition-state structure resembles an acylium ion and has $\delta = -1$ because the leaving oxygen *gains* negative charge (one unit) from ground to transition state. The transition state for the concerted mechanism where changes in effective charge on entering and departing oxygens are balanced has $\delta = 0$.

(1) Ba-Saif, S.; Luthra, A. K.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 6362.

(2) Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040.

(3) (a) Williams, A. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; p 127. (b) This diagonal is called the "disparity mode" by Grunwald (Grunwald, E., *J. Am. Chem. Soc.* **1985**, *107*, 125).