Raman Spectroscopic Studies of Halide-ion Complexes of Carbon Tetrahalides in Solution

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The Raman spectra of solutions containing tetra-alkylammonium chlorides or bromides and CCl_4 or CBr_4 in non-hydrogen bonding solvents show evidence of 1 : 1 complexes $X^-.CBr_4$ present in ion pairs with the cation. From Raman intensity measurements the formation constant for $[Bu_4N]^+CBr_4Cl^-$ at 20 °C is 4·8 l mol^{-1} in MeCN and 2·0 l mol^{-1} in CH_2Cl_2 solution. Evidence is presented from changes in vibration frequencies and Raman depolarization ratios of CBr_4 on complexing that in CBr_4Cl^- the chloride ion is bound to a face rather than an apex or edge of the CBr_4 tetrahedron.

ELECTRONIC absorption studies of dilute solutions of tetra-alkylammonium halides in mixed solvents containing carbon tetrachloride have provided evidence for weak 1 : 1 complexes between a halide ion (probably present as an intimate ion pair with the cation in solvents of low polarity) and a CCl_4 molecule.[1,2] The stability constants measured in acetonitrile solution showed the expected decrease from the iodide to the bromide ion complex, consistent with their formulation as donor–acceptor complexes with halide ion as donor.[2] Recently the vibrational spectra and structures of crystalline complexes of tetra-alkylammonium halides with CCl_4, CBr_4, and CI_4 have been reported and further evidence provided that these are predominantly donor–acceptor rather than electrostatic complexes.[3] This paper reports Raman observations on solutions containing halide ions and CCl_4 or CBr_4. The results for the CBr_4 solutions clearly demonstrate the presence of a 1 : 1 halide ion–CBr_4 complex and provide stability-constant data and evidence of its structure.

RESULTS

While tetramethyl-, tetraethyl-, and tetrapropyl-ammonium halides have low solubilities in carbon tetrachloride, tetrabutylammonium chloride and bromide give viscous saturated solutions containing *ca.* 2 mol l^{-1} at room temperature. The Raman spectra of these solutions show small differences from the spectrum of pure CCl_4 and more closely resemble the spectra of the solid compounds Et_4NX,CCl_4 (X = Cl, Br, or I). Thus as shown in Figure 1, the ν_1 band is broadened on the low-frequency side, and may be curve-resolved into a broad ν_1 band of complexed CCl_4 at 453 cm^{-1} superimposed on the isotope components of ν_1 of free solvent CCl_4. There is also a change in the Fermi doublet ν_3, $\nu_1 + \nu_4$, the upper component becoming more intense than the lower (see Figure 1), and the ν_2 band is less intense relative to ν_1 and ν_4 than in the spectrum of pure CCl_4.

The previous studies[3] showed that the crystalline halide-ion complexes of CBr_4 are more stable than those of CCl_4 and show greater changes in the vibrational spectra when compared with the spectra of the free carbon tetrahalides. Raman spectra of solutions of CBr_4 and tetrapropyl- or tetrabutyl-ammonium chloride or bromide in carbon tetrachloride, chloroform, dichloromethane, nitromethane, acetonitrile, and methanol have therefore been examined, and except in methanol these all show a new sharp polarized band at *ca.* 260 cm^{-1} due to ν_1 of complexed CBr_4. Although this band is clearly resolved from the ν_1 band of free CBr_4 (269 cm^{-1}) as shown in Figure 1, the other modes of complexed CBr_4 overlap the modes of the free molecule, as was readily shown by intensity measurements relative to the free CBr_4 ν_1 band. Further evidence of this overlapping may also be seen in the small shifts in the band maxima of ν_2 and ν_4 compared with their frequencies in pure CBr_4 solutions. The frequencies measured for the solutions are given in the Table, and were obtained from spectra of solutions in which the concentration of free CBr_4, as judged from the intensity of ν_1, was very low relative to that of the complexes.

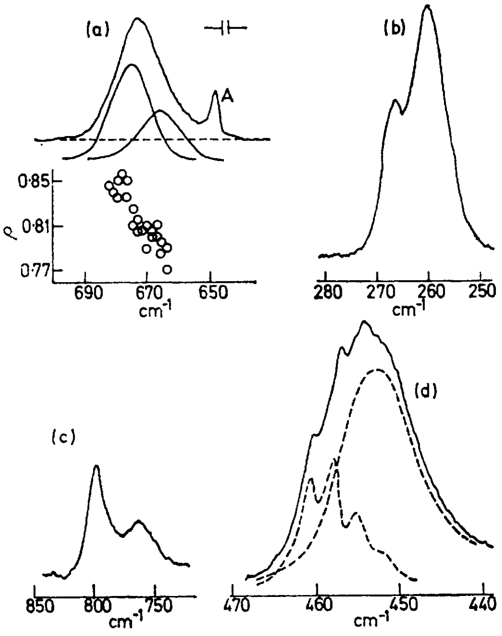

FIGURE 1 Raman bands of carbon tetrahalides in solutions containing halide ions: (a) ν_3 $CBr_4 + Cl^-$; Bu_4NCl (1·6M), CBr_4 (1·3M) in MeCN; (b) ν_1 $CBr_4 + Cl^-$; Pr_4NCl (0·54M), CBr_4 (0·24M) in MeCN; (c) ν_3 $CCl_4 + Cl^-$; (d) ν_1 $CCl + Cl^-$; (c) and (d) Bu_4NCl (2·0M) in CCl_4. In (a) the depolarization ratio ρ is also shown; the peak marked A is due to neon at 6598·95 Å

The ν_1 bands of the free and complexed CBr_4 were sufficiently well resolved to enable accurate peak height measurements to be made on both bands. Job plots of the peak height of the ν_1 band of the chloride or bromide ion complex were therefore made by use of solutions of CBr_4 and Bu_4NCl

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[1] M. J. Blandamer, T. E. Gough, and M. C. R. Symons, *Trans. Faraday Soc.*, 1964, **60**, 488.

[2] P. C. Dwivedi and C. N. R. Rao, *Spectrochim. Acta*, 1970, **26**, *A*, 1535.

[3] J. A. Creighton and K. M. Thomas, (*a*) *J.C.S. Dalton*, 1972, 403; (*b*) *J. Mol. Structure*, 1971, **7**, 173.

or Bu_4NBr in carbon tetrachloride, in which the sum of the concentrations of CBr_4 and Bu_4NX was 0·31M for X = Cl and 0·19M for X = Br. The ν_2 band of the solvent was used as an internal intensity standard. These measurements clearly showed that both the chloride- and bromide-ion complexes of CBr_4 are $n : n$ in these solutions and this was confirmed by Job plots of electrical conductances by use of similar solutions of total concentrations 0·08 and 0·19M respectively. [The specific conductances at the Job maxima were $0{\cdot}56 \times 10^{-6}$ and $0{\cdot}30 \times 10^{-6}$ ohm^{-1} respectively, consistent with the expected high degree of ion association of these concentrations.] Job plots were also made of peak heights of the complexed CBr_4 ν_1 band for solutions of Bu_4NCl and CBr_4 in acetonitrile, nitromethane, and dichloromethane of total solute concentrations 0·25, 0·24, and 0·28M respectively, and of Bu_4NBr and CBr_4 in acetonitrile of total concentration 0·20M. These measurements also indicated $n : n$ stoicheiometry for the halide ion–CBr_4 complex in each solution.

Raman frequencies/cm^{-1} of carbon tetrahalide complexes in solution

	ν_1	ν_2	ν_3	ν_4
CCl_4	459	218	762, 790	314
Cl^-,CCl_4 [a]	453	220	758, 792	313
Br^-,CCl_4 [a]	453	220	757, 789	313
CBr_4 [b]	267	128	675	183
Cl^-,CBr_4 [b]	260	*d*	673 [c]	182
Br^-,CBr_4 [b]	259	*d*	667	180

[a] Solution in CCl_4. [b] Solution in MeCN. [c] Curve resolution gives $\nu_3(a_1)$ = 666 cm^{-1}, $\nu_3(e)$ = 675 cm^{-1}. [d] Not observed.

In order to demonstrate that at these concentrations of 0·1—0·3M the complexes are the simplest species 1 : 1, equilibrium studies were carried out by use of Raman peak height measurements on the ν_1 bands of both free and complexed CBr_4. The measurements were made on a series of 12 solutions of different molar ratios of Bu_4NCl and CBr_4 in acetonitrile at 20 °C in which the total solute concentration was 0·29M, and on a similar series of 12 solutions in dichloromethane in which the total solute concentration was 0·33M. The solvent bands at 380 cm^{-1} (MeCN) and 283 cm^{-1} (CH_2Cl_2) were used as internal intensity standards.

For each solution the equilibrium concentration of free CBr_4 was first calculated by comparison of the height of the free CBr_4 ν_1 band with that from a standard solution of CBr_4 in the same solvent. The number of moles l^{-1} of complexed CBr_4 was then given by the difference between the initial and equilibrium concentrations of free CBr_4, and this was fitted by a least-squares procedure to a linear function of the height of the complexed CBr_4 ν_1 band to give the constant relating the ν_1 peak height to the concentration of complexed CBr_4. It was thus found that the molar intensity of the ν_1 band of complexed CBr_4 is $3{\cdot}27 \pm 1{\cdot}56$ times that of free CBr_4 in dichloromethane solution and $2{\cdot}67 \pm 0{\cdot}63$ in acetonitrile. From these averaged values for the molar intensities of the ν_1 band of complexed CBr_4 and also that for free CBr_4, the concentrations of free and complexed CBr_4 for each solution were calculated from the experimental peak heights, and Figure 2 shows a plot of $[CBr_4]_{complexed}/[CBr_4]_{free}$ against $[Bu_4NCl]_{free}$ with the best least-squares lines through the calculated points. It is clear from the linearity of the plots that at these concentrations the equilibrium is $Bu_4NCl + CBr_4 \rightleftharpoons Bu_4NCl,CBr_4$, and from the gradients the formation constants of the 1 : 1 complex at 20 °C are 2·03 and 4·78 l mol^{-1} in dichloromethane and acetonitrile respectively. This difference in the formation constants in the two solvents parallels that reported previously for the iodide-ion complex of CCl_4.[2] The least-squares standard deviation in both the formation constants from the linear plots in Figure 2 was 0·05 l mol^{-1}, but in view of the large standard deviation in the molar intensity of the complexed CBr_4 ν_1 band, somewhat larger error limits should probably be placed on the formation constants.

The 1 : 1 stoicheiometry requires that the symmetry of CBr_4 in the complexes is lower than T_d, and likely configurations are those in which a chloride ion is bound to a face, edge, or apex of a CBr_4 tetrahedron, whose symmetry is then C_{3v}, C_{2v}, and C_{3v} respectively. A distinction between these symmetries may be made by examining the contour of the ν_3 band of the complex. The effect of a C_{2v} distortion is to split ν_3 into three components $[f_2(T_d) \longrightarrow a_1 + b_1 + b_2(C_{2v})]$, and it can be shown[4] that, for a small perturbation, the a_1 component always lies approximately centrally between the b_1 and b_2 components, *i.e.*, the overall band contour remains symmetric. A C_{3v} distortion however splits ν_3 into two components $[f_2(T_d) \longrightarrow a_1 + e(C_{3v})]$, and since for a small effect the intensity of the e is approximately twice that of the a_1 component, the overall contour of ν_3 is then asymmetric. As shown in Figure 1(a), which is a trace of the ν_3 band of the complex in a solution in which the concentration of free CBr_4 (as judged by the intensity of ν_1) was too low to contribute measurable intensity to ν_3, the observed contour of ν_3 is asymmetric, and is consistent with a C_{3v} perturbation but not in accord with C_{2v}.

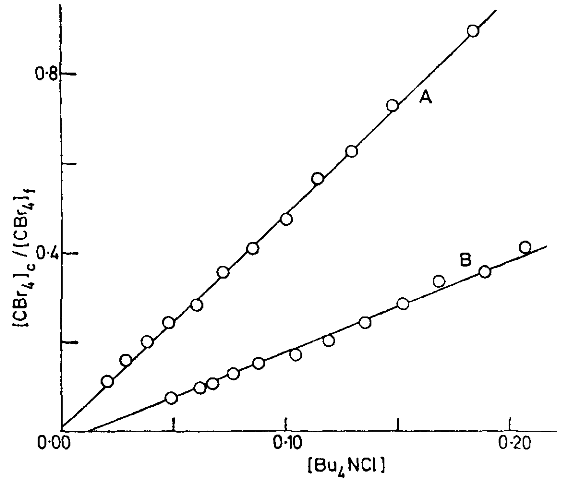

FIGURE 2 A plot of the ratio of concentrations of complexed and free CBr_4, $[CBr_4]_c/[CBr]_f$, against the free Bu_4NCl concentration at equilibrium (20 °C) in solutions in A, MeCN; and B, CH_2Cl_2

In order to investigate further whether the chloride ion is bound to an apex or face, the effect of the chloride ion on the stretching force constants of CBr_4 was studied. It was first necessary to assign the a_1 and e components of ν_3, and though the lower and weaker component may be presumed to be a_1 on intensity grounds, this assignment was conclusively established by measuring the depolarization ratio ρ through the ν_3 band. The results for several separate scans are shown in the lower part of Figure 1(a), and it may be seen that ρ is less on the low-frequency side of the

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[4] J. A. Creighton, to be published.

band, due to the a_1 component, than it is at the band-maximum. The observed band was therefore decomposed by use of a Dupont Curve Analyser into two bands of the same half-width and with heights in the ratio 1 : 2 as shown in Figure 1(a), giving $\nu_3(a_1) = 666\,\mathrm{cm}^{-1}$ and $\nu_3(e) = 675\,\mathrm{cm}^{-1}$. The curve analysis showed that though $\rho < 6/7$ at the band maximum, this is due to a contribution at this frequency from the side of the a_1 component, and does not indicate that the more intense component is a_1 as was previously believed.[3b]

It can be shown[4] that if the changes in the stretch–stretch interaction force constants on complex formation is very small and the a_1 component of ν_3 is *lower* than the e component, then the stretching force constant of the bond along the C_3 axis is *less* than that of the other three bonds, consistent with apical binding of the tetrahedral molecule. Such a situation has recently been found for example for the contact ion pair $Na^+[Co(CO)_4^-]$ in tetrahydrofuran solution.[5] One may test the importance of the stretch–stretch interaction force constant changes with the relationship (1)

$$3\Delta\lambda_1(\mu_{\mathrm{Br}} + \tfrac{4}{3}\mu_{\mathrm{C}}) = [\Delta\lambda_3(a_1) + 2\Delta\lambda_3(e)]\mu_{\mathrm{Br}} \qquad (1)$$

which holds approximately[4] only if the interaction constant changes are negligible, where $\lambda_i = 4\pi^2\nu_i^2$ and μ_{C} and μ_{Br} are the inverse masses. It is thus clear that on formation of CBr_4,Cl^- there is a considerable change in the stretch–stretch interaction force constants of CBr_4. The simple argument indicated above for deducing the configuration from the relative positions of the a_1 and e components of ν_3 is therefore not applicable to CBr_4,Cl^-, and indeed as shown below the conclusion which would be drawn is probably erroneous.

The observed frequencies (Table) were used to calculate the fractional changes α_{VF} and a in the bond stretching and stretch–stretch interaction constants involving the C–Br bond along the C_3 axis, and the corresponding changes γ_{VF} and c in the force constants involving only the three equivalent bonds. There are only three C–Br stretching frequencies from which to calculate four force constants, and it was therefore necessary to use one force constant as a variable parameter. The off-diagonal element f_{12} in the a_1 block of the $\mathscr{F}$ matrix of CBr_4,Cl^- was chosen for this purpose, since it must be small for a small perturbation and its value may therefore be used to define the limits of acceptable solutions. Details of the calculation are given in the Appendix, and Figure 3 shows the variation of α_{VF}, γ_{VF}, a, and c within a range of assumed values of f_{12} of roughly $\pm 5\%$ of the diagonal elements of $\mathscr{F}$. It may be seen that close to $f_{12} = 0{\cdot}09$ mdyne $\mathrm{\AA}^{-1}$ there are solutions with $\alpha_{\mathrm{VF}} \doteqdot a \doteqdot 0$ and γ_{VF} and c negative, consistent with face-centred co-ordination of CBr_4, but also close to $f_{12} = -0{\cdot}16$ mdyne $\mathrm{\AA}^{-1}$ are solutions consistent with apical co-ordination with $\gamma_{\mathrm{VF}} \doteqdot c \doteqdot 0$ and α_{VF} and a negative. Two arguments favour the solutions in the range consistent with the face-centred configuration. First, off-diagonal elements of symmetrized force constant matrices, such as f_{12}, are normally positive. Secondly α_{VF} and γ_{VF} are of course fractional changes in force constants of a valence force field. It has been suggested[6] that a Urey–Bradley force field provides a better description of the vibrations of CBr_4, and α_{VF} and γ_{VF} were therefore analysed in terms of a and c, which are also the fractional changes in the non-bonded repulsion constants F, and of the fractional changes α_{UB} and γ_{UB} in the Urey–Bradley bond-stretching constant K (see Appendix). As Figure 3 shows, solutions near $f_{12} = 0{\cdot}09$ mdyne $\mathrm{\AA}^{-1}$ have $\alpha_{\mathrm{UB}} \doteqdot a \doteqdot 0$ and thus correspond to face-centred co-ordination also in a Urey–Bradley field, whereas there is no solution with small values of both γ_{UB} and c. Indeed $|\gamma_{\mathrm{UB}}| > |\alpha_{\mathrm{UB}}|$ throughout the whole range of Figure 3, and the small values of γ_{VF} near $f_{12} = -0{\cdot}16$ mdyne $\mathrm{\AA}^{-1}$ are interpreted in the Urey–Bradley field as due to fairly large but opposing values of γ_{UB} and α.

Clearly a detailed interpretation of the force-constant changes depends on the type of force field assumed, but the valence-force and Urey–Bradley fields represent two extremes in which respectively none and all the stretch–stretch interaction is attributed to non-bonded repulsions. It thus seems clear that with intermediate force fields, as with the two extremes, the force-constant changes indicate a face-centred structure as the more probable configuration of CBr_4,Cl^- in solution.

Attempts were also made to study solutions of tetra-alkylammonium iodides with CBr_4, but new strong bands appeared in the Raman spectra during a few hours owing to halogen-exchange. In contrast the tetra-alkylammonium chloride solutions with CBr_4 showed no evidence of halogen-exchange at room temperature during several weeks. The exchange reaction with iodide ions was more rapid in methanol than in acetonitrile solution, and initially the spectra of the acetonitrile solutions showed a band at 259 cm^{-1} due to ν_1 of I^-,CBr_4, which was not present in the solutions in methanol. There was evidence from the spectra of two exchange products formed at different rates,[7] but the exchange was not studied in detail.

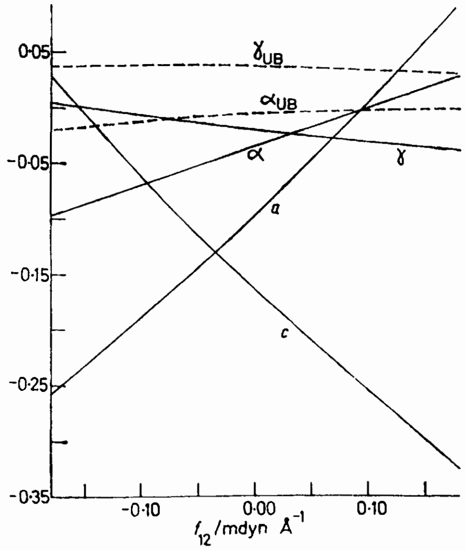

FIGURE 3 The fractional changes in the force constants of CBr_4 on complexing with chloride ions in solution in acetonitrile (see text)

DISCUSSION

The configuration of CBr_4,Cl^- and presumably also of the other halide ion–carbon tetrahalide complexes in solution thus appears to be similar to that of the halide ion complexes of iodoform in solution, where it has been

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[5] W. F. Edgell and J. Lyford, *J. Amer. Chem. Soc.*, 1971, **93**, 6407.

[6] T. Shimanouchi, *Pure Appl. Chem.*, 1963, **7**, 131.

[7] K. M. Thomas, Ph.D. Thesis, University of Kent, 1971.

shown[8] that a halide ion is facially bound to all three iodine atoms of an HCI_3 molecule, rather than to the configuration of the solid tetra-alkylammonium halide–CBr_4 complexes, where the halide ions interact with the apices of the CBr_4 tetrahedra.[3] The order of stability of the iodoform complexes, $Cl^- > Br^- > I^-$, indicates that the interaction there is mainly electrostatic,[8] whereas in the solution complexes of CCl_4 (and presumably also of CBr_4) the order of stability is $I^- > Br^-$,[2] showing that here the interaction is due mainly to either donor–acceptor or dispersion forces. It thus appears that facial binding of a halide ion to a tri- or tetra-halogenomethane is more stable than apical binding whichever of these forces is dominant. It is perhaps surprising therefore that apical binding is found in the solid CBr_4 complexes, but this is probably forced in the lattice structure by the bulky R_4N^+ ions. The greater shifts in the CBr_4 vibration frequencies in these solid complexes than in those observed in the solutions may simply be a consequence of the greater number of halide ions per CBr_4 molecule,[3] and not an indication of a stronger interaction.

APPENDIX

If the same symmetry co-ordinates are used for both free and complexed CBr_4 we may define $\mathscr{F}_1 = \mathscr{F}(CBr_4Cl^-) - \mathscr{F}(CBr_4)$. The changes in the individual valence force constants are then the elements of $\mathbf{F}_1 = \tilde{\mathbf{U}}\mathscr{F}_1\mathbf{U}$, where all the components of degenerate symmetry co-ordinates must be included in $\mathbf{U}$.

For the purpose of deducing the configuration of CBr_4Cl^-, the mixing of stretching and bending motion was neglected. This seemed justified here since ν_3 and ν_4 are well separated for CBr_4 and since only large differences in the elements of $\mathbf{F}_1$ were taken as significant evidence in support of a particular configuration. The $\mathscr{G}$ matrix elements used to evaluate the elements f_{ij} of $\mathscr{F}_1$ were $g_{11} = \mu_{Br}$, $g_{12} = 0$, $g_{22} = g_{33} = \mu_{Br} + 4/3\ \mu_C$, and from the symmetry co-ordinates $S_1(a_1) = \frac{1}{2}(r_1 + r_2 + r_3 + r_4)$, $S_2(a_1) = (3r_1 - r_2 - r_3 - r_4)/\sqrt{12}$, $S_3(e) = (2r_2 - r_3 - r_4)/\sqrt{6}$, and $S_3'(e) = (r_3 - r_4)/\sqrt{2}$ where r_k are bond-length displacements, relationships (2)—(5) follow from $\mathbf{F}_1 = \tilde{\mathbf{U}}\mathscr{F}_1\mathbf{U}$.

$$\alpha_{VF}f_r = f_{11}/4 + 3f_{22}/4 + 3f_{12}/\sqrt{12} \qquad (2)$$

$$\gamma_{VF}f_r = f_{11}/4 + f_{22}/12 - f_{12}/\sqrt{12} + 2f_{33}/3 \qquad (3)$$

$$a_{VF}f_{rr} = f_{11}/4 - f_{22}/4 + f_{12}/\sqrt{12} \qquad (4)$$

$$c_{VF}f_{rr} = f_{11}/4 + f_{22}/12 - f_{12}/\sqrt{12} - f_{33}/3 \qquad (5)$$

The changes in the valence-force constants can be reinterpreted in terms of a Urey–Bradley force field by use of the relationships for a tetrahedral XY_4 molecule[9] $f_r = K + 1{\cdot}9F$, $3f_{rr} = 2{\cdot}1F$. We thus find: $a_{UB} = a_{VF} = a$, $c_{UB} = c_{VF} = c$, $K\alpha_{UB} = f_r\alpha - 1{\cdot}9Fa$, and $K\gamma_{UB} = f_r\gamma - 1{\cdot}9F(a + 2c)/3$, where f_r, K, and F are the force constants for free CBr_4.

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[9] G. W. Chantry and L. A. Woodward, *Trans. Faraday Soc.*, 1960, **56**, 1110.