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Ionisation and Dissociation of Diarylmethyl Chlorides in BCl_3/CH_2Cl_2 Solution: Spectroscopic Evidence for Carbenium Ion Pairs

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The ionisation equilibria of diarylmethyl chlorides Ar_2CHCl (Ar = p-$CH_3O-C_6H_4$, p-$PhO-C_6H_4$, p-$CH_3-C_6H_4$) reacting with BCl_3 in CH_2Cl_2 to give ion-pairs $Ar_2CH^+BCl_4^-$ (K_I), and the dissociation of these (K_D) were studied by conductimetry and spectro-photometry. The molar conductivities are almost independent of the nature of the aryl group ($\approx 3.5 \cdot 10^{-3}$ Sm^2/mol at −70°C). The ionisation constants K_I increase strongly with increasing electron releasing ability of the p-substituents. The standard ionisation enthalpies and entropies for $(p\text{-}CH_3-C_6H_4)_2CHCl$ and $(p\text{-}PhO-C_6H_4)(Ph)CHCl$, calculated from the K_I at different temperatures are negative. The dissociation constants K_D [$(1.9-2.9) \cdot 10^{-4}$ mol/L at −70°C] do not show a systematic dependence on the electron donating abilities of the substituents in the aryl groups. Small differences between the UV-vis absorption spectra of unpaired and paired ions were used to confirm the conductimetrically determined values of K_D.

Introduction

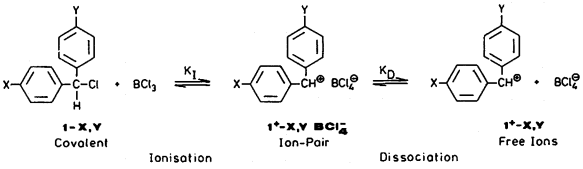
Diarylcarbenium ions have been studied extensively in solvents of low nucleophilicity, mostly by NMR and UV spectroscopy [1], and several species have been isolated as crystalline hexachloroantimonates from CCl_4 solution [2]. The ionisation equilibria of various diarylmethanols have been determined in sulfuric acid/water mixtures (Eq. (1)) [3].

$$Ar_2CH^+ + H_2O \overset{K_{R^+}}{\rightleftharpoons} Ar_2CHOH + H^+. \quad (1)$$

The K_{R^+} values show a linear correlation with the rates of the solvolyses of the corresponding diarylmethyl chlorides [4] and the enthalpies of ionisation of diarylmethyl chlorides and alcohols in superacidic media [5].

$$Ar_2CH^+BCl_4^- + H_2C{=}CR'R'' \rightarrow Ar_2CH-CH_2-CR'R''Cl + BCl_3. \quad (2)$$

In the context of kinetic studies on the addition of carbenium tetrachloroborates to alkenes (Eq. (2)) [6], the Lübeck group required information on the ionisation and dissociation equilibria (3), the equilibrium constants of which are given by Eqs. (4) and (5).



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$$K_I = \frac{[Ar_2CH^+BCl_4^-]}{[Ar_2CHCl][BCl_3]} \quad (4)$$

$$K_D = \frac{[Ar_2CH^+][BCl_4^-]}{[Ar_2CH^+BCl_4^-]}. \quad (5)$$

The investigation involved conductimetric and spectrophotometric measurements, and the results were analysed by means of the theory of Binary Ionogenic Equilibria [7]. A new and unexpected finding is, that there are small but quite definite differences between the UV-vis spectra of paired and unpaired diarylmethyl cations, which can be used to confirm the conductimetrically derived value of K_D.

Experimental

Dichloromethane was purified and dried as described by Heublein and Bauerfeind [8]. Boron trichloride (>99%) was commercially available and was used without further purification. Benzyltriethylammonium chloride was dried for 24 h in high vacuum at 130°C and stored under dry nitrogen. The diarylmethyl chlorides were prepared from diarylketones, which were obtained by the Friedel-Crafts reaction of suitably substituted benzoyl chlorides with benzene derivates according to a standard literature procedure [9]. The reduction of the ketones was carried out with Zn/KOH in ethanol, following the method of Davies [10a]. Subsequent treatment of the diarylmethanols with gaseous HCl in dichloromethane at 0°C in the presence of $CaCl_2$ yielded the diarylmethyl chlorides. After recrystallization or distillation colourless materials were obtained. 1-CH_3,H: bp. 110–112°C/7 Pa (160–164°C/(8–9) · 10^2 Pa [10a]); 1-CH_3,CH_3: pentane, mp. 45–46°C (45–46°C [10b]); 1-OPh,H: ether, mp. 52–53.5°C; 1-OCH_3,H: pentane, mp. 61–62°C (62–63°C [10c]); 1-OPh,CH_3: ether, mp. 67–68.5°C; 1-OCH_3,CH_3: pentane, mp. 43–44°C; 1-OPh,OCH_3: pentane, mp. 54–56°C; 1-OCH_3,OCH_3: ether, mp. 80–82°C (83–84°C [10d]).

The UV-vis-Spectra were taken with the KONTRON UVIKON 860 spectrometer at ambient temperature. Photometric measurements were carried out with a fibre optic system (Schölly KGS III). The light of a 30 W halogen lamp is conducted in a liquid fibre, which splits the light into a probe channel and a reference channel. The probe (Fig. 1) consists of two parallel quartz rods, inserted into twin quartz sleeves, which dip into the solution to be analysed. The light travels down one rod, is totally reflected at its lower end to pass through the solution (≈5 mm) and then returns by the second rod, whence a liquid fibre conducts it through an interference filter (Bandpass-Filter Corion) with a band width of 10 nm to the signal monitor.

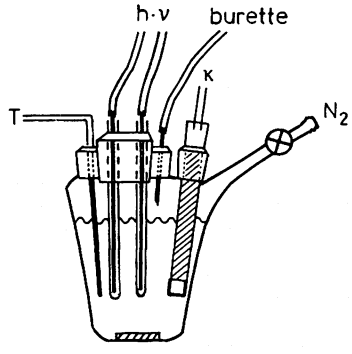

Fig. 1
Diagram of the reaction vessel

Conductimetric measurements were carried out with a Tacussel CD 810 conductimeter and Pt plate electrodes. The cell constants, determined with 0.01 M and 0.001 M KCl solutions, ranged from 53 to 85 m^{-1}. Conductances below 10 μS were determined with 62.5 Hz AC, and for those between 10 and 50 μS an AC of 250 Hz was used.

All experiments were carried out in a dry nitrogen atmosphere. All the concentrations quoted are those at the actual operating temperatures, the adjustments having been calculated from the coefficient of thermal expansion of dichloromethane, 0.00137 K^{-1} [11].

Results and Discussion

Ionisation of Diarylmethyl Chlorides by BCl_3 in Dichloromethane

The reactions of diarylmethyl chlorides 1-X,Y with $3Cl_3$ yield ion-pairs 1^+-X,Y BCl_4^- in equilibrium with the free ions 1^+-X,Y and BCl_4^- (Eqs. (3)–(5)). Consequently, the UV-vis absorbance and the conductivity will grow when BCl_3 is added progressively to solutions of 1-X,Y.

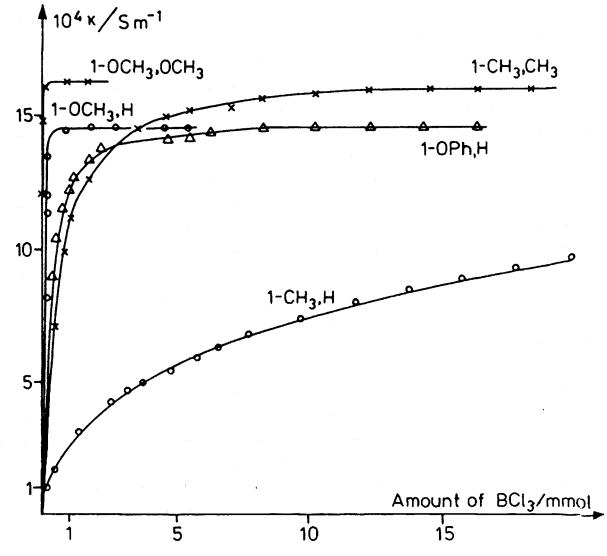

Fig. 2
Conductance of $1.1 \cdot 10^{-3}$ M diarylmethyl chloride solutions in the presence of various amounts of BCl_3 (CH_2Cl_2, −70°C)

As shown in Fig. 2, the conductance increases rapidly, when 1-OCH_3,OCH_3 is titrated with BCl_3 and reaches a limiting value after the addition of 1 equivalent of BCl_3. These findings indicate a large value of K_I and a dissociation equilibrium, which is independent of the concentration of BCl_3, as required by theory (Eqs. (3)–(5)).

When 1-OCH_3,OPh, 1-OCH_3,CH_3 (not shown in Fig. 2) and 1-OCH_3,H are titrated, 1–3 equivalents of BCl_3 are sufficient to reach the plateau in the titration curves, i.e., K_I is large for all of these systems. For 1-OPh,H and 1-CH_3,CH_3, 100–120 equivalents of BCl_3 are needed to achieve complete ionisation, and 1-CH_3,H is not completely ionised even with 200 equivalents of BCl_3. Note that "200 equivalents of BCl_3" amounts to only ≈ 2 vol% of BCl_3, so that any effect on the macroscopic dielectric constant of the mixture is in fact negligible.

When the titrations were monitored photometrically, curves closely similar to those in Fig. 2 were obtained. Photometric studies over a range of temperatures showed, that 1-OCH_3,OCH_3, 1-OCH_3,OPh and 1-OCH_3,CH_3 in the presence of excess BCl_3 remain fully ionised from −70 up to −20°C, whereas for the less stabilised cations 1^+-OCH_3,H, 1^+-OPh,H, and 1^+-CH_3,CH_3 the formation of

the molecules 1-X,Y becomes noticeable at the higher temperatures (Fig. 3).

As discussed below, 10^{-5} M solutions of diarylcarbenium tetrachloroborates contain less than 10% of ion-pairs, and therefore the absorbances shown in Fig. 3 are almost entirely due to unpaired ions. If deviations from Lambert-Beer's law, which are caused by the use of non-monochromatic light [12], are neglected, $K' = K_I \cdot K_D$ for the dilute solutions of 1-CH_3,CH_3, and 1-OPh,H can be derived from Fig. 3. From a plot of $\ln K'$ vs. $1/T$ the thermodynamic parameters ΔH^0 and ΔS^0 for the equilibrium (6) were calculated (Table 1).

$$Ar_2CHCl + BCl_3 \underset{CH_2Cl_2}{\overset{K'}{\rightleftharpoons}} Ar_2CH^+ + BCl_4^- . \quad (6)$$

Table 1
Standard-enthalpies and entropies for the ionogenic equilibrium (6) from photometric studies at different temperatures

1-X, Y	ΔH^0/kJ mol^{-1}	ΔS^0/JK^{-1} mol^{-1}
1-OPh, H	−47.5	−260
1-CH_3, CH_3	−46.4	−260

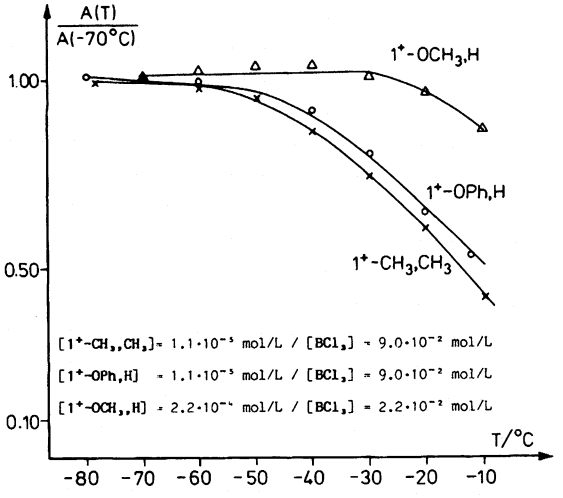

Fig. 3
Temperature dependence of the UV-vis-absorbance of diarylcarbenium tetrachloroborate solutions in dichloromethane (λ = 490 nm)

Quantitative Analysis of the Conductivity Results [7]

If the system is described by Eq. (3), the total concentration (c_0) of diarylmethyl species is

$$c_0 = [Ar_2CHCl] + [Ar_2CH^+BCl_4^-] + [Ar_2CH^+]. \quad (7)$$

Substitute $[Ar_2CH^+BCl_4^-]$ from (4) into (7):

$$[Ar_2CHCl] = \frac{c_0 - [Ar_2CH^+]}{1 + K_I[BCl_3]}. \quad (8)$$

The product $K_I K_D$ is formed from Eqs. (4) and (5), $[Ar_2CHCl]$ substituted from (8), and $[BCl_4^-]$ set equal to $[Ar_2CH^+]$ (electroneutrality); we thus obtain Eq. (9):

$$K_D K_I = \frac{[Ar_2CH^+]^2}{[BCl_3](c_0 - [Ar_2CH^+])/(1 + K_I[BCl_3])}. \quad (9)$$

As discussed by Grattan and Plesch [7a], the ionic conductivity Λ_i can be considered to be independent of the concentration in dilute solutions, so that $\Lambda_i = \Lambda_0 = \kappa/[Ar_2CH^+]$. With this substitution, Eq. (9) can be rewritten to give:

$$\frac{c_0}{\kappa} = \frac{1 + 1/K_I[BCl_3]}{K_D \Lambda_i^2} \cdot \kappa + \frac{1}{\Lambda_i}. \quad (10)$$

This equation is equivalent to Eq. (C.2.14) of Ref. [7a], if $[BCl_3] \approx [BCl_3]_0$.

For fully ionised systems, in which $K_I[BCl_3] \gg 1$, Eq. (10) is reduced to (11).

$$\frac{c_0}{\kappa} = \frac{1}{K_D \Lambda_i^2} \cdot \kappa + \frac{1}{\Lambda_i}. \quad (11)$$

Eqs. (10) and (11) can be used to derive the equilibrium constants and the molar conductivities as described [7].

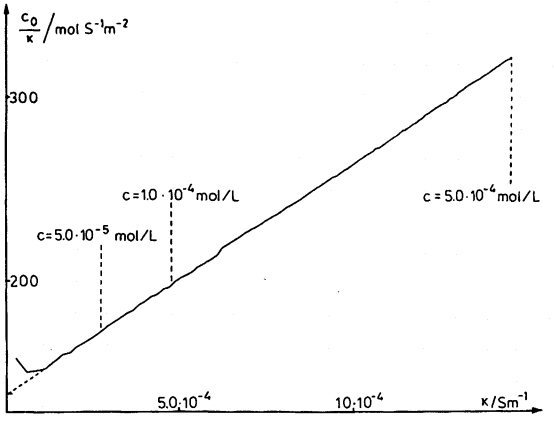

Fig. 4
Evaluation of Λ_i and K_D for 1$^+$-OCH_3,OCH_3 in dichloromethane at −30°C

In a first series of experiments, diarylmethyl chlorides 1-X,Y were added gradually to solutions of BCl_3 in CH_2Cl_2 while the conductance was determined. The concentration of BCl_3 and the temperature were selected so that ionisation was complete. A plot according to Eq. (11) (Fig. 4) was linear for $c_0 < 5 \cdot 10^{-4}$ mol/L, and its intercept yields $1/\Lambda_i$. With this value, the dissociation constant K_D can be derived from the slope.

The dissociation constants thus obtained are of the same order as the K_D values of other types of carbenium salts in CH_2Cl_2 previously reported (Table 2). As expected, variations of the substituents have little effect on the molar conductivities. The temperature dependence of K_D indicates negative dissociation enthalpies and entropies. The positive ΔG^0 value of the ion-pair dissociation is thus due to the unfavourable dissociation entropy. The paucity of data obtained at different temperatures inhibits a detailed discussion. It seems, however, that for the less stabilised carbenium

Table 2
Molar conductivities, ion-pair dissociation constants and thermodynamic parameters for the dissociation of carbenium ion salts in dichloromethane

Salt[b]	T/°C	No of Expts.	$\Lambda_i \cdot 10^3$/ S m^2 mol^{-1} [a]	$10^4 K_D$/ mol L^{-1} [a]	ΔH^0/ kJ mol^{-1}	ΔS^0/ JK^{-1} mol^{-1}	Lit.
$1^+ -OCH_3, OCH_3 BCl_4^-$	−70	6	3.50 ± 0.14	2.2 ± 0.2	−2.3	−81	[c]
	−60	1	4.23	2.1			
	−50	2	5.33 ± 0.03	1.9 ± 0.3			
	−40	2	6.17 ± 0.08	1.8 ± 0.0			
	−30	6	7.15 ± 0.09	1.8 ± 0.2			
	−20	1	8.42	1.6			
$1^+ -OCH_3, OPh\, BCl_4^-$	−70	2	3.15 ± 0.06	2.1 ± 0.4			[c]
$1^+ -OCH_3, CH_3 BCl_4^-$	−70	9	3.49 ± 0.14	2.4 ± 0.3	−3.8	−88	[c]
	−60	1	4.34	2.3			
	−50	2	5.21 ± 0.20	2.0 ± 0.1			
	−30	2	7.18 ± 0.08	1.7 ± 0.1			
$1^+ -OPh, CH_3 BCl_4^-$	−70	3	2.99 ± 0.17	2.9 ± 0.5			[c]
$1^+ -OCH_3, H\, BCl_4^-$	−80	5	2.45 ± 0.05	2.7 ± 0.2	−7.0	−105	[c]
	−70	15	3.37 ± 0.12	1.9 ± 0.2			
	−65	2	3.95 ± 0.05	1.8 ± 0.1			
	−60	3	4.29 ± 0.13	1.7 ± 0.1			
	−50	4	5.28 ± 0.17	1.4 ± 0.2			
	−40	3	6.09 ± 0.09	1.3 ± 0.1			
	−30	4	7.03 ± 0.06	1.0 ± 0.1			
$1^+ -OPh, H\, BCl_4^-$	−70	7	3.16 ± 0.14	2.0 ± 0.3			[c]
$1^+ -CH_3, CH_3 BCl_4^-$	−70	3	3.31 ± 0.25	1.9 ± 0.1			[c]
$Tr^+ SbCl_6^-$	−45		6.17	0.73	−10.5	−126	[13a]
$Pyr^+ SbCl_6^-$	−45		5.95	0.88	−13.0	−138	[13a]
$Et_4N^+ SbCl_6^-$	−45		5.53	1.2	−6.3	−100	[13a]
$Ph_3C^+ SbCl_6^-$	−45		4.13	2.9	−3.3	−71	[13b]
	−45		4.43	5.3	−8.4	−96	[13a]
	0		8.21	3.1			
	25		10.8	1.9			
$Ph_3C^+ SbF_6^-$	0		9.71	2.4	−9.2	−105	[13c]
$Ph_3C^+ AsF_6^-$	0		9.69	1.9	−9.2	−105	[13c]
$Ph_3C^+ Cl^-$	0		–	–	≈0	−152	[8]

[a] With standard deviations.
[b] Tr = Tropylium; Pyr = 2,4,6-Trimethylpyrylium; Et = Ethyl; Ph = Phenyl.
[c] This work, derived from Eq. [11].

Table 3
Molar conductivities and ionisation constants for solutions of diarylmethyl chlorides and BCl_3 in CH_2Cl_2 at −70°C derived from conductivity measurements on partially ionised systems

1-X, Y	No of Expts.	$\Lambda_i \cdot 10^3$/ S m^2 mol^{-1} [a]	K_I/ L mol^{-1} [a]	ΔG_I^0(70°C) kJ mol^{-1}
1-OPh, H	2	2.97 ± 0.08	145 ± 7	−8.4
1-CH_3, CH_3	3	3.64 ± 0.99	64 ± 10	−7.0
1-CH_3, H[b]	3	1.94 ± 0.43	0.49 ± 0.05 (0.17)	+1.2 (+3.0)

[a] With standard deviations.
[b] Calculated for $K_D = 2.0 \cdot 10^{-4}$ mol/L; values in parentheses calculated for $\Lambda_i = 3.20 \cdot 10^{-3}$ Sm^2/mol (see text).

ions both ΔH^0 and ΔS^0 are more negative, which indicates that in these systems the solvation of the free ions is more important.

In a second series of experiments, diarylmethyl chlorides 1-X,Y were added gradually to solutions of BCl_3 under conditions of incomplete ionisation. Large concentrations of BCl_3 were again used, and the changes of $[BCl_3]$ during the titrations were negligible. Again, linear plots of c_0/κ vs. κ were obtained (Eq. (10)), but the intercepts $(1/\Lambda_i)$ observed in different experiments varied considerably, which diminished the accuracy of the Λ_i values. However, the Λ_i values of 1^+-OPh,H and 1^+-CH_3,CH_3 (Table 3) agree well with those in Table 2. Since Table 2 showed Λ_i to be almost independent of the nature of the para-substituents, we consider the low Λ_i value found for 1^+-CH_3,H to be an artefact of unexplained origin.

The K_I values can be calculated from the slopes of the plots, $[BCl_3]$, Λ_i and K_D (Eq. (10)). These values together with the K_D in Table 2 give $K' = K_I \cdot K_D$ for 1-OPh,H + BCl_3 (0.029) and 1-CH_3,CH_3 + BCl_3 (0.0122), corresponding to ΔG^0 (−70°C) of 6.0 and 7.4 kJ mol^{-1}, respectively. These numbers are closely similar to those derived from the temperature dependence of absorbance (5.3 and 6.4 kJ mol^{-1}, Table 1).

Furthermore, the difference between the ΔG_I^0 values of the lower two compounds of Table 3 (8 − 10 kJ/mol) agrees

well with the corresponding value (7–11 kJ/mol) derived from the pK_{R^+} values of 1-CH_3,CH_3 (pK_{R^+} = −10.4 [3b]) and 1-CH_3,H (pK_{R^+} = −12.3 [3c]; −11.6 [3d]) at 25°C.

Spectroscopic Evidence for Ion-Pair ⇋ Free Ions Equilibria

It has long been known that the UV-vis absorption spectra of carbocations are influenced only slightly by the solvent and the state of the ions [14]. Consequently, many analyses of ionogenic equilibria have been based on the identity of the absorption spectra of unpaired and paired ions [15]. The differences in the absorption spectra shown in Fig. 5 enable us to progress beyond these conventional approximations and to extract information on ion-pair dissociation from absorbance measurements.

The absorption spectrum A (Fig. 5) can be attributed to unpaired 1^+-OCH_3,OCH_3 ions, since at a concentration of 10^{-5} M, the degree of dissociation exceeds 90% (from K_D in Table 2). The same solution, but containing also 10^{-2} M benzyltriethylammonium tetrachloroborate gave spectrum B, which showed a 2 nm blue shift of λ_{max} and a decrease of ε_{max} (Fig. 5). Similar changes have been observed for the absorption spectrum of 1^+-OCH_3,CH_3.

This effect may be attributed a priori either to the formation of ion-pairs or to a more general solvatochromic

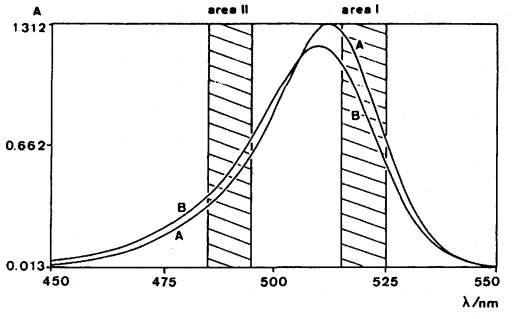

Fig. 5
Absorption spectrum of 1^+-OCH_3,OCH_3 ($1.0 \cdot 10^{-5}$ M) in CH_2Cl_2 at 20°C (curve A) in presence of benzyltriethylammonium tetrachloroborate ($1.0 \cdot 10^{-2}$ M) (curve B)

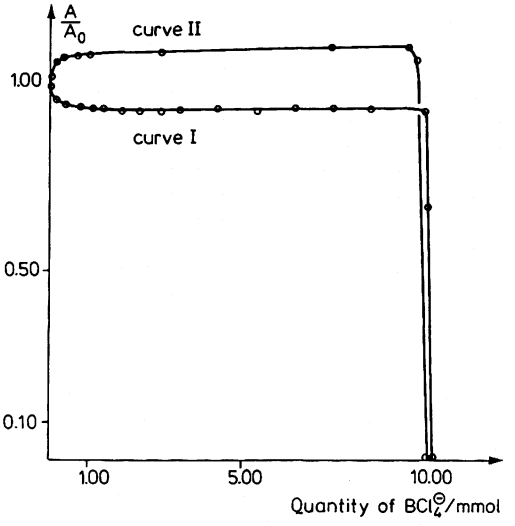

Fig. 6
Titration of 1^+-OCH_3,OCH_3 BCl_4^- ($2.0 \cdot 10^{-5}$ mmol) and BCl_3 (10 mmol) in 92 mL of CH_2Cl_2 with benzyltriethylammonium chloride at −70°C. Upper curve: 485–495 nm, lower curve: 515–525 nm

effect caused by the change of the medium. Since all spectra were taken in the presence of a large excess of BCl_3, the differences are unlikely to arise from nucleophilic impurities.

In order to assign these spectral effects, solutions of 1^+-X,Y BCl_4^- with excess of BCl_3 were titrated with benzyltriethylammonium chloride. When the ammonium chloride is added, the BCl_3 accepts Cl^- ions so that [BCl_4^-] increases at the expense of [BCl_3]. According to Eqs. (4) and (5), these concentration changes reduce the degree of ionisation of 1-X,Y and the degree of dissociation of the 1^+-X,Y BCl_4^- ion pairs.

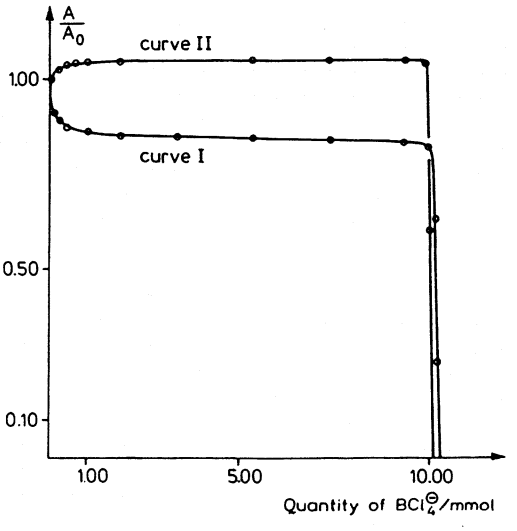

Fig. 7
Titration of 1^+-OCH_3,CH_3 BCl_4^- ($2.0 \cdot 10^{-5}$ mmol, λ_{max} = 488 nm in CH_2Cl_2) and BCl_3 (10 mmol) in 92 mL of CH_2Cl_2 with benzyltriethylammonium chloride at −70°C. Upper curve: 465–475 nm; lower curve: 505–515 nm

Fig. 6 shows the change of the absorbance during the titration of 1^+-OCH_3,OCH_3/BCl_3 with Cl^- in two different spectral regions. If the titration is monitored in the 515–525 nm range (Fig. 5, area I) one observes an initial 8% decrease in absorbance, then a wide range in which the absorbance remains constant, and finally an abrupt decrease (Fig. 6, curve I). A similar behaviour was observed when the absorbance was measured at 485–495 nm (Fig. 5, area II); the only difference is that now an increase in absorbance was observed during the first phase of the titration (Fig. 6, curve II). Similar titration curves were obtained with 1^+-OCH_3,CH_3 (Fig. 7).

With all systems, an abrupt decrease of the absorbance occurs when the BCl_3 is used up and the chloride ions are then trapped by the 1^+-X,Y. This finding supports the previous conclusion that the diarylmethyl chlorides with X = OCH_3 and Y = OCH_3 or CH_3 are completely ionised by one equivalent of BCl_3, i.e. K_I is relatively great.

It remains to find the reason for the changes of absorbance in the initial phase of the titration. If they were due to a change of the medium, i.e. a general solvatochromic effect, one would not expect the absorbance to remain constant while 90–95% of the ammonium chloride is added. However, the noticeable change in the absorbance at the beginning and the long plateau while most of the Cl^- is added,

are readily compatible with our explanation in terms of ion-pairs.

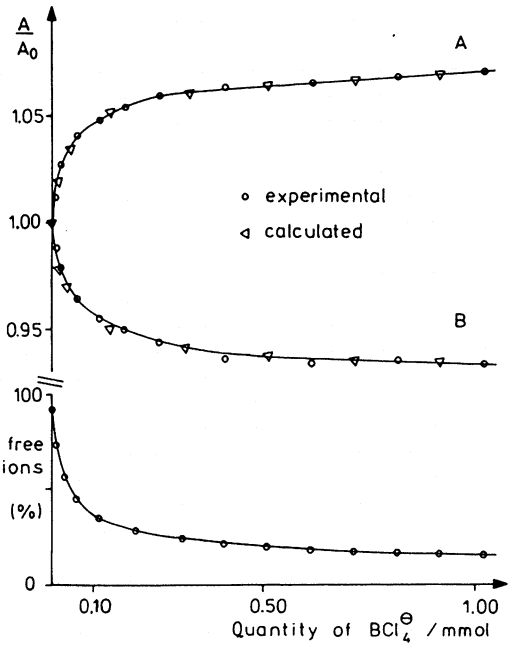

Fig. 8
Upper part: Spread out section of Fig. 6 and calculated changes of absorbance (see text). Lower part: percentage of free ions

Fig. 8 shows an enlargement of the left part of Fig. 6 and the percentage of unpaired ions calculated by means of K_D [16]. It is obvious that the changes of absorption take place in the same range in which the percentage of unpaired ions decreases from ≈90% to less than 13%. From the absorbance observed before Cl^- was added (92% free ions and 8% ion-pairs) and the absorbance at the plateau (5% free ions and 95% ion-pairs), we can calculate the absorbance at different stages of the titration and, as Fig. 8 shows, the experimental and the calculated curves superimpose. The participation of 1:1 ion-pairs in binary ionogenic equilibria has thus been supported by an independent method.

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[16] For the calculation of the percentage of free ions we assumed K_D of $1^+BCl_4^-$ and $R_4N^+BCl_4^-$ to be equal (see Table 2 and corresponding discussion).

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