

The energetics of the $X_2 + X^- \rightarrow X_3^-$ equilibrium ($X = \text{Cl, Br, I}$) in aqueous and nonaqueous solution

Evan Crawford, J. Scott McIndoe, and (the late) Dennis G. Tuck

Abstract: The magnitude of the stability constants (K) for the formation of X_3^- from X^- and X_2 ($X = \text{Cl, Br, I}$) in aqueous and nonaqueous solution depends strongly on both X and solvent. Thermodynamic arguments establish that for aqueous solutions this is not the result of differing bond strengths in the X_3^- anion but rather depends on the solvation energies of the relevant anions and halogens. The experimental results for K in different organic solvents can also be rationalized in terms which emphasise solvation effects. Electrospray ionization mass spectrometry (ESI-MS) has been used to qualitatively probe relative bond strengths in the absence of solvent.

Key words: trihalides, stability constants, solvation, electrospray ionization, mass spectrometry.

Résumé : En solutions aqueuses ou non aqueuses, l'amplitude des constants de stabilité (K) pour la formation de X_3^- à partir de X^- et X_2 ($X = \text{Cl, Br, I}$) dépend fortement de la nature de X ainsi que de celle du solvant. Des arguments thermodynamiques permettent d'établir que, dans les cas de solutions aqueuses, cette situation ne résulte pas de différences dans les forces de liaison dans l'anion X_3^- , mais plutôt des énergies de solvation des anions et des halogènes appropriés. Les résultats expérimentaux pour les valeurs de K dans divers solvants organiques peuvent aussi être rationalisés en fonction d'effets qui mettent l'accent sur la solvation. On a utilisé la spectrométrie de masse avec ionisation par électronébulisation pour évaluer qualitativement les forces relatives des liaisons en absence de solvant.

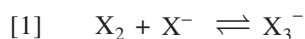
Mots clés : trihalogénures, constantes de stabilité, solvation, ionisation par électronébulisation, spectrométrie de masse.

[Traduit par la Rédaction]

Introduction

Many polyhalide anions have been characterized in recent years and the X_3^- ions ($X = \text{Cl, Br, I}$) have been the focus of special interest. Over the last 100 years, many different techniques have been used in attempts to establish reliable values for the equilibrium constant for the formation of these ions in aqueous and nonaqueous solutions. The related X_2Y^- anions ($X \neq Y = \text{Cl, Br, I, SCN}$) are also known and their dissociative and redistribution equilibria in solution have been investigated (1).

One feature which has aroused interest is that in aqueous solution the equilibrium constants for



$$[2] \quad K_3 = \frac{[X_3^-]}{[X_2][X^-]}$$

are in the order $\text{I} > \text{Br} > \text{Cl}$, which has prompted speculation about the bonding in the X_3^- anions. A second point is that in nonaqueous solvents this order is reversed and the numerical values are all higher by several orders of magnitude. A recent paper by Landrum et al. (2) has shown that there is, in fact, little difference between the bonding energies in the three trihalide ions ($X = \text{Cl, Br, I}$) and these results form the basis of a satisfactory analysis of those factors that do affect the value of K_3 in different solvents.

The present paper addresses the energetics of the $X_2 + X^- \rightarrow X_3^-$ equilibrium in three related ways. In the first place, we show that the value reported by Landrum et al. (2) for the binding energy of I_3^- is compatible with related experimental values; secondly, we compare this and other calculated binding energies for X_3^- and X_2Y^- anions ($X \neq Y = \text{Cl, Br, I}$) with mass spectrometric determinations of the decomposition potential; and finally, the effect of solvent on the stability constants of the X_3^- anions is discussed in terms of the relevant solvation parameters.

The bonding energy of I_3^- (g)

The bonding in the X_3^- anions has been the subject of a number of theoretical treatments prompted by the fact that X^- , X_2 , and X_3^- are all closed shell species. Landrum et al. (2) have reviewed previous attempts at estimating the bonding energy for



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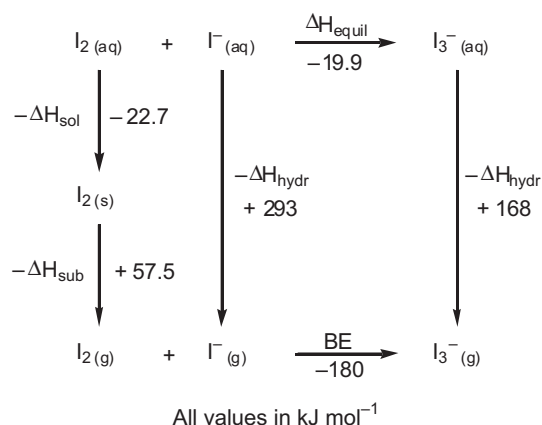
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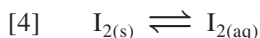
Table 1. Thermodynamic parameters in the $X_2 + X^- \rightarrow X_3^-$ cycle (in kJ mol^{-1}) (Scheme 1).

	Cl	Br	I	Reference
$\Delta EB(X_3^-(g))$	-164	-166	-180	2, and text
$\Delta H_f^\circ(X_{2(g)})$	0	29.6	57.5	1b, 1c
$\Delta H_{\text{soln}}(X_{2(g)})$	23.3	2.6	22.7	1b, 1c
$\Delta H_{\text{hydr}}(X^-(g))$	-368	-335	-293	7
$\Delta H^\circ_{\text{equil}}$	~8	-12.8	-19.9	4, 9, 10
$\Delta H_{\text{hydr}}(X_3^-(g))$	-225	-210	-168	7, 16, and text
$\Delta H[X_{2(s)} \rightarrow X_{2(aq)}]$	23.3	32.2	80.2	—
$\Delta H_{\text{hydr}}(X^-) - \Delta H_{\text{hydr}}(X_3^-)$	-143	-125	-125	—

Scheme 1.

for which a range of values have been proposed. Their calculations give -164 , -166 , and -157 kJ mol^{-1} for Cl_3^- , Br_3^- , and I_3^- , respectively, and this small range of values immediately emphasizes that factors other than bond energy must affect the value of K_3 . The authors comment on the lack of experimental data against which these numbers can be tested. Fortunately, it is possible to obtain a value for the iodine system from published information and this provides a starting point for the present discussion. The appropriate thermodynamic cycle is shown in Scheme 1.

The thermodynamic parameters for the formation of I_3^- in aqueous solution (eq. [1], $X = \text{I}$) have been studied by several authors using a variety of experimental techniques, and the results have been reviewed by Ramette and Sandford (3) who recommend the spectrophotometric results of Daniele (4), namely $K_3 = 723$ at 25°C , $\Delta H^\circ = -19.9 \text{ kJ mol}^{-1}$, $\Delta G^\circ = -16.3 \text{ kJ mol}^{-1}$, $\Delta S^\circ = -12.0 \text{ J K}^{-1} \text{ mol}^{-1}$. These values are used in Scheme 1 and later. The enthalpy of solution of I_2 in water reported by Ramette and Sandford is $\Delta H^\circ = +22.7 \text{ kJ mol}^{-1}$ for



with $\Delta G^\circ = +16.4 \text{ kJ mol}^{-1}$. Earlier studies by Davies and Gwynne (5) gave $\Delta H^\circ = +25.7 \text{ kJ mol}^{-1}$; the lower value is used in Scheme 1. The standard enthalpy of formation of $\text{I}_{2(g)}$ (i.e., ΔH_{sub}) is $+57.5 \text{ kJ mol}^{-1}$. The thermodynamics of the hydration of ions has been reviewed by Marcus (6); the work of Halliwell and Nyburg (7) gives values for the halide

ions and for I_3^- ($\Delta H_{\text{hydr}}(\text{I}^-) = -293 \pm 4 \text{ kJ mol}^{-1}$, $\Delta H_{\text{hydr}}(\text{I}_3^-) = -168 \pm 20 \text{ kJ mol}^{-1}$).

The resultant value for the dissociation energy of I_3^- is 180 kJ mol^{-1} , ca. 8% higher than the 157 kJ mol^{-1} calculated by Landrum et al. (2). The largest experimental uncertainties are in the enthalpies of hydration; any errors related to the fact that these necessarily depend on $\Delta H^\circ_{\text{hydr}}$ of the proton fortunately cancel in the summation around the cycle. The largest uncertainty in the calculation of the bond energy relates to the size of the basis set and to possible relativistic effects.³ In general, the agreement between the two approaches seems satisfactory.

Equilibrium constants in aqueous solution

As noted earlier, there is a wide range of values for K_3 in contrast to the calculated bond energies. For $X = \text{I}$, the value quoted (4) earlier is $K_3 = 723$. For $X = \text{Br}$, Dubois and Garnier (8) found $K_3 = 16.3$ at 25°C , in good agreement with an earlier result (1a), which gave $\Delta H = -12.8 \text{ kJ mol}^{-1}$. The corresponding values (9) for $X = \text{Cl}$ are $K_3 = 0.191 \pm 0.016$ and $\Delta H = -8 \text{ kJ mol}^{-1}$, again in keeping with earlier investigation (1a, 10) of this experimentally difficult system.

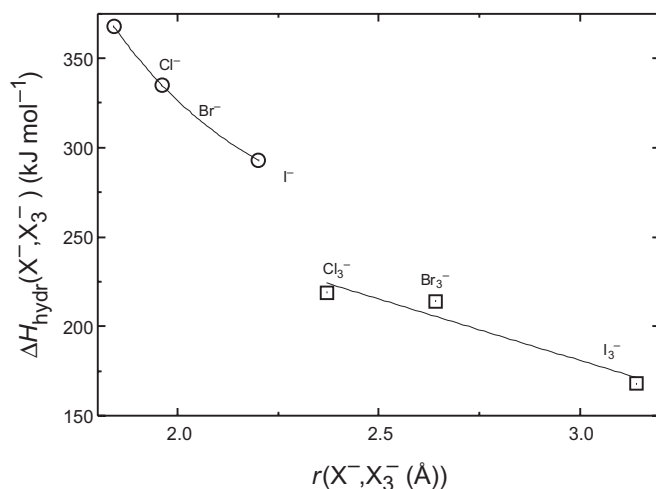
To identify the reasons for the differences in K_3 , it is necessary to use the hydration enthalpies of Cl^- and Br^- and the enthalpies of solutions of $\text{Cl}_{2(g)}$ and $\text{Br}_{2(g)}$, which are available from the sources used for iodine. The corresponding terms for Cl_3^- and Br_3^- are not available and so must be estimated, which can be done by using a cycle analogous to that in Scheme 1, but now relying upon the calculations of Landrum et al. (2) for the Cl_3^- and Br_3^- dissociation energies. The relevant numerical values are shown in Table 1 and the appropriate summation leads to $\Delta H_{\text{hydr}}(\text{Cl}_3^-(g)) = -219 \text{ kJ mol}^{-1}$ and $\Delta H_{\text{hydr}}(\text{Br}_3^-(g)) = -214 \text{ kJ mol}^{-1}$. The size dependence of the resultant ΔH_{hydr} for X_3^- is shown in Fig. 1, using the calculated $X-X$ distances as a measure of ionic size; the analogous values for X^- are plotted against $r(X^-)$ for comparison.

The value for $\Delta H_{\text{hydr}}(\text{Cl}_3^-)$ appears to be lower than one would predict from Fig. 1 and this may well be related to the large uncertainty in ΔH_{equil} for the formation of $\text{Cl}_3^-(aq)$. In what follows, we assume the values of the enthalpy of hydration to be -168 , -210 , and -225 kJ mol^{-1} for I_3^- , Br_3^- , and Cl_3^- , respectively, derived from Fig. 1.

Table 1 makes it immediately obvious that the $X_3^-(g)$ bonding energies are not the dominant terms determining the

³Private communications from Prof. Hoffmann and Dr. Goldberg.

Fig. 1. Size dependence of ΔH_{hydr} for X^- (circles) and X_3^- (squares) anions ($X = \text{Cl}, \text{Br}, \text{I}$).



value of $\Delta H_{\text{equil}}^{\circ}$ for eq. [1]. The derived parameters given in the last two lines of this Table show that while the differences between the enthalpy of hydration of $X^-_{(g)}$ and $X_3^-_{(g)}$ are similar, there is a much larger variation in the enthalpy of solution of the elements from their standard states. In sum, the important enthalpy terms relate to the solution and hydration of the various solute species and do not reflect differences in the bond energy of the X_3^- anions.

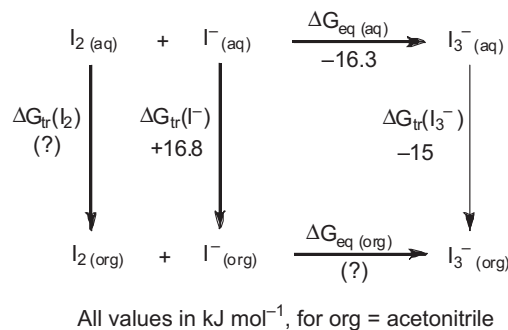
This last conclusion is relevant to the purported estimate of the stability of X_3^- based on the thermal stabilities of crystalline $M^+X_3^-$ salts (ref. 1a, p. 241). These results are better understood as a reflection of the different lattice energies of the salts in question and must depend only slightly on the bond energy of X_3^- . Equally, they can have little to do with the symmetry of the cation involved (ref. 1b) other than to the extent that this affects the lattice energy.

Comparison of aqueous and nonaqueous solutions

As noted earlier, K_3 is substantially larger for all three trihalide anions in nonaqueous solutions, and in the order $\text{Cl} > \text{Br} > \text{I}$. It is immediately obvious from the previous discussion that neither of these conclusions can be the result of bond energy factors and therefore it is incumbent to examine the solvation energies involved. As in the aqueous solution case, the I_3^- equilibrium is the only case for which adequate data are available and these are free energy rather than enthalpy values. A comparison of aqueous and nonaqueous systems can be made through the cycle shown in Scheme 2.

Where the numerical values refer to acetonitrile, Nelson and Iwamoto (11) have measured K_3 for Cl , Br , and I^- in this and other polar solvents and we use their value of $\log K_3 = 6.6$ for the formation of I_3^- . The free energy of transfer of I^- from H_2O to CH_3CN is given as $+16.8 \text{ kJ mol}^{-1}$ by Marcus (6) and the corresponding ΔG_{tr} for I_3^- is -15 kJ mol^{-1} . There appears to be no direct measurement of $\Delta G_{\text{tr}}(\text{I}_2)$ from aqueous solution to acetonitrile, but Hildebrand et al. (12) have published an extensive set of values for the solubility of I_2 in organic solvents and their data show that iodine is more soluble in polar organic solvents than in water by a factor of

Scheme 2.



ca. 10^3 . The value of ΔG_{tr} calculated from the result for ethanol at 25°C is $-18.6 \text{ kJ mol}^{-1}$ and in the absence of other information this value is used for acetonitrile in the first iteration. The equilibrium constant for K_3 for I_3^- in aqueous solution is 723, with $\Delta G^\circ = -16.3 \text{ kJ mol}^{-1}$ (see earlier), so that Scheme 2 gives ΔG° for eq. [1] in acetonitrile as $-29.5 \text{ kJ mol}^{-1}$ and $\log K_3(\text{CH}_3\text{CN}) = 5.2$. As noted above, the reported experimental value is $\log K_3 = 6.6$ and the agreement seems reasonable given the uncertainty in ΔG_{tr} . Nelson and Iwamoto do not give values for their equilibrium constants, so that the reality of the difference cannot be explored.

The agreement justifies an extension of the argument to seek an explanation of the order of K_3 in organic solvents. Ideally, a series of cycles analogous to Scheme 2 for each solvent and each halogen would lead to a detailed understanding of the factors involved, but unfortunately the numerical data required for this approach are not available; in particular, there is an absence of results for the solution properties of X_3^- . It is however possible to go some way in comparing the equilibrium constants for the three different trihalides, in acetonitrile in the first place, with the corresponding aqueous systems by using Scheme 2. The appropriate numerical data are in Table 2, in which the final column is the sum

$$[5a] \quad \Delta G^\circ(\text{CH}_3\text{CN}) - \Delta G^\circ(\text{H}_2\text{O}) + \Delta G_{\text{tr}}(X^-)$$

which from Scheme 2 obviously equates to

$$[5b] \quad \Delta G_{\text{tr}}(X_3^-) - \Delta G_{\text{tr}}(X_2)$$

The value of K_3 taken for the iodine system is that reported by Nelson and Iwamoto ($\log K = 6.6$) and not that calculated in the paragraph above.

The values for bromine and iodine in the final column of Table 2 are quite close and as noted earlier any conclusions about the value for chlorine are conditioned by the experimental uncertainties. Beyond that, an inspection of the parameters in this table suggests that the single most significant factor predicting the order $\text{Cl} > \text{Br} > \text{I}$ for K in acetonitrile and the change from the reverse order in water is the free energy of transfer of X^- from aqueous to nonaqueous solution.

To further examine this conclusion and its possible application to other solvents (e.g., S), we make the assumption that the term in eq. [5b], which equates to the last column of Table 2, is effectively constant within experimental error and lies in the range $0 \pm 15 \text{ kJ mol}^{-1}$, corresponding to ± 2.6 in

Table 2. Thermodynamic parameters (in kJ mol⁻¹) for X₂ + X⁻ → X₃⁻ in water and in acetonitrile.

X	K _{aq} ^a	ΔG°(H ₂ O) (A)	log K(CH ₃ CN) ^b	ΔG°(CH ₃ CN) (B)	ΔG _{tr} (X ⁻) ^c (C)	(B)+(C)-(A)
Cl	0.19	4.1	10	-57	42.1	-19
Br	16.3	-6.9	7	-40	31.3	-1.8
I	721	-16.3	6.6	-38	16.8	-4.8

^aSee text.^bRef. 13.^cH₂O → CH₃CN; ref. 6.

the accumulated errors for log K(H₂O) and log K(S). Experimental values have been reported for K₃ for each trihalide in the solvents acetonitrile, nitromethane, and acetone, and Marcus has published ΔG values for the transfer of X⁻ from aqueous to nonaqueous solution for these and other solvents. Equation [5] can be rewritten as

$$[6] \quad \Delta G^\circ(\text{H}_2\text{O}) - \Delta G^\circ(\text{S}) = -\Delta G_{\text{tr}}(\text{X}) - [\Delta G_{\text{tr}}(\text{X}_2) - \Delta G_{\text{tr}}(\text{X}_3)]$$

and following the assumption above that the term in square brackets is effectively constant within the uncertainties of the data, we have

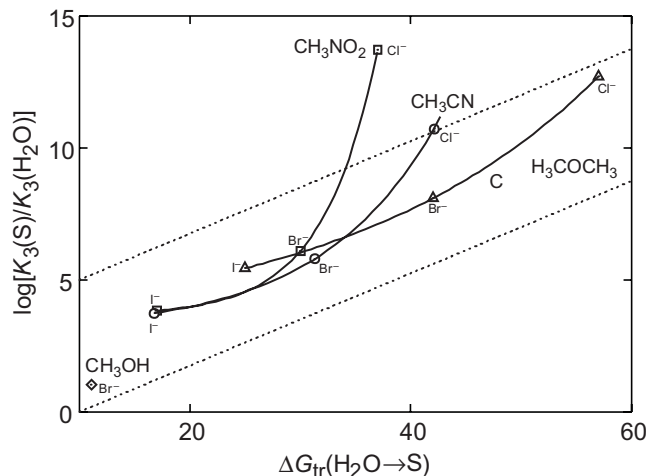
$$[7] \quad RT \log [K_3(\text{S}) / K_3(\text{H}_2\text{O})] = -\Delta G_{\text{tr}}(\text{X}^-) - \text{constant}$$

Figure 2 shows a plot of log [K₃(S) / K₃(H₂O)] against ΔG_{tr}(X⁻) for acetonitrile, nitromethane, and acetone, using the data in Table 2, and in refs. 6 and 11.

With one exception, the points fall within a band (indicated with dotted lines on Fig. 2) with a slope of 2.303RT on log [K₃(S) / K₃(H₂O)]. The exception is for Cl⁻-CH₃NO₂ and the value for Cl⁻-CH₃CN is barely within the upper limit. Given the experimental problems in measuring K₃ for the Cl₃⁻ system in aqueous solution and apparently in organic solvents (9), it is not surprising that this is where the largest deviations are found. In spite of the considerable assumptions made in deriving eq. [8], it is reasonable to conclude that the main factor predicting the value of K₃ in organic solvents relates to the free energy of transfer of X⁻ from H₂O to the solvent in question. In essence, since the X⁻ anions are much less strongly solvated in organic solvents than in water, equilibrium (3) is driven to the right relative to the situation in aqueous solution. This conclusion is in keeping with that reached earlier that solvation forces are more important than bond energies in both aqueous and nonaqueous systems.

The Br₃⁻ system in aqueous methanol

Two papers by Dubois and coworkers (8, 14) report results for the Br₂-Br⁻-Br₃⁻ system in water, methanol, and aqueous methanol over the whole range of compositions. The ratio K₃(MeOH)-K₃(H₂O) is 176:16.3; ΔG_{tr} for Br⁻ from H₂O to MeOH is +11.1 kJ mol⁻¹, leading to the point shown in Fig. 2. Dubois and Garnier (8) show that the change in log K₃ with H₂O-CH₃OH mole ratio is a linear function of the reciprocal of the dielectric constant of the solvent mixture. Any comparison of this conclusion with the arguments used in deriving Fig. 2 is negated by the absence of the necessary data (e.g., ΔH_{sol} of Br₂ in H₂O-MeOH mixtures). It is clear, however, that within the limits of the argu-

Fig. 2. Log (K₃(S) / K₃(H₂O)) as a function of ΔG_{tr} (H₂O → S) for X⁻ ions (X = Cl, Br, I). The dotted lines have slope = 2.303RT.

ment the change in K₃ with solvent composition is explicable in terms of the changing free energy of solvation of the Br⁻ ion, even in a system involving a highly polar nonaqueous solvent.

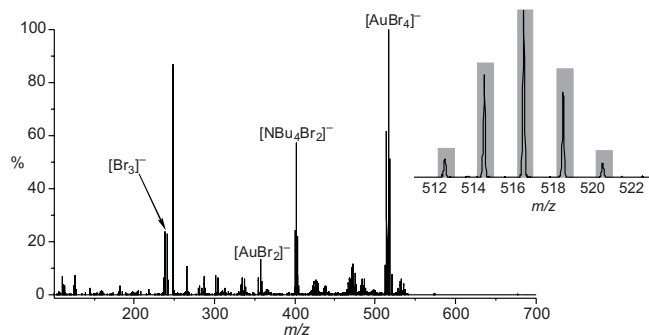
Mass spectrometry

We were interested in the speciation of Br₃⁻ in methanol. One useful technique for the analysis of charged species in polar solvents is electrospray ionization mass spectrometry (ESI-MS) (15). This technique is most prominent in the study of biomolecules (16) but has also become widely used in the analysis of a huge range of inorganic compounds (17). The power of the technique is probably best demonstrated in the analysis of complex mixtures, because the extensive fragmentation common to other mass spectrometric ionization methods is essentially absent from ESI mass spectra. A result of this is that each signal in the spectrum is due to a different parent ion corresponding to a unique solution species. We have already demonstrated the utility of the technique with respect to solutions of polyhalides (1d).

Examination of the negative-ion ESI mass spectrum of Br₃⁻ in methanol revealed rather complicated solution speciation (Fig. 3). While Br₃⁻ can be observed in the spectrum, it makes up only a small percentage of the total ion current. Close inspection of the isotope patterns revealed a complex series of polybrominated ions. These could not be assigned to simple combinations of Br, solvent, and counterion and so other possibilities were considered. The key to this puzzle was an ion at 517 m/z that had the exact

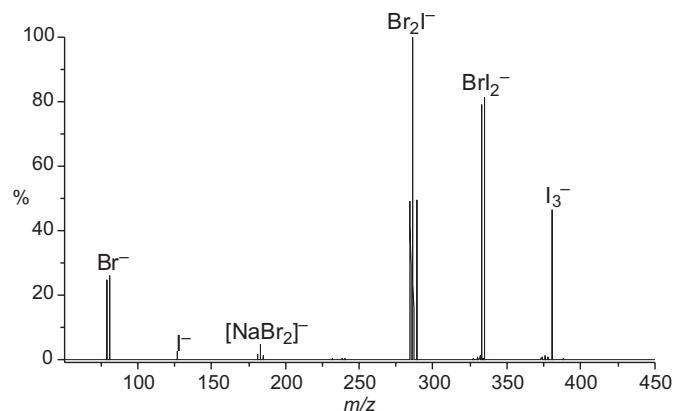
Table 3. Results of MS–MS decomposition studies of X_3^- and X_2Y^- species.

Anion	m/z	Product ion(s)	Neutral fragment	E_{COM} (eV)		Bonding E^a (kJ mol $^{-1}$)
				50% decomposition	50% appearance	
Br_2I^-	254.7	Br^-	BrI	1.7	1.4	
I_3^-	380.7	I^-	I_2	1.5	1	157
Cl_2I^-	196.8	Cl^-	ClI	1.4	1	
Br_2Cl^-	192.6	Br^-	BrCl	1.4	0.7	
ClI_2^-	289.8	I^-	ClI	1.2	0.8	155, 119
Br_3^-	236.5	Br^-	Br_2	1.2	0.9	166
BrI_2^-	332.7	I^- (58%)	IBr (58%)	1.1	1.4	153, 141
		Br^- (42%)	I_2 (42%)		1.1	
BrClI_2^-	148.9	Cl^-	BrCl	1	0.6	
$[\text{Br}_2(\text{SCN})]^-$	217.8	SCN^- (30%)	Br_2 (30%)	0.8	0.4	
		Br^- (70%)	BrSCN (70%)		0.6	
$[\text{I}_2(\text{SCN})]^-$	311.8	SCN^- (98%)	I_2 (98%)	0.6	0.4	
		I^- (2%)	ISCN (2%)		3.0	
$[\text{I}(\text{SCN})_2]^-$	242.8	SCN^-	ISCN	0.5	0.3	

^aValues from ref. 2.**Fig. 3.** Negative-ion ESI-MS of $[\text{NBu}_4][\text{Br}_3]$ in methanol. The inset shows the calculated (grey bars) and experimental isotope pattern of $[\text{AuBr}_4]^-$.

isotope pattern for Br_4^- , with all other contributors being monoisotopic (see inset pattern in Fig. 3). A single isotope with the correct mass is ^{197}Au and the pattern matches perfectly for $[\text{AuBr}_4]^-$. Chemically, this is perfectly reasonable as this complex is quite stable (18), but where did it come from? The answer provided itself when the mass spectrometer stopped functioning and after dismantling the source we found that the stainless steel capillary from which the spray emerges had been completely corroded. $[\text{AuBr}_4]^-$ is present in an appreciable quantity; its abundance in the spectrum is surprising and suggests that corrosion elsewhere in the source is an issue because it is unlikely the stainless steel capillary contains sufficient gold to provide the strength of signal observed (the brass components of the ion block assembly are a likely source of the gold; some parts may also be gold-plated, though this information is proprietary). Br_3^- in methanol is clearly too reactive to be studied routinely using ESI-MS and viable conclusions cannot be drawn using this method of analysis.

However, we found ESI-MS of acetonitrile solutions of X_3^- ($X = \text{I}, \text{Br}, \text{Cl}$, and the pseudohalide SCN) to provide entirely explicable spectra (Fig. 4), with no sign of any species

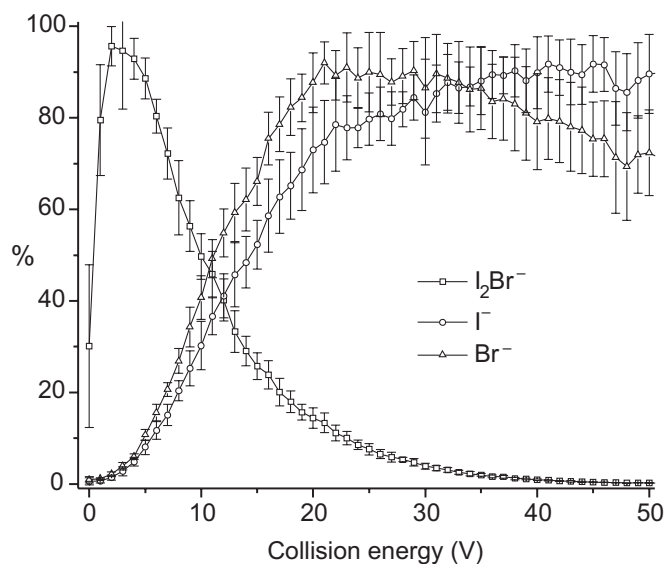
Fig. 4. Negative-ion ESI-MS of $\text{NaBr} + \text{I}_2$ in acetonitrile.

attributable to corrosion of parts of the source. Prominent peaks in the negative-ion mode include X^- , X_3^- , and $[\text{CX}_2]^-$ ($\text{C} = \text{cation}$) (Fig. 4). The thiocyanates were investigated, but spectra were dominated by $X_2(\text{SCN})^-$ ions and an $X(\text{SCN})_2^-$ ion was detected only in the case of $X = \text{I}$.

All X_3^- species undergo collision-induced dissociation (CID) in the argon-filled collision cell of the mass spectrometer to form X_2 (neutral, so not observed) and X^- in a simple MS–MS experiment. As collision energies may be smoothly varied, this process offers qualitative insight into the relative bonding energy by assessing the voltage required to fragment X_3^- . Table 3 summarizes the results obtained from these experiments. Figure 5 illustrates the type of raw data obtained for each of the species using I_2Br^- as the example (only I_2Br^- , $\text{I}_2(\text{SCN})^-$, and $\text{Br}_2(\text{SCN})^-$ generated both possible X^- ions upon CID; the remainder exclusively formed the ions listed in Table 3).

Essentially, X_3^- was selected using the first mass analyser (MS1) of a hybrid quadrupole time-of-flight (Q-TOF) mass spectrometer. The ion was fragmented in the collision cell using a collision voltage that increased by an increment of

Fig. 5. Breakdown graph of I_2Br^- showing traces for the disappearance of I_2Br^- and the appearance of I^- and Br^- . The error bars represent the variability between five independent experiments. The collision energy, E_{LAB} is the value of the offset voltage for the central hexapole.



1 V for each spectrum that was recorded, in exactly the same way as in energy-dependent ESI mass spectra (EDESIMS) (19). However, the simplicity of the spectra are such that breakdown graphs (20) convey the same information in a readily comprehensible fashion. Half of the maximum intensity of the X_3^- ion was used as a convenient point to assess the relative energy required to break apart the X_2 and X^- fragments (Table 3, 50% decomposition). Half of the maximum intensity of the X^- ion was also recorded (Table 3, 50% appearance; also see Fig. 6). The energies are recorded as centre-of-mass, where $E_{COM} = E_{LAB}(m / (m + M))$, where E_{LAB} is the value of the offset voltage for the central hexapole (the collision energy), m is the mass of the stationary Ar atom, and M is the mass of the precursor ion.

Figure 7 shows a spectrum obtained by summing all spectra used in the collection of the breakdown graphs depicted in Fig. 5 (note that all ions appear monoisotopic because of the fact that the lowest mass isotopomer of X_3^- was selected for fragmentation in all cases). Note that trace amounts of I_2^- and IBr^- are also present; these imply loss of Br^- and I^- , respectively. The radical decomposition channel was always a minor one.

There is sufficient error in the values obtained for appearance and decomposition voltages (ca. ± 0.3 V) that in-depth analysis of the values obtained is not prudent; the experiments we describe are very much qualitative. However, two useful general conclusions can be drawn. First, all mixed species X_2Y^- tended to lose XY as the primary neutral fragment, generating X^- . Three examples also lost X_2 , namely $I_2(SCN)^-$, $Br_2(SCN)^-$, and BrI_2^- , but in all of these cases this decomposition pathway was in competition with XY loss. On purely statistical grounds, one would expect that X_2Y^- species should produce XY as the neutral fragment twice as often as X_2 ; the selectivity for the mixed fragment suggests that the XY bond is marginally stronger than the X_2 bond

Fig. 6. Breakdown plots of the appearance of I^- from I_3^- , BrI_2^- , ClI_2^- , and $I_2(SCN)^-$. $E_{COM} = E_{LAB}(m / (m + M))$, where E_{LAB} is the value of the offset voltage for the central hexapole, m is the mass of the stationary Ar atom, and M is the mass of the precursor ion. Dotted lines indicate the 50% appearance potential for each trace. Note that for BrI_2^- and $I_2(SCN)^-$, Br^- and SCN^- were being concurrently generated.

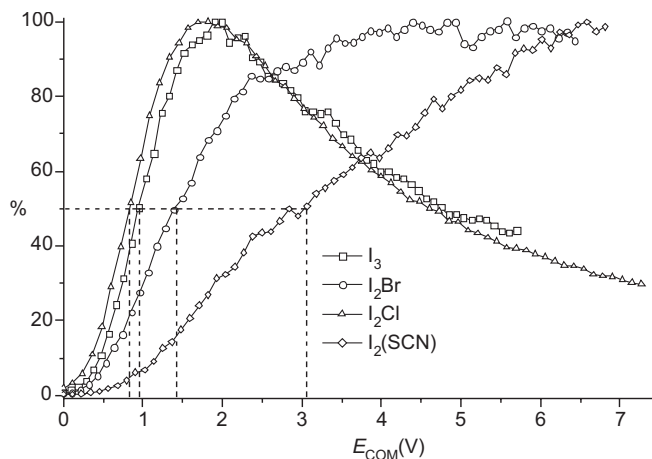
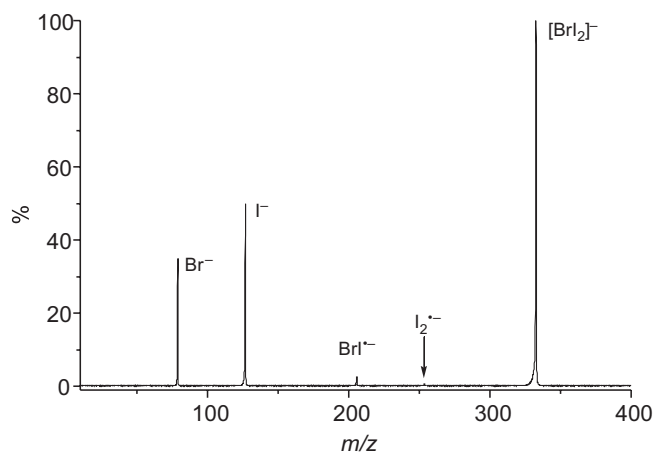


Fig. 7. ESI-MS-MS of BrI_2^- summed over collision voltages of 0–50 V.



(though in the case of BrI_2^- , $I-Br$, and $I-I$ it must be of comparable strength). Second, the thiocyanate-containing species $I_2(SCN)^-$, $Br_2(SCN)^-$, and $(SCN)_2I^-$ clearly have the lowest bonding energies, being the easiest to decompose. Both $I_2(SCN)^-$ and $Br_2(SCN)^-$ produced both possible decomposition products (SCN^- and the appropriate halide ion), though in the case of $I_2(SCN)^-$, I^- was a very minor product and the spectrum was dominated by the appearance of SCN^- . The remaining species have values that are not dramatically different to one another and accurate quantitative assessments of the bond energies are required, e.g., by guided ion beam tandem mass spectrometry (21), before any firm conclusions can be drawn about the exact ordering of bond strengths.

General conclusion

The variation of K_3 in the Cl, Br, I triad is not a function

of any wide variation in the X_3^- bonding energy, but rather reflects the solvation energies of the solutes in question. Within the limits of the available thermodynamic information, it is possible to rationalize the range of equilibrium constants and the effect of changes of solvent on these constants. ESI-MS-MS studies confirm that bond strengths do not vary wildly between different species and also suggest that for mixed X_2Y^- trihalides the XY bond is marginally stronger than the X_2 bond. Mixed halogen-thiocyanate species exhibit the weakest bonding.

Experimental

Electrospray ionization mass spectra were collected using a Waters Micromass Q-ToF micro with Z-Spray source with the following settings: the nebuliser tip was set at 2900 V and 100 °C and nitrogen was used as the bath gas; samples were introduced directly to the source at 5 $\mu\text{L min}^{-1}$ as acetonitrile solutions via a syringe pump; data collection was carried out in continuum mode. For the breakdown graphs, the cone voltage was set at 15 V and MS1 was set at the appropriate m/z value for the species of interest. The collision voltage was initially set at 0 V and spectra collected at every 1 V increment until MS2 showed no change in the daughter ion spectrum (typically ~ 60 V). The collision gas was argon at a pressure of 10^{-4} mbar (1 bar = 100 kPa).

All chemicals were purchased from Sigma-Aldrich (99% purity or better) and used as received. Solutions of the trihalides were typically prepared by adding the appropriate potassium or sodium (pseudo)halide salt to an acetonitrile solution of I_2 or Br_2 . To get spectra of $[Cl_2Br]^-$ and $[Br_2Cl]^-$, equimolar amounts of Br_2 and $[Et_4N]Cl \cdot H_2O$ were heated to complete liquification. The cooled solid was then dissolved in acetonitrile. The spectrum of $[Br_2(SCN)]^-$ was collected by mixing an acetonitrile solution of Br_2 with 0.2 mL of a saturated acetonitrile solution of KSCN. Solution concentrations of each species were of the order of ca. 0.1 mg mL^{-1} .

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