

Studies of polyhalide ions in aqueous and non-aqueous solution by electrospray mass spectrometry

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Solutions of $I_2 + X^-$ ($X = Cl, Br, I, NCS$) in both water and acetonitrile have been studied by electrospray mass spectrometry in order to identify the anions present. For I_2/I^- , there is no evidence of the I_5^- anion proposed earlier to explain deviations from ideality in the formation of I_3^- in aqueous solution; rather, the equilibrium $I_3^- + I^- \rightleftharpoons I_4^{2-}$ is shown to be compatible with the mass spectrometric results, and with the earlier literature. With Cl^- , Br^- and NCS^- , both classes of solution contain members of the series $X_3^- \rightleftharpoons X_2I^- \rightleftharpoons XI_2^- \rightleftharpoons I_3^-$; this is ascribed to rapid redistribution processes rather than to the redox and/or photochemical reactions suggested by earlier workers. There is little qualitative difference between aqueous and acetonitrile solutions, except that aqueous I_2/Cl^- systems contain the ICl_4^- anion, whose decomposition in the gas phase produces the previously unknown $ICl_3^{\cdot-}$ radical anion. No I_2X^- adducts were identified when $X = OH^-, NCO^-, N_3^-$ or NO_2^- .

The solid state and solution phase chemistry of polyhalide anions has been studied for many years.¹⁻⁴ The stable salts which have been prepared, and in many cases characterised crystallographically,⁴ include those of X_3^- ($X = Cl, Br, I$), I_n^- ($n = 5, 9$), I_n^{2-} ($n = 4, 8, 9$) and I_{16}^{4-} . Mixed halogens species are also known, and several XY_n^- salts have been reported, as have those of higher XY_n^- species. The appropriate description of the bonding in the X_3^- ions has prompted considerable discussion, since both X_2 and X^- have closed shell configurations. A paper by Landrum, Goldberg and Hoffmann⁵ reviews earlier work, and reports calculated values for the bonding energy in X_3^- ($X = Cl, Br, I$) and I_2X^- ($X = Cl, Br$) anions.

The stability of X_3^- and XY_2^- anions in solution has been widely investigated by UV-vis spectrophotometry, by a variety of electrochemical techniques, and by solubility and two-phase distribution measurements.¹ In aqueous solution, the stability constants are in the order $I_3^- > Br_3^- > Cl_3^-$, but this order is reversed in aprotic organic solvents; in addition, the latter values are solvent dependent and are higher than those in aqueous solution by several orders of magnitude.

Since there is little direct evidence on the species present in solutions of polyhalides, the interpretation of spectroscopic and other investigations has largely depended on analogies with known solid state structures. We now report studies of a variety of solutions containing X_3^- , X_2Y^- and related anions, using electrospray ionisation mass spectrometry (ESI-MS). With one exception (see below), instrumental limitations, related to the possible corrosion of the instrument, restricted the work to anions derived from elemental iodine.

Experimental

General

Iodine, salts of alkali metals and substituted ammonium cations were Reagent Grade, and were used as supplied. Stock solutions in either water or acetonitrile were prepared gravimetrically, and diluted as appropriate. An aqueous solution of I_2 was prepared by equilibrating the solid with water at room temperature over several days, and then carefully collecting the solution phase. Acetonitrile was used without further purification.

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Mass spectrometry

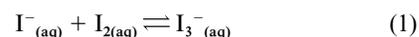
Mass spectra were collected using a Micromass Quattro LC triple quadrupole instrument. The nebuliser tip was set at 3100 V and 100 °C, and nitrogen was used as the bath gas. Samples were introduced directly to the source at 2–4 $\mu\text{L min}^{-1}$ via a syringe pump. The cone voltage was set at 20 V in order to minimise fragmentation. The MS/MS experiment was carried out using argon as the collision gas.

Results and discussion

Aqueous solutions

(i) **Aqueous iodine.** A saturated solution of I_2 (concentration at 25 °C = 1.33 mM, following Ramette and Sandford)⁶ gave an ESI mass spectrum in which I^- was the only detectable iodine species. A repeat spectrum taken 2 months later showed additional traces (<3%) of I_3^- and I_2^- (see below), but neither IO^- nor IO_3^- was detected, showing that hydrolysis was negligible over this length of time.

(ii) **Aqueous $I_2 + KI$.** The system



is amongst the most frequently studied of aqueous phase equilibria, with a history of publications (see ref. 1) going back about 100 years.⁷ The results obtained by a variety of experimental methods have been reviewed by Popov,¹ and for the present purposes we use the thermodynamic parameters obtained by Daniele;⁸ K_3 at 298 K = 723, $\Delta H^\circ = -19.9 \pm 1.7$ kJ mol⁻¹. Experiments involving distribution or solubility measurements necessarily involve higher concentrations than do spectroscopic studies, and there are marked deviations from these values under such conditions, and this has been attributed to the competing formation of higher species.^{5,9} We return to this point below.

Fig. 1 is a typical negative ion ESI-MS over the range $m/z = 200$ –700 from an aqueous solution of $I_2 + I^-$, molar ratio 1 : 9. The dominant features correspond to I^- (not shown), I_2^- (or I_4^{2-} ; see below) and I_3^- , together with KI_2^- and $K_2I_3^-$. The assignments are based on m/z values, and on comparison of the peak pattern with that calculated from the known isotopic composition. Similar spectra were obtained over a wide range of mole ratios of 1 : 90 – 1 : 09, with no qualitative change in the species detected. Substitution of Et_4NI for KI caused no

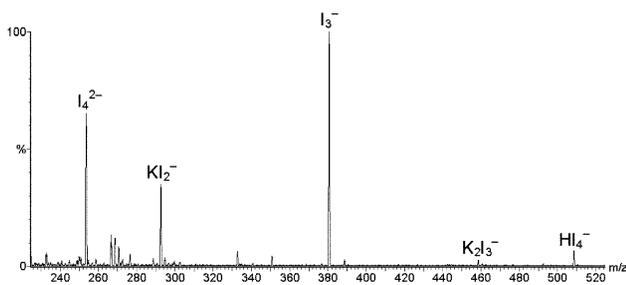


Fig. 1 ESI-MS of an aqueous solution of I_2 (0.56 mM) + KI (5 mM), over the range $m/z = 200$ –700.

change in the $I^-/I_2^-/I_3^-$ portion of the spectrum. The appearance of cluster ions of the type $[M_nX_{n+1}]^-$ in solutions of alkali metal salts MX is a well-studied phenomenon,¹⁰ and such clusters are in fact often used to calibrate mass spectra,¹¹ aggregates of quaternary ammonium cations form in analogous fashion.¹² Of special interest is the highest species observed in this experiment at $m/z = 508.6$, unambiguously identified as HI_4^- , the protonated form of the I_4^{2-} anion.

In the first place, these results confirm the reality of eqn. (1), if such confirmation be needed, but more importantly raise other issues. The first concerns the existence in aqueous solution of I_5^- , which has been postulated to explain deviations from the ideality of eqn. (1) at high iodide concentrations. Partial support for this comes from the existence of crystalline salts of this anion,¹³ whose structure can be described as $[I(I_2)_2]^-$. The processes by which this might be formed in aqueous solution are either



or



each of which implies the co-existence of I_2 and either I^- or I_3^- . These seem unlikely circumstances, since the presence of excess KI (e.g. 0.5 M KI + 0.67 mM I_2) must cause the formation of I_3^- by eqn. (1), thereby lowering the concentration of I_2 . The derived equilibrium constant⁶ for eqn. (3) is ca. 10, much smaller than K_3 (see above), and hence formation of I_5^- by either eqn. (2) or (3) should be decreasingly probable with increasing iodide concentration. In fact, the formation of I_5^- should be favoured by the co-existence of both I_2 and I_3^- , a situation which holds only at low I^- concentrations. Fig. 2

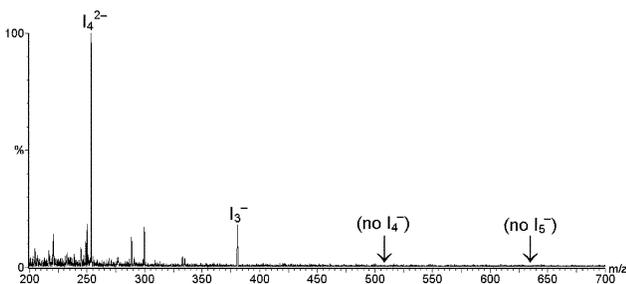


Fig. 2 ESI-MS of an aqueous solution of I_2 (0.56 mM) + KI (0.05 mM).

shows the ESI-MS of a solution in which the initial $I_2 : I^-$ mole ratio was 1 : 9. Calculations using $K_3 = 723$ for eqn. (1), and the constant $K_5 = 10$ suggested by Ramette and Sandford,⁶ show that the equilibrium concentrations should be $[I_3^-] \sim 1.5 \times 10^{-5}$ M, and $[I_5^{2-}] \sim 10^{-7}$ M. The spectrum in Fig. 2 shows no evidence of I_5^{2-} ($m/z = 634.5$) even at this calculated ratio of $[I_5^{2-}] : [I_3^-] \sim 0.02$, and we therefore conclude that the deviations found by Davies and Gwynne⁹ cannot be explained in terms of I_5^{2-} .

We suggest that the presence of the peak with $m/z = 253.8$ in the ESI-MS offers a more probable explanation for the deviations from ideality observed by Davies and Gwynne,⁹ Ramette and Sandford,⁶ and earlier workers.⁴ This anion is identified as I_4^{2-} , rather than I_2^- . Since iodine is mono-isotopic, it is not possible to distinguish between these species mass-spectrometrically.

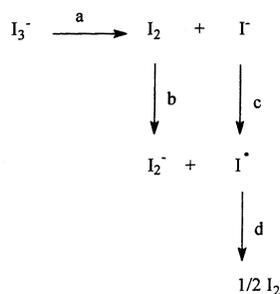
It is first necessary to eliminate the formation of I_2^- by the ionisation of I_2 in the collector core of the mass spectrometer. Such a process is possible in principle; the electron affinity of I_2 has been estimated¹⁴ at $+164 \pm 50$ kJ mol⁻¹, but the absence of the $m/z = 253.8$ peak in the ESI-MS of an aqueous solution of I_2 argues against this. Another route to I_2^- in the gas phase might be



The energetics of eqns. (4) + (5) can be estimated from the sequence in Scheme 1 from which ΔE for the overall process



is $+213$ kJ mol⁻¹. There is no energy source of this magnitude in the ESI-MS experiment, and taken with the above arguments, we conclude that the peak at $m/z = 253.8$ is that of I_4^{2-} . The presence of HI_4^- in aqueous I_2/KI solutions (Fig. 1) confirms this identification.



All species in the gas phase. Numerical values (in kJ mol⁻¹), and references:

a. Dissociation energy of I_3^-	+157	ref. 5
b. (-) Electron affinity of I_2	+164	ref. 14
c. (-) Electron affinity of I	-295	ref. 4
d. (1/2) Bond energy of I_2	-75	ref. 4

Scheme 1

The presence of the I_4^{2-} ion in aqueous solutions of I^- and I_3^- was suggested some time ago by French and Effenberger¹⁵ to explain their spectrophotometric results for this system, and by Genser and Connick¹⁶ from NMR studies of solution phase exchange processes. In the present work, the ESI-MS of all $I_2/I^-/I_3^-$ solutions showed the peak at $m/z = 253.8$ only when both I_3^- and I^- were present, and only with aqueous solutions. Salts of I_4^{2-} have been structurally characterised;^{17,18} in each case, the anion is linear, and one result¹⁷ gives almost constant I–I bond distances [3.17 ± 0.84 (av.) Å], close to that calculated for I_3^- ($r = 3.14$ Å) by Hoffmann *et al.*⁵

The equilibrium



will obviously be favored in solutions of relatively high $[I^-]$, and we have explored the possibility that the results reported by Davies and Gwynne⁹ can be explained by the presence of the

Table 1 Re-calculation of results on the equilibrium $I_2 + I^- = I_3^-$, from ref. 9

Expt. in Table I of ref. 9	$[I^-]_{\text{total}}/M$	K_3'	$[I_4^{2-}]/M$	K_4
1	1.069	1287	Negative value	—
2	1.059	1086	0.27	23 (!)
3	1.059	1058	0.064	0.67
4	1.039	954	0.065	0.66
5	1.032	906	0.035	0.35
6	1.014	863	0.013	0.18
7	1.008	798	0.0019	0.45
8	1.004	784	3.94×10^{-4}	0.23
9	0.101	791	Negative value	—
10	0.1002	773	5.03×10^{-4}	0.48

I_4^{2-} anion, rather than I_5^- or I_6^{2-} . If the dissolution of I_2 in aq. KI leads to the formation of I_3^- and I_4^{2-} , their values for $[I_3^-]$ should be corrected to

$$[I_3^-] = [I_3^-]' - [I_4^{2-}] \quad (8)$$

where $[I_3^-]'$ represents the reported concentration of I_3^- . Equally, their values of concentration of I^- are too high by the quantity $2[I_4^{2-}]$, since

$$[I^-]_{\text{total}} = [I^-]' + [I_3^-] + 2[I_4^{2-}] \quad (9)$$

One can then write

$$K_3 = \frac{([I_3^-]' - [I_4^{2-}])}{[I_2]([I^-]' - 2[I_4^{2-}])} \quad (10)$$

where $[I_3^-]'$ and $[I^-]'$ are the experimental values in Table I of the paper by Davies and Gwynne. For internal consistency, we have taken the value $K_3 = 767$ at 25 °C from this paper. The results of these calculations are shown in Table 1, in which K_3' is the uncorrected experimental value found in ref. 9, and K_4 is the equilibrium constant for eqn. (7). The average value of K_4 (ignoring the value $K_4 = 23$) is 0.43 ± 0.13 . By way of comparison, French and Effenberger report $K_4 = 0.184$ in 2 M KNO_3 .¹⁵

The spread of the derived values for K_4 is not surprising; a feature of the calculation is that the subtraction of two similar numbers (in the order of 0.5 M) to give a concentration of I_4^{2-} in the order of 0.01 M or less, and this obviously introduces a large uncertainty into the final value of K_4 . It should also be noted that Table I of ref. 10 appears to contain some misprints, since K_3' cannot always be derived from the experimental results reported. Finally, we note that the experiments at the highest $[I^-]_{\text{total}}$ give either a negative value for $[I_4^{2-}]$, or an unacceptably high value, which may be evidence of the presence of yet further species in addition to I^- , I_3^- and I_4^{2-} in such solutions. This concentration region is not accessible to investigation by ESI-MS under the conditions available to us.

(iii) Aqueous $I_2 + KCl, KBr$. These two systems are conveniently considered together. Fig. 3 is a typical ESI-MS, in this

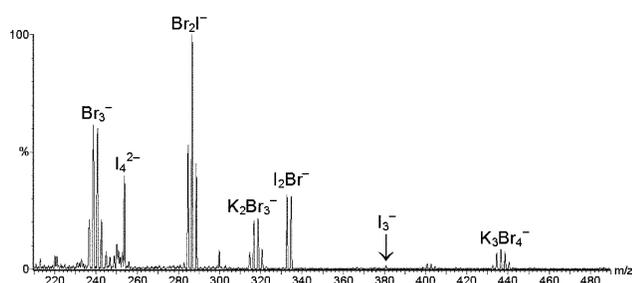
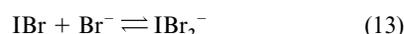


Fig. 3 ESI-MS of an aqueous solution of I_2 (0.56 mM) + KBr (0.25 mM).

case of saturated $I_2 + KBr$ (mole ratio $I_2 : Br = 1 : 446$); in addition to Br^- and I^- (not shown), the spectrum identifies the presence of Br_3^- , Br_2I^- , I_2Br^- and I_3^- , together with $[K_nBr_{n+1}]^-$ clusters up to $n = 3$; each of these assignments was confirmed by matching with the calculated isotopic distribution. An analogous $I_2 + KCl$ mixture had peaks from $I^- > ICl_2^- > I_2Cl^- > I_3^-$ in the intensity order shown.

The reactions which can lead to these results, as exemplified by the I_2/Br^- system, are of the type

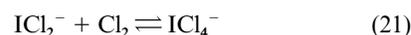


and the overall effect is to establish the series $X_3^- \rightleftharpoons X_2Y^- \rightleftharpoons XY_2^- \rightleftharpoons Y_3^-$. Such redistribution processes, rapid on the time scale of this work, are common in main group solution chemistry. It is unnecessary to identify such processes as redox reactions, as other authors have done,^{1,2,19} and we return to this point in more detail for the I_2 /thiocyanate system. It is equally inappropriate, in the light of the ESI-MS results, to consider the dissociation of an XY_3^- polyhalide anion in terms of a single process



since the solution equilibria are more complicated than this, as set out in eqns. (11)–(15). The nature of the ESI-MS analysis does not allow any quantification of these equilibria.

(iv) Aqueous I_2/KCl ; the ICl_4^- anion. An unexpected feature of the ESI-MS of $I_2 + 0.5$ M KCl was a series of peaks centred at $m/z = 268.7$, identified by the isotopic composition as being ICl_4^- . The presence of this iodine(III) species, which was not apparently identified in previous work on I_2/Cl^- systems clearly, demonstrates the oxidation of I_2 , and we tentatively suggest the sequence (*cf.* eqns. 11, 12 and 14)

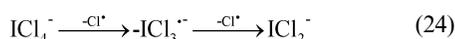


The thermal stability of crystalline salts of ICl_4^- has been studied by Smyth and Culter²⁰ who have reviewed earlier work on these compounds. The dissociation vapour pressure over the

temperature range 35–90 °C was interpreted in terms of the decomposition processes



which correspond to the solution processes (21) + (20). In contrast, Caglioti and Centola²¹ reported that dissociation gives KCl directly without the intermediate formation of KICl₂. Fig. 4 shows that the decomposition of [I(³⁵Cl)₄]⁻ under the conditions of ESI-MS goes by the sequence



while a corresponding study of ICl₂⁻ demonstrated that this ion is stable under analogous conditions. These results confirm reaction (22), although the loss of Cl₂ is identified as involving successive elimination of two chlorine atoms rather than of Cl₂. The radical anion ICl₃^{•-} has not been identified previously, although the neutral analogue ICl₃ is well known.^{2,4}

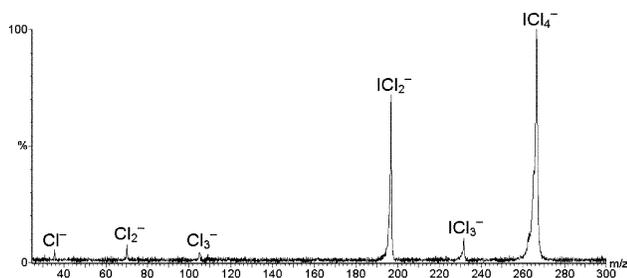
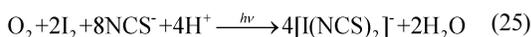


Fig. 4 ESI-MS study of the decomposition of [I(³⁵Cl)₄]⁻.

(v) **Aqueous I₂ + KNCS.** As with the halide anions, the addition of excess aqueous KNCS solution (0.1 M) to I₂ gives rise to an ESI-MS in which a series of [K_n(NCS)_{n+1}]⁻ anions accompany the species [I(NCS)₂]⁻ and [I₂(NCS)]⁻. There is no evidence of I₃⁻ and very little of the ion at m/z = 253.8, but the presence of I⁻ indicates the reduction of I₂ by NCS⁻, a known reaction.²

Both [I(NCS)₂]⁻ and [I₂(NCS)]⁻ have been identified spectrophotometrically by Skoog and Long,^{22,23} the latter was formulated as the 1 : 1 adduct of I₂ and NCS⁻, but the formation of [I(NCS)₂]⁻ was attributed²¹ to the photochemically initiated redox reaction.



We do not believe that it is necessary to invoke such processes, given the evidence of redistribution reactions in I₂X⁻ systems (see above), and the identification of both anionic species in non-aqueous solution. It is also worth noting that attempts to prepare salts of [I(NCS)₂]⁻ gave a mixture of this and [I₂(NCS)]⁻ derivatives,²⁴ in keeping with the proposed facile redistribution processes.

(vi) **Aqueous I₂ + other anions.** We also investigated the possible interaction of I₂ with other pseudohalides (NCO⁻, N₃⁻), and with NO₂⁻ and OH⁻, but in no case were I₂X⁻ or IX₂⁻ adducts detected. The anion I₂OH⁻ has been invoked in discussions of the kinetics of the reaction of I₂ with H₂O in alkaline solution;²⁵ it is possible that this anion is sufficiently hydrophilic to be undetectable under the conditions of the ESI-MS experiment.

Acetonitrile solutions

(i) **Iodine.** The only anions detected in the ESI-MS of a solution of I₂ in CH₃CN (1 mM) were I₃⁻ (100%) and I⁻ (10%),

with essentially no (<1%) peak at m/z = 253.8. We argue above that this species is only found when both I₃⁻ and I⁻ are present in solution, but in this case the presence of I₃⁻ and I⁻ ions may be the result of trace amounts of I⁻ present either in the mass spectrometer or in the iodine sample. The sensitivity of the instrument is such that it can detect extremely low concentrations of charged species, and the ion current observed in this spectrum was several orders of magnitude lower than that observed in samples with added X⁻.

(ii) **I₂ + I⁻.** A mixture of I₂ and Et₄NI (approx. 1 mM in each) showed a strong peak for I⁻, and much weaker features for I₃⁻ (~10%) and [Et₄N·I₂]⁻ (~5%). There was no detectable intensity at m/z = 253.8, and no anions higher than I₃⁻. This is readily understandable; the stability constant for eqn. (1) in acetonitrile has been found to be in the order of 10⁷, so that under the experimental conditions I₂ is essentially completely consumed and only I₃⁻ and excess I⁻ are present.^{26–28}

(iii) **I₂ + Cl⁻, Br⁻.** A solution of equimolar (~1 mM) I₂ and BzEt₃NCl in CH₃CN gave the ESI-MS shown in Fig. 5. The

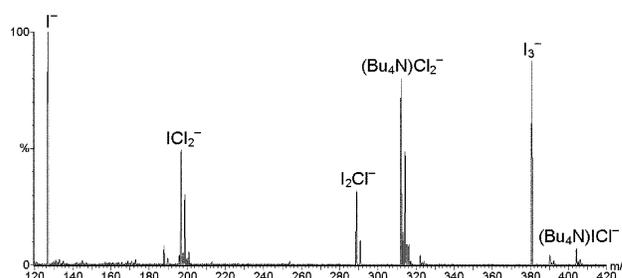


Fig. 5 ESI-MS of a solution of I₂ + BzEt₃NCl (each ~ 1 mM) in acetonitrile.

series I₃⁻ – I₂Cl⁻ – ICl₃⁻ is apparent, as are [BzEt₃NCl₂]⁻, and [(BzEt₃N)₂Cl₃]⁻; I⁻ is also detected but there is no intensity at m/z = 253.8. The anion ICl₄⁻ (m/z = 268) is apparently absent. Similar results were found from a solution of I₂ + Bu₄NBr, with I⁻, I₂Br⁻ and I₃⁻ being detected, together with [Bu₄NBr₂]⁻.

(iv) **I₂ + NCS⁻.** Fig. 6 confirms that an acetonitrile solution of I₂ + Bu₄NNCS contains both [I(NCS)₂]⁻ and [I₂(NCS)]⁻, together with I₃⁻ and I₃, in agreement with the results from the corresponding aqueous solution.

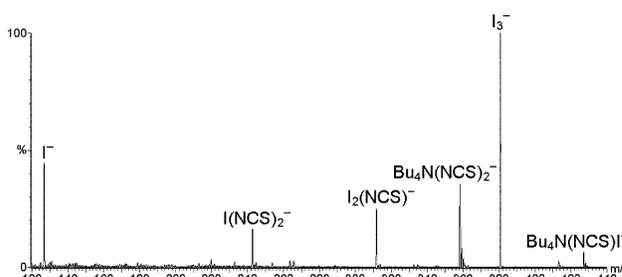


Fig. 6 ESI-MS of a solution of I₂ + Bu₄NNCS (each ~ 1 mM) in acetonitrile.

(v) **Br₃⁻.** The ESI-MS of a dilute solution of n-Bu₄NBr₃ in acetonitrile showed Br₃⁻ as the only significant anion in the region m/z > 100, together with traces of Bu₄NBr₂⁻; there was no evidence of higher species such as Br₄²⁻. When Cl⁻ (in the form of BzMe₃NCl) was added to this solution, the ions Cl₃⁻, BrCl₂⁻ and Br₂Cl⁻ were also observed, together with the appropriate anionic cluster derivatives of Bu₄N⁺ and BzMe₃⁺.

General conclusions

Electrospray ionisation mass spectrometry is clearly a very useful technique for identifying the anionic species present in aqueous and non-aqueous solutions containing I_2 and various halide and pseudohalide salts. The results show that in each case I_2X^- and IX_2^- ($X = Cl, Br, NCS$) species co-exist, being formed by redistribution processes; redox and/or photochemically induced reactions need not be invoked to explain this. Similar conclusions apply to the formation of Br_2Cl^- and $BrCl_2^-$ from Br_3^- and Cl^- in acetonitrile. Although the ESI-MS results cannot yield quantitative information as to the speciation in such solutions, it is clear that the dissociation of I_2X^- species, and by extension of other XY_2^- anions, cannot be satisfactorily explained in terms of a single $XY_2^- \rightleftharpoons X^- + Y_2$ process, since the solutions in question contain both the products of the primary dissociation and those derived from the subsequent redistribution process.

This caveat is well exemplified by the identification of the ICl_4^- anion in aqueous solutions of $I_2 + KCl$. The decomposition to the hitherto unreported $ICl_3^{\cdot-}$ radical anion is another unusual feature of this system.

Finally, deviations from ideality in the I_2/I^- aqueous system at high I^- concentrations cannot be explained in terms of I_5^- (or I_6^-), for whose existence we find no evidence under conditions which should favour the formation of this anion. The observations of a significant species at $m/z = 253.8$, and of HI_4^- , show that this long-standing problem can be explained in terms of the formation of I_4^{2-} by the interaction of I_3^- and I^- at high ionic strength.

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