

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

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Received 15th August 2002, Accepted 20th November 2002

First published as an Advance Article on the web 9th December 2002

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.<sup>1-4</sup> The stable salts which have been prepared, and in many cases characterised crystallographically,<sup>4</sup> 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 Hoffmann<sup>5</sup> 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.<sup>1</sup> 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

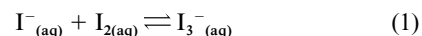
Mass spectra were collected using a Micromass Quattro LC triple quadrupole instrument. The nebuliser tip was set at 3100 V and 100 °C, and nitrogen was used as the bath gas. Samples were introduced directly to the source at 2–4  $\mu\text{L min}^{-1}$  via a syringe pump. The cone voltage was set at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

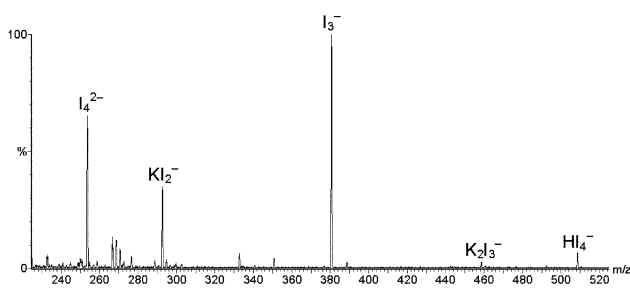
(i) **Aqueous iodine.** A saturated solution of  $I_2$  (concentration at 25 °C = 1.33 mM, following Ramette and Sandford)<sup>6</sup> gave an ESI mass spectrum in which  $I^-$  was the only detectable iodine species. A repeat spectrum taken 2 months later showed additional traces (<3%) of  $I_3^-$  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.<sup>7</sup> The results obtained by a variety of experimental methods have been reviewed by Popov,<sup>1</sup> and for the present purposes we use the thermodynamic parameters obtained by Daniele;<sup>8</sup>  $K_3$  at 298 K = 723,  $\Delta H^\circ = -19.9 \pm 1.7$  kJ  $\text{mol}^{-1}$ . 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.<sup>5,9</sup> 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  $\text{Et}_4\text{NI}$  for  $\text{KI}$  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,<sup>10</sup> and such clusters are in fact often used to calibrate mass spectra,<sup>11</sup> aggregates of quaternary ammonium cations form in analogous fashion.<sup>12</sup> 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.

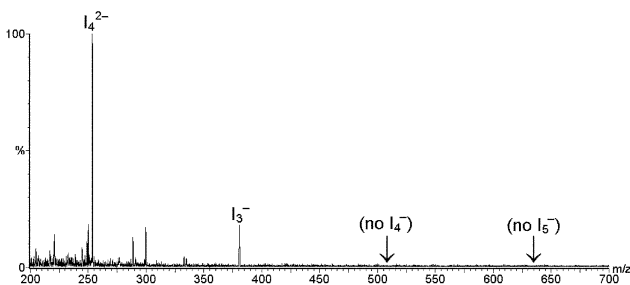
In the first place, these results confirm the reality of eqn. (1), if such confirmation be needed, but more importantly raise other issues. The first concerns the existence in aqueous solution of  $I_5^-$ , which has been postulated to explain deviations from the ideality of eqn. (1) at high iodide concentrations. Partial support for this comes from the existence of crystalline salts of this anion,<sup>13</sup> 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 constant<sup>6</sup> 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,<sup>6</sup> 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 Gwynne<sup>9</sup> 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,<sup>9</sup> Ramette and Sandford,<sup>6</sup> and earlier workers.<sup>4</sup> 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.

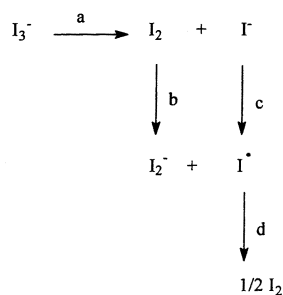
It is first necessary to eliminate the formation of  $I_2^-$  by the ionisation of  $I_2$  in the collector core of the mass spectrometer. Such a process is possible in principle; the electron affinity of  $I_2$  has been estimated<sup>14</sup> at  $+164 \pm 50$  kJ mol<sup>-1</sup>, but the absence 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  $\Delta E$  for the overall process



is  $+213$  kJ mol<sup>-1</sup>. 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<sup>-1</sup>), 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 Effenberger<sup>15</sup> to explain their spectrophotometric results for this system, and by Genser and Connick<sup>16</sup> 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;<sup>17,18</sup> in each case, the anion is linear, and one result<sup>17</sup> gives almost constant I–I bond distances [ $3.17 \pm 0.84$  (av.) Å], close to that calculated for  $I_3^-$  ( $r = 3.14$  Å) by Hoffmann *et al.*<sup>5</sup>

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 Gwynne<sup>9</sup> 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	$3.94 \times 10^{-4}$	0.23
9	0.101	791	Negative value	—
10	0.1002	773	$5.03 \times 10^{-4}$	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

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

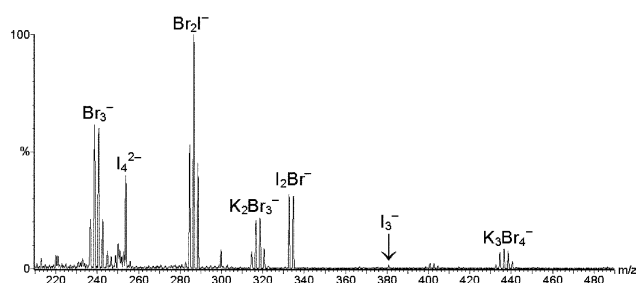
One can then write

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

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  $0.43 \pm 0.13$ . By way of comparison, French and Effenberger report  $K_4 = 0.184$  in 2 M  $KNO_3$ .<sup>15</sup>

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.

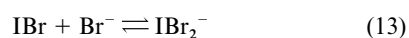
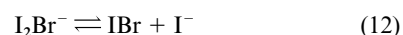
**(iii) Aqueous  $I_2 + KCl, KBr$ .** These two systems are conveniently considered together. Fig. 3 is a typical ESI-MS, in this



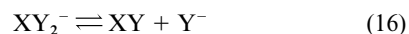
**Fig. 3** ESI-MS of an aqueous solution of  $I_2$  (0.56 mM) +  $KBr$  (0.25 mM).

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

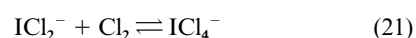
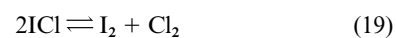


and the overall effect is to establish the series  $X_3^- \rightleftharpoons X_2Y^- \rightleftharpoons XY_2^- \rightleftharpoons Y_3^-$ . Such redistribution processes, rapid on the time scale of this work, are common in main group solution chemistry. It is unnecessary to identify such processes as redox reactions, as other authors have done,<sup>1,2,19</sup> 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



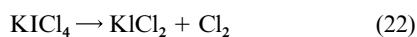
since the solution equilibria are more complicated than this, as set out in eqns. (11)–(15). The nature of the ESI-MS analysis does not allow any quantification of these equilibria.

**(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)

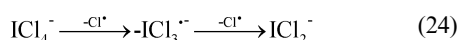


The thermal stability of crystalline salts of  $ICl_4^-$  has been studied by Smyth and Culter<sup>20</sup> who have reviewed earlier work on these compounds. The dissociation vapour pressure over the

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 Centola<sup>21</sup> reported that dissociation gives KCl directly without the intermediate formation of KICl<sub>2</sub>. Fig. 4 shows that the decomposition of [I(<sup>35</sup>Cl)<sub>4</sub>]<sup>-</sup> under the conditions of ESI-MS goes by the sequence



while a corresponding study of ICl<sub>2</sub><sup>-</sup> demonstrated that this ion is stable under analogous conditions. These results confirm reaction (22), although the loss of Cl<sub>2</sub> is identified as involving successive elimination of two chlorine atoms rather than of Cl<sub>2</sub>. The radical anion ICl<sub>3</sub><sup>•-</sup> has not been identified previously, although the neutral analogue ICl<sub>3</sub> is well known.<sup>2,4</sup>

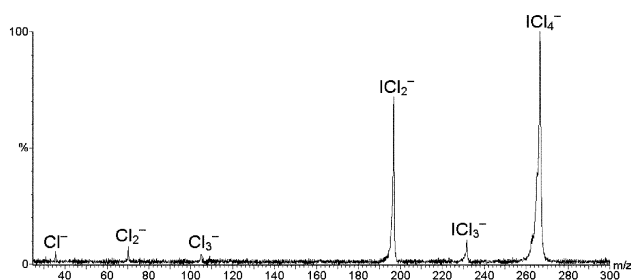
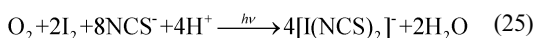


Fig. 4 ESI-MS study of the decomposition of [I(<sup>35</sup>Cl)<sub>4</sub>]<sup>-</sup>.

(v) **Aqueous I<sub>2</sub> + KNCS.** As with the halide anions, the addition of excess aqueous KNCS solution (0.1 M) to I<sub>2</sub> gives rise to an ESI-MS in which a series of [K<sub>n</sub>(NCS)<sub>n+1</sub>]<sup>-</sup> anions accompany the species [I(NCS)<sub>2</sub>]<sup>-</sup> and [I<sub>2</sub>(NCS)]<sup>-</sup>. There is no evidence of I<sub>3</sub><sup>-</sup> and very little of the ion at m/z = 253.8, but the presence of I<sup>-</sup> indicates the reduction of I<sub>2</sub> by NCS<sup>-</sup>, a known reaction.<sup>2</sup>

Both [I(NCS)<sub>2</sub>]<sup>-</sup> and [I<sub>2</sub>(NCS)]<sup>-</sup> have been identified spectrophotometrically by Skoog and Long,<sup>22,23</sup> the latter was formulated as the 1 : 1 adduct of I<sub>2</sub> and NCS<sup>-</sup>, but the formation of [I(NCS)<sub>2</sub>]<sup>-</sup> was attributed<sup>21</sup> 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 I<sub>2</sub>X<sup>-</sup> 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)<sub>2</sub>]<sup>-</sup> gave a mixture of this and [I<sub>2</sub>(NCS)]<sup>-</sup> derivatives,<sup>24</sup> in keeping with the proposed facile redistribution processes.

(vi) **Aqueous I<sub>2</sub> + other anions.** We also investigated the possible interaction of I<sub>2</sub> with other pseudohalides (NCO<sup>-</sup>, N<sub>3</sub><sup>-</sup>), and with NO<sub>2</sub><sup>-</sup> and OH<sup>-</sup>, but in no case were I<sub>2</sub>X<sup>-</sup> or IX<sub>2</sub><sup>-</sup> adducts detected. The anion I<sub>2</sub>OH<sup>-</sup> has been invoked in discussions of the kinetics of the reaction of I<sub>2</sub> with H<sub>2</sub>O in alkaline solution;<sup>25</sup> 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 I<sub>2</sub> in CH<sub>3</sub>CN (1 mM) were I<sub>3</sub><sup>-</sup> (100%) and I<sup>-</sup> (10%),

with essentially no (<1%) peak at m/z = 253.8. We argue above that this species is only found when both I<sub>3</sub><sup>-</sup> and I<sup>-</sup> are present in solution, but in this case the presence of I<sub>3</sub><sup>-</sup> and I<sup>-</sup> ions may be the result of trace amounts of I<sup>-</sup> 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<sup>-</sup>.

(ii) **I<sub>2</sub> + I<sup>-</sup>.** A mixture of I<sub>2</sub> and Et<sub>4</sub>NI (approx. 1 mM in each) showed a strong peak for I<sup>-</sup>, and much weaker features for I<sub>3</sub><sup>-</sup> (~10%) and [Et<sub>4</sub>N·I<sub>2</sub>]<sup>-</sup> (~5%). There was no detectable intensity at m/z = 253.8, and no anions higher than I<sub>3</sub><sup>-</sup>. This is readily understandable; the stability constant for eqn. (1) in acetonitrile has been found to be in the order of 10<sup>7</sup>, so that under the experimental conditions I<sub>2</sub> is essentially completely consumed and only I<sub>3</sub><sup>-</sup> and excess I<sup>-</sup> are present.<sup>26–28</sup>

(iii) **I<sub>2</sub> + Cl<sup>-</sup>, Br<sup>-</sup>.** A solution of equimolar (~1 mM) I<sub>2</sub> and BzEt<sub>3</sub>NCl in CH<sub>3</sub>CN gave the ESI-MS shown in Fig. 5. The

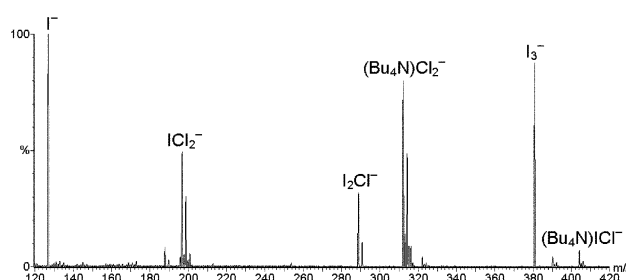


Fig. 5 ESI-MS of a solution of I<sub>2</sub> + BzEt<sub>3</sub>NCl (each ~ 1 mM) in acetonitrile.

series I<sub>3</sub><sup>-</sup> – I<sub>2</sub>Cl<sup>-</sup> – ICl<sub>3</sub><sup>-</sup> is apparent, as are [BzEt<sub>3</sub>NCl<sub>2</sub>]<sup>-</sup>, and [(BzEt<sub>3</sub>N)<sub>2</sub>Cl<sub>3</sub>]<sup>-</sup>; I<sup>-</sup> is also detected but there is no intensity at m/z = 253.8. The anion ICl<sub>4</sub><sup>-</sup> (m/z = 268) is apparently absent. Similar results were found from a solution of I<sub>2</sub> + Bu<sub>4</sub>NBr, with I<sup>-</sup>, I<sub>2</sub>Br<sup>-</sup> and I<sub>3</sub><sup>-</sup> being detected, together with [Bu<sub>4</sub>NBr<sub>2</sub>]<sup>-</sup>.

(iv) **I<sub>2</sub> + NCS<sup>-</sup>.** Fig. 6 confirms that an acetonitrile solution of I<sub>2</sub> + Bu<sub>4</sub>NNCS contains both [I(NCS)<sub>2</sub>]<sup>-</sup> and [I<sub>2</sub>(NCS)]<sup>-</sup>, together with I<sub>3</sub><sup>-</sup> and I<sub>3</sub>, in agreement with the results from the corresponding aqueous solution.

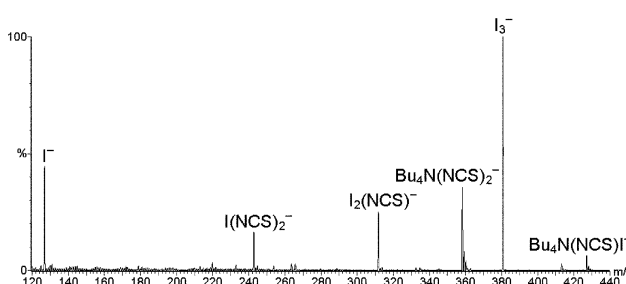


Fig. 6 ESI-MS of a solution of I<sub>2</sub> + Bu<sub>4</sub>NNCS (each ~ 1 mM) in acetonitrile.

(v) **Br<sub>3</sub><sup>-</sup>.** The ESI-MS of a dilute solution of n-Bu<sub>4</sub>NBr<sub>3</sub> in acetonitrile showed Br<sub>3</sub><sup>-</sup> as the only significant anion in the region m/z > 100, together with traces of Bu<sub>4</sub>NBr<sub>2</sub><sup>-</sup>; there was no evidence of higher species such as Br<sub>4</sub><sup>2-</sup>. When Cl<sup>-</sup> (in the form of BzMe<sub>3</sub>NCl) was added to this solution, the ions Cl<sub>3</sub><sup>-</sup>, BrCl<sub>2</sub><sup>-</sup> and Br<sub>2</sub>Cl<sup>-</sup> were also observed, together with the appropriate anionic cluster derivatives of Bu<sub>4</sub>N<sup>+</sup> and BzMe<sub>3</sub><sup>+</sup>.

## 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.

## Acknowledgements

One of us (D. G. T.) gratefully acknowledges financial support from the Royal Society of Chemistry for a Journals Grant. Thanks are also due to Newnham and Trinity Colleges, Cambridge for a college lectureship (J. S. M.).

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