HALOGEN CATIONS

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1. Introduction

MUCH confusion has arisen in the literature over the terms "positive halogen" and "halogen cations". This confusion appears to arise from the fact that elements of Group VII, apart from fluorine, form covalently bonded compounds in which the halogen is in the +1 oxidation state. Thus positively-charged halogen compounds, where the halogen will migrate to the cathode in electrolysis, are common. At an early stage in chemical history[1] these compounds were confused with the free halogen cation. Since the alkali metals do not readily form covalently bonded complexes, no such confusion has arisen in this case, and, whereas Cl^+, Br^+, and I^+ are often postulated in systems where their presence is chemically improbable, references to the equally improbable Li^-, Na^-, and K^- are unknown to the authors.

(a) **Definitions and Scope.**—Since fluorine does not readily form compounds in which it is normally considered to be in the +1 oxidation state, the term "halogens" in this review will refer to chlorine, bromine, and iodine. For convenience we shall employ the following conventions when referring to their oxidation states:

The total sum of the oxidation states of the elements forming a molecule or ionic species is equal to the charge on the species.

Elements bonded to a more electronegative element are in a positive oxidation state and *vice versa*.

Halogen compounds in which the element is in the +1 oxidation state can be divided into three classes:

(*i*) *Neutral or negatively-charged species.* These consist principally of the hypohalous acids and their anions, and binuclear interhalogen compounds such as iodine monochloride.

(*ii*) *Species which have a unit positive charge.* These include protonated hypohalous acids such as H_2OBr^+, and aromatic heterocyclic nitrogen complexes such as $pyI^+NO_3^-$ (py = pyridine). These compounds can be referred to as "cationic halogen compounds" or "positive halogen compounds". The latter nomenclature will be used since this prevents confusion with (iii).

(*iii*) *The simple cations.* These will have an electronic configuration ns^2np^4. We will refer to them as halogen cations, and it is with solutions of these ions that this Review is principally concerned.

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[1] See, *e.g.*, Caven and Lander, "Systematic Inorganic Chemistry," Blackie and Son, London, 1906, p. 301.

(b) Historical Significance of this Topic.—One of the first trends noted in the Periodic Table was the increase in the electropositive character of succeeding elements in a given group. The desire to illustrate this trend stimulated a search for iodine species in which the element had an electropositive character. This, in turn, led to an almost obsessive desire to prove the existence and comparative stability of the iodine cation in chemical systems. This obsession appears to have been mainly responsible for the confusion, which is still apparent in current literature, regarding the chemical nature of halogen cations.

The discovery[2] that iodine and iodine monochloride formed conducting solutions in ethanol, and, later,[3] that iodine itself conducted in the vapour phase and in the molten state, led to the conclusion that the iodine cation was present in these systems. Since the cation has only six electrons in its outermost shell, its existence could not be accounted for by the octet theory. This contributed to the concept that it was electron-pairing, and not octet formation, that resulted in stable configurations.[4]

Recently, investigations of aromatic nitration have shown that the nitronium ion is a comparatively stable entity and is the reactive intermediate in many electrophilic nitrations.[5] As a result of this work a rash of postulates arose concerning the existence of positively-charged intermediates involved in electrophilic attack of aromatic compounds. Amongst these intermediates, halogen cations were prominent. A paper by Bell and Gelles,[6] concerned with thermodynamic aspects of the formation of halogen cations in aqueous solution, has tended to curb enthusiasm for reaction mechanisms involving their participation.

(c) Reviews.—Many Reviews, which purport to be directly concerned with halogen cations as well as halogen compounds in the +1 oxidation state, have appeared both in periodicals[7] and in text-books.[8] Unfortunately, in most of these, confusion between halogen cations and positive-halogen compounds is apparent. For example the phrase "solvated iodine cation" is often used when referring to protonated hypoiodous acid. Also, the phrase "stabilised halogen cation" may be found in reference to cations such as the *N*-iodopyridinium ion. These criticisms do not apply to a recent extensive review of aromatic halogenation and nitration.[9]

[2] Walden, *Z. phys. Chem.*, 1903, **43**, 385.

[3] Thomson, "The Corpuscular Theory of Matter," Constable, London, 1907, pp. 130, 131.

[4] Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762.

[5] Ingold, "Structure and Mechanism in Organic Chemistry," Bell, London, 1953, 274.

[6] Bell and Gelles, *J.*, 1951, 2734.

[7] See, *e.g.*, Mischenko, *Zhur. priklad. Khim.*, 1957, **30**, 665.

[8] See, *e.g.*, Heslop and Robinson, "Inorganic Chemistry," Elsevier, Amsterdam, 1960, p. 384; Kleinberg, Argersinger, and Griswold, "Inorganic Chemistry," Heath and Co., Boston, 1960, p. 483.

[9] de la Mare and Ridd, "Aromatic Nitration and Halogenation," Academic Press, London, 1959.

2. Properties

Halogen cations, particularly that of iodine, have been clearly identified in the gas phase by emission and mass spectroscopy. The spark spectrum of iodine[10] shows lines attributable to electronically-excited iodine cations, from which it is possible to show that the ground state of the cation is $^3P_2$ of the configuration $\cdots 5s^25p^4$, as expected. We can quite safely assume from this that there is also no departure from Hund's rule of maximum multiplicity in the case of bromine and chlorine cations. The cations will thus have two unpaired electrons and we will see later that this fact is of importance when considering methods of identification.

Because there are only four *p*-electrons in the outer shell, halogen cations must be extremely powerful electrophiles, though electrophilic activity will be partly governed by the energy required to pair the two unpaired *p*-electrons.[11] However, this energy, which (from data for iodine cations in the gas phase[10]) must be of the order of 10 kcal. mole^{-1}, will not be sufficient to lower their reactivity to a value below that of such covalently bonded species as H_2OI^+.

Two other properties that are relevant to the study of halogen cations are their unit positive charge and the fact that the halogen is in the $+1$ oxidation state. Detection of a species having these two properties together with high electrophilicity is often used as proof of the presence of halogen cations in the system. It should be emphasised that these properties are shared with most positive halogen compounds. In fact there would only be a difference in electrophilic power, a property that it is very difficult to measure quantitatively. Further, since halogen cations are such powerful electrophiles, their presence in nucleophilic solvents such as water,[6] ethanol[12], and nitrobenzene[2] is most unlikely.

Fortunately, another property of halogen cations, namely their paramagnetism, is more diagnostic of their presence in solution than those listed above, since solutions which might conceivably contain halogen cations are unlikely to contain other unidentifiable paramagnetic entities. The magnitude of the magnetic moment for these ions in solution will be difficult to predict since it will surely depend considerably upon the mode of interaction with nearest-neighbour solvent molecules. However, a strongly paramagnetic halogen species having the properties listed above will almost certainly be the corresponding cation.

The electronic absorption spectrum of halogen cations will not be so useful for purposes of identification. Analysis of the spectrum of the iodine cation in the vapour phase[10] shows that there are no permitted electronic transitions above 200 mμ. By extrapolation this will also be the case for bromine and chlorine cations. However, in any interacting medium the

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[10] Murakawa, *Z. Physik.*, 1948, **5C**, 84.

[11] Millen, quoted in ref. 5.

[12] Brasset and Kikindai, *Compt. rend.*, 1951, **232**, 1840; Kikindai and Cassel, *ibid.*, 1110.

configuration of the cations will be more or less perturbed. The situation is closer to that of solvated transition-metal ions than that of ions with a rare-gas configuration. Thus the medium may perturb the energy levels in the cation in such a manner that transitions similar to those between the *d*-levels of transition-metal complexes can occur.

Since halogen cations will not, by definition, be strongly bonded to other species, there should be no infrared or Raman absorption bands attributable to them.

(a) **Thermodynamic Considerations.**—In 1951 an important paper by Bell and Gelles[6] appeared concerning the probable existence of halogen cations in aqueous media. Equilibrium constants for reactions shown in Table 1 were estimated from free-energy data computed by means of typical thermodynamic cycles (Table 2). Inevitably, numerical values for ionic radii and solvation energies of the cations under consideration have been derived from only partly justifiable extrapolations and hence may be considerably in error.

This treatment of the equilibria has been subjected to some criticism. In particular, Bell and Gelles made no allowance for the fact that, since halogen cations have an incomplete outer *p*-level, some "ligand field

TABLE 1. *Free energies and equilibrium constants for some reactions of the halogens (from Bell and Gelles[6]).*

$$X_2\,(aq.) \rightleftharpoons X^+\,(aq.) + X^-\,(aq.) \qquad (1)$$

X	Cl	Br	I
ΔG° (kcal. mole^{-1})	84(56)	67(39)	55(27)
K	$10^{-60}(10^{-40})$	$10^{-50}(10^{-30})$	$10^{-40}(10^{-21})$

The values in parentheses incorporate our approximate ligand field correction of 28 kcal. mole^{-1}.

$$X_2\,(aq.) + H_2O \rightleftharpoons H^+ + HOX + X^- \qquad (2)$$

X	Cl	Br	I
ΔG° (kcal. mole^{-1})	4·5	11·2	17
K	10^{-3}	10^{-8}	10^{-13}

$$X_2\,(aq.) + H_2O \rightleftharpoons H_2OX^+ + X^- \qquad (3)$$

X	Cl	Br	I
ΔG° (kcal. mole^{-1})	42	30	14
K	10^{-30}	10^{-20}	10^{-10}

TABLE 2. *The Born–Haber cycle for the determination of the free energy of:*

$$X_2\,(aq.) = X^+\,(aq.) + X^-\,(aq.) \qquad (4)$$

$$\begin{tikzcd}
X_2\,(gas) \arrow[r] & 2X\,(gas) \arrow[r] & X^+\,(gas) \arrow[d] & + & X^-\,(gas) \arrow[d] \\
X_2\,(aq.) \arrow[u] \arrow[rr] & & X^+\,(aq.) & + & X^-\,(aq.)
\end{tikzcd}$$

stabilisation" must occur, giving higher solvation energies for the cations than was originally estimated. Secondly, there is strong evidence that H_2OX^+ (X = Br, Cl) is an intermediate in aromatic halogenations,[9] but the equilibrium constants estimated by Bell and Gelles for reaction (3) of Table 1 lead to concentrations of protonated hypohalous acids which are so small that they could hardly act as important intermediates in the relevant halogenations.

A considerable body of evidence has now been advanced[13–16] for the existence of iodine cations in oleum solutions. From the spectra of these solutions we estimate a value of about 28 kcal. mole^{-1} for the "ligand field stabilisation" of the iodine cation due to the oriented field of solvent molecules.[17] It is unlikely that this stabilisation energy will vary extensively from iodine to chlorine since ligand-field stabilisation energies of transition elements appear to depend more on their configuration and charge than on their size. We have therefore included this figure with the data of Bell and Gelles (Table 1). As a result of this extra solution energy the iodine cation appears to be sufficiently stable to be a reasonable intermediate in chemical reactions. The participation of chlorine and bromine cations in halogenations still appears unlikely.

On the question of the reaction described by equation (3) Bell and Gelles had to make rather gross approximations, both for the free-energy of reaction between halogen cations and water and for the solvation energy of hypohalous acids. One or both of these approximations appear to us to be somewhat in error for the following reasons. First, kinetic evidence for the participation of protonated hypohalous acids in electrophilic substitutions is strong. Secondly, it seems possible to obtain approximate values for the acidities of all the protonated hypohalous acids by relating the known value for hypoiodous acid with the differences between the pK values for the acidities of the neutral acids, and the results are very different from those which can be derived from the data of Bell and Gelles.[6] Thus the difference in the pK values for hypoiodous and hypochlorous acid is of the order of −5, and, since this reflects the difference in electronegativities of iodine and chlorine, we suggest that a similar difference in the pK values for the protonated acids is probable. The pK value for hypoiodous acid [equation (25)] is about 1·3.[18] Hence the pK value for protonated hypochlorous acid is probably in the region of from −3 to −4. This is in marked contrast with the value of −26 implicit in the data of Bell and Gelles.[6] Many other common intermediates in reactions, such

[13] Symons, *J.*, 1957, 387.
[14] Symons, *J.*, 1957, 2186.
[15] Arotsky, Mishra, and Symons, *J.*, 1961, 12.
[16] Arotsky, Mishra, and Symons, *J.*, 1962, 2582.
[17] Orgel, "An Introduction to Transition-Metal Chemistry," Methuen, London, 1961, p. 72.
[18] Buckles and Mills, *J. Amer. Chem. Soc.*, 1953, **75**, 552; Bowers and Scott, *ibid.*, 3582.

as the t-butyl carbonium ion,[19] have pK values in this region, and thus our calculations support the postulate that protonated hypohalous acids could be reactive intermediates in electrophilic hologenations. This reasoning in no way reflects upon calculations relating to the formation of free halogen cations as has previously been intimated.[9] Even when one adds an extremely large free-energy term for the "ligand field" stabilisation of free chlorine cations, their significant existence in chemical systems is energetically unlikely. Finally, even if free halogen cations were formed in aqueous systems, the free energy of reaction (1) in Table 1 would require the immediate formation of the corresponding protonated hypohalous acid. The argument that the energy of activation of reaction (1) would be large, resulting in the stabilisation of free halogen cations in aqueous systems,[11] is not compelling since this effect would merely lower the electrophilic reactivity of the halogen cations generally, as the *p*-electrons must pair for the halogen cation to react as an electrophile with any system. Besides, the quantitative reasoning given in Section 2 suggests that this barrier is not large. We conclude therefore that, although protonated hypohalous acids may well be reactive species involved in electrophilic substitution reactions, the participation of halogen cations, except possibly iodine cations, is improbable in any reaction in aqueous media.

It is perhaps significant that we have failed to detect chlorine or bromine cations in sulphuric acid and oleum solutions[15] [Section 3(b)] and that, if our conclusions regarding the electronic absorption spectrum of solvated iodine cations [Section 3(b)] are correct, we can put a limiting value of 10^{-4}M to the concentration of iodine cations in acidified aqueous solutions of hypoiodous acid and related compounds. This conclusion is based upon the fact that no absorption in the 640 mμ region could be found for such solutions. By using the data of Bell and Gelles,[6] and this value for the concentration of the iodine cation, we calculate that the concentration of chlorine cations in comparable solutions is about 10^{-33}M. This result, since it rests upon differences in energies rather than absolute values, cannot be in error by many powers of ten.

3. Preparation

The preparation of halogen cations can be discussed in terms of the hypothetical equilibrium:

$$\mathrm{HalX} \rightleftharpoons \mathrm{Hal}^+ + \mathrm{X}^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

where X^- might be halide, hydroxide, or other suitable anions.

In view of the thermodynamic considerations already discussed, physical constraints are unlikely to influence such equilibria sufficiently to give detectable amounts of halogen cations. However, the equilibrium could be moved to the right if there is either a suitable nucleophilic reagent present to react preferentially with the halogen cations, or an electrophile to react

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[19] Rosenbaum and Symons, *Mol. Phys.*, 1960, 3, 205.

with the anions. The first alternative is trivial since our aim is to prepare halogen cations; we mention it here since it seems that such reactions have often occurred in attempts to make halogen cations, and failure to recognise this mode of reaction has led to many erroneous conclusions (Section 4).

The latter alternative must therefore be used, and it will also be a necessary requirement that no nucleophiles be present which can react with the halogen cations formed. For an electrophile Y the sequence:

$$X^- + Y \rightleftharpoons XY^- \quad \ldots\ldots \quad (6)$$

$$XY^- \rightarrow \text{Further products} \quad \ldots\ldots \quad (7)$$

is suggested, step (7) being necessary if (6) is reversible or if halogen cations can react with XY^- to re-form HalX. In the reactions that we have studied, a second step of this type appears to be necessary for the formation of appreciable concentrations of halogen cations.

(a) Suitable Media.—Halogen cations are very powerful electrophiles and will exist in media containing only the weakest of nucleophiles. Another necessary prerequisite is that the ionizing power of the solvent be high. There should be no reducing agents capable of converting the cations into the halogen, or oxidizing agents of sufficient power to oxidize them to the ter- or quinque-valent state. This latter condition is particularly important in the case of iodine.

One medium which appears to fill the above requirements is sulphuric acid, and the solution chemistry of the halogens in this solvent has received considerable attention. However, much of this work has been on iodine compounds in the $+3$ and $+5$ oxidation states, with which we are not at present concerned.

(b) Solutions of Iodine and its Compounds in Sulphuric Acid and Oleums.—When potassium iodate is mixed with an excess of iodine in sulphuric acid a solution is formed having a brown-red colour which contains a powerful electrophilic iodinating agent. This is thought to be the cation I_3^+ formed by the reaction:

$$HIO_3 + 7I_2 + 8H_2SO_4 \rightarrow 5I_3^+ + 3H_3O^+ + 8HSO_4^- \quad \ldots\ldots \quad (8)$$

Masson [20] found that, when nitrobenzene or chlorobenzene is shaken with such a solution, high yields of the *m*-iodo-compounds are formed together with molecular iodine, according to reactions of the type:

$$C_6H_5NO_2 + I_3^+ \rightarrow I_2 + C_6H_4I{\cdot}NO_2 + H^+ \quad \ldots\ldots \quad (9)$$

$$C_6H_5NO_2 + I_5^+ \rightarrow 2I_2 + C_6H_4I{\cdot}NO_2 + H^+ \quad \ldots\ldots \quad (10)$$

The presence of the cations I_3^+ and I_5^+ is also indicated by cryoscopic, spectrophotometric, and conductometric measurements.[15,16] The formation and comparative stability of such ions is considered in detail in Section 6.

[20] Masson, *J.*, 1938, 1708.

Iodine dissolves in sulphuric acid to give pink solutions having an absorption spectrum similar to that of iodine vapour[18] (see however ref. 15). The solubility of iodine is increased from about 10^{-3}M to 0·5M by addition of silver sulphate, the solubility of which is concurrently enhanced. The resulting solutions contain a powerful electrophilic iodinating agent which reacts in a manner comparable with I_3^+ except that silver iodide is precipitated instead of iodine.[21]

$$AgI_2^+ + C_6H_5NO_2 \rightarrow C_6H_4I{\cdot}NO_2 + AgI + H^+ \quad . \; . \; . \; . \; . \quad (11)$$

Cryoscopic and conductimetric measurements indicate that a 1:1 complex is formed between silver ions and iodine molecules.[16] These facts indicate that the iodine is entirely converted into AgI_2^+ and hence that these complexes have considerable stability. Although the geometry of such complexes is unknown, it is noteworthy that silver ions readily form complexes with olefins and aromatic hydrocarbons, and hence we feel that a similar form of bonding, giving rise to a structure in which the silver is symmetrically placed with respect to the two iodine atoms, may be favoured. Alternatively, the structure may be more comparable to that of I_3^+, in whose formation the role of molecular iodine is again that of a donor rather than an acceptor. In accord with results for other complexes of silver[22] the spectrum of "iodine" in AgI_2^+ is shifted to low energies relative to that of "free" iodine, and there is a new intense absorption in the near-ultraviolet region probably associated with an intramolecular charge-transfer transition.[16]

A possible role of halogen complexes with silver ions in aromatic halogenations is discussed in Section 7.

None of these solutions contains an appreciable concentration of paramagnetic species and therefore we conclude that iodine cations are not an important constituent.

When sulphur trioxide is added to sulphuric acid the medium is changed in two ways; first, the acidity is increased, and, secondly, there is an increasing concentration of powerful oxidant. These effects are reflected in the behaviour of iodine in such solvents.[13]

The apparent solubility of iodine in dilute oleums (30%)* is about 0·5M. Spectrophotometric studies[15] of these brown solutions show that they contain I_3^+ and sulphur dioxide. If potassium iodate in the stoicheiometric amount required by reaction (12) is added to the brown solutions,

$$HIO_3 + 2I_3^+ + 8H_2SO_4 \rightarrow 7I^+ + 3H_3O^+ + 8H_2SO_4^- \quad . \; . \; . \; . \quad (12)$$

the colour changes to a deep blue. This change can also be effected by other oxidizing agents such as potassium persulphate or hydrogen perox-

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* The concentration of oleums will be expressed in terms of the percentage by weight of sulphur trioxide in 100% sulphuric acid.

[21] Derbyshire and Waters, *J.*, 1950, 3694.

[22] Tetlow, *Z. phys. Chem.*, 1938, *B*, **40**, 397; 1939, B, **43**, 198.

ide. The visible absorption spectra of the blue solutions are characterised by three bands with maxima at 645, 500, and 410 mμ.

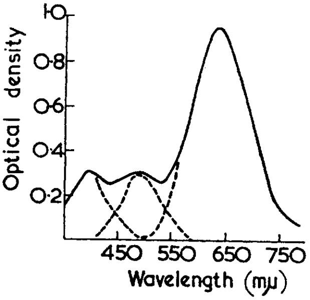

FIG. *Electronic spectrum assigned to the iodine cation.*
(Broken curve was derived as described in ref. 15.)

Similar blue solutions are obtained by direct dissolution of iodine in 65% oleum.[13] The apparent solubility of iodine in this medium is extremely large, being greater than 10M. These solutions contain an exceptionally powerful iodinating agent, such inert compounds as pyridine,[23] picoline,[24] and phthalic anhydride[25] being readily iodinated in positions expected for electrophilic attack. The spectrum of these blue solutions is very similar to that described above, and is quite different from that of blue solutions of sulphur in oleum,[26] with which these solutions might be confused. An early analysis[13] has now been modified[15] to give the following conclusions.

A band at 280 mμ is ascribed to sulphur dioxide, since addition of sulphur dioxide merely increases its intensity whilst addition of an oxidizing agent such as potassium persulphate decreases its intensity, the rest of the spectrum remaining unaltered. Also, when iodine monochloride is dissolved in this medium the spectrum is identical with that of solutions of iodine except that there is no absorption band at 280 mμ.[15] From the value of the extinction coefficient of sulphur dioxide in this medium, it has been shown that one molecule of sulphur dioxide is formed per molecule of iodine dissolved.[15] This is in accord with the postulate that all the iodine is in the +1 oxidation state, in agreement with chemical analysis.[13] A careful study of the visible spectrum of these solutions under a variety of conditions suggests strongly that all three bands in the visible region are a property of a single substance.[15]

The blue solutions in both dilute and concentrated oleums contain a paramagnetic species[14,16] having a magnetic moment corresponding to 1·44 B.M. per iodine atom as estimated by the Gouy technique,[16] and 1·5 B.M.

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[23] Plazek and Rodewald, *Roczniki Chem.*, 1947, **21**, 150.
[24] Plazek and Rodewald, *Ber.*, 1937, **70**, 1159.
[25] Allen, Homer, Cressman, and Johnson, *Org. Synth.*, 1947, **27**, 78.
[26] Symons, *J.*, 1947, 2440.

by using nuclear magnetic resonance.[27] The latter measurements showed that the paramagnetic entity is not protonated.[27]

Conductometric measurements of both dilute[28] and concentrated oleums[15] and conductometric titrations of these solutions with appropriate solutions of boric acid[15,28,29] showed that there is one positive charge per iodine atom. Similar results were obtained for solutions of iodine monochloride.[15]

4. Evidence for the Iodine Cation

In summary, it has been shown that there is a single coloured species containing iodine in the +1 oxidation state in the blue solutions, having the spectrum shown in the Figure. This species has one positive charge per iodine atom, is not protonated, and is paramagnetic, having a moment of about 1·5 B.M. per iodine atom at room temperature. These results are consistent with the concept that the blue species is the cation I+, formed by reactions such as:

$$I_2 + 2H_2S_2O_7 + 2SO_3 \rightarrow 2I^+ + HS_2O_7^- + SO_2 \quad \ldots\ldots \quad (13)$$

$$ICl + H_2S_2O_7 + SO_3 \rightarrow I^+ + HS_2O_7^- + HSO_3Cl \quad \ldots\ldots \quad (14)$$

However, since this ion has two unpaired electrons, an explanation must be found for the relatively small magnetic moment, which is much smaller than the "spin-only" value of 2·8. Also, since there are no allowed transitions for iodine cations in the gas phase above 200 mμ,[10] the visible spectrum also requires interpretation. Furthermore, in view of the discussion in Section 2(a) it will be necessary to show that this postulate is not contrary to thermodynamic requirements.

(a) Solvation of the Iodine Cation.—To a first approximation, the solvent stabilisation energy of the iodine cation will be comparable with that of a rare-gas cation having the same radius. Solvation energies in sulphuric acid are not known but must surely be large. In addition there will be a "crystal field" stabilisation since the cation has a ^3P ground state. This is expected to give rise to a distorted solvation in which the solvent molecules specifically avoid the filled *p*-orbital. Comparison with theory and results for transition-metal complexes suggests that this extra stabilisation may be as large as 28 kcal. mole^{-1}. The simplest reaction for iodine cations in oleum is

$$I^+(\text{solv.}) + HS_2O_7^-(\text{solv.}) \rightleftharpoons IHS_2O_7 \quad \ldots\ldots \quad (15)$$

and this must be compared with the reaction

$$I^+(\text{aq.}) + H_2O \rightleftharpoons IOH_2^+ \quad \ldots\ldots \quad (16)$$

of Bell and Gelles.[6] In addition to the "crystal field" stabilisation, which was not taken into account by Bell and Gelles, reaction (15) is inherently less probable than (16) since two strongly solvated ions are thereby destroyed, and $HS_2O_7^-$ ions are far weaker nucleophiles than water.

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[27] Connor and Symons, *J.*, 1959, 963.

[28] Mishra and Symons, unpublished results.

[29] Arotsky and Symons, *Trans. Faraday Soc.*, 1960, **56**, 1426.

(b) **Effect of Solvation on Spectra.**—As has been pointed out[15] an asymmetric solvent-field of the type depicted, which results in a splitting of the *p*-orbitals into a lower singlet and an upper doublet, creates a situation which is comparable with that for transition-metal complexes. Hence *p–p* transitions must be considered, and, for simplicity, this problem was treated as one involving a linear Stark field.[15] Thus, using the symbolism of linear molecules, the ground state of the solvated ion is $^3\Sigma^-$ and there are three low lying $^3\Pi$ excited states. The transitions under consideration are then $^3\Pi i \leftarrow {}^3\Sigma^-$, where $i = 0, 1,$ or 2. These transitions are formally forbidden since the model has inversion symmetry. However, in comparable systems involving second- or third-row transition-metal complexes, relatively intense transitions are often observed, such factors as mixing with higher-energy orbitals of opposite parity, such as the 5*d* level, or "borrowing" from charge-transfer transitions involving orientated solvent molecules, tending to increase the intensity.[15] The treatment by Jevons[30] shows that the energy difference between these transitions should be equal, and about half that between the $^3P_2$ and $^3P_1$ levels for the ion in the gas phase. Furthermore, the lowest energy-transition should be more intense than the others. We therefore postulate that the bands at 640, 500, and 410 mμ are due to these transitions: the band at 640 mμ is indeed about three times as intense as the others, and the equal spacing of 4400 cm.$^{-1}$ is close to the value of 3600 cm.$^{-1}$ derived from the data for the ion in the gas phase.[10]

(c) **Effect of Solvation upon Magnetic Susceptibility.**—To continue our analogy with compounds of transition metals, we find that experimental susceptibilities are often far smaller than the value predicted by using the "spin-only" approximation. A possible approach to this question was given[15] using the theory of Kotani.[31] Alternatively, one can postulate that as a result of coupling with excited singlet states, the $^3\Sigma^-$ state is split so that the $M_S = 0$ level lies slightly below the $M_S = \pm 1$ level. This would have the effect of lowering the measured susceptibility. A similar argument could be used to account for the very weak paramagnetism attributed to the ion IO^+.[16]

(d) **Alternative Postulates.**—A variety of alternatives were considered, and rejected because of known properties of the blue solutions.[15] However the possibility that ISO_3^+ was the coloured paramagnetic species could not be eliminated,[15] although qualitative considerations made it seem less likely than the original theory. The ion ISO_3^+ could be paramagnetic for the same reasons as IO^+, in that it has local axial symmetry. Also, other things being equal, it might have a visible spectrum qualitatively similar to that postulated above for solvated iodine cations.

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[30] Jevons, "Report on The Band Spectra of Diatomic Molecules," Physical Society, London, 1932, p. 100.

[31] Kotani, *J. Phys. Soc. Japan*, 1949, **4**, 293.

Since, in our view, the cation ISO_3^+ is the only important alternative to the iodine cation an experiment was devised which would enable us to draw a clear distinction between them. The conductivities of solutions of sodium chloride and iodine monochloride in dilute oleums have been measured,[28] and the results provide the required distinction. The conductivities of the latter solutions, which have the same visible spectrum as that of solutions of iodine monochloride in 65% oleum, vary markedly as the medium is changed, and hence an uptake of sulphur trioxide greater than that required by reactions (17) and (18) would be readily detected. In fact the

$$ICl + 2H_2S_2O_7 \rightarrow I^+ + HSO_3Cl + HS_2O_7^- + H_2SO_4 \quad . \; . \; . \; . \quad (17)$$

$$H_2SO_4 + H_2S_2O_7 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad . \; . \; . \; . \; . \; . \; . \; . \quad (18)$$

conductivity of equimolar solutions of sodium chloride and iodine monochloride were the same within experimental error.[28] This result, whilst being in accord with the iodine cation theory, eliminates the concept that ISO_3^+ is an important constituent of these solutions.

5. Chlorine and Bromine Cations in Strong Acids

In view of the apparently successful preparation of concentrated solutions of iodine cations, attempts have been made to detect cations of chlorine and bromine under similar conditions.[16] These elements dissolve unchanged in 65% and other oleums, and on oxidation give tervalent derivatives, in the case of bromine *via* the cation Br_3^+. No indication of a stable species containing halogen in the +1 oxidation state was detected. Most significantly, no paramagnetic species could be detected, which result means that the concentration of solvated chlorine or bromine cations was always less than 10^{-2}M. Again, no trace of an absorption band which could be assigned to the ion was detected. Since, had they been formed, they would surely be solvated in a manner comparable to that of the iodine cation, we would expect to find bands of low energy. However, especially for the chlorine cation, the intensities would be expected to be greatly reduced and thus it is difficult to predict a detection limit. This result, that the iodine cation is considerably more stable than those of chlorine and bromine, is in accord with expectation.

6. Trihalogen Cations

These ions have the general formula Hal_3^+ and known examples are given in Table 3. A consideration of electronic structure[32] suggests that

TABLE 3. *Trihalogen cations.*

Cation	I_3^+	ICl_2^+	BrF_2^+	Br_3^+
Anion	HSO_4^-	$SbCl_6^-$	BrF_4^-	$HS_2O_7^-$
Reference	20	33	*	28

* See, *e.g.*, Woolf and Emeléus, *J.*, 1949, 2865.

[32] Walsh, *J.*, 1953, 2,260.

these ions should be bent and have considerable stability since, as was stressed by Masson,[20] they have a "closed-shell" configuration. Recent structural studies of salts such as (ICl_2^+) ($SbCl_6^-$)[33] have shown that these ions have a bond angle of about 90°. So far as we are aware the first ion in this class to be discovered was I_3^+ which Masson identified in solution in sulphuric acid.[20] They are of significance to the subject matter of this Review in that they are powerful electrophilic halogenating agents, and have thus often been confused with simple halogen cations.

7. Summary of Other Work

In this section we shall consider reports, other than those discussed above, purporting to demonstrate the presence of halogen cations in various systems. There is a considerable mass of work in the literature on this topic, much of it a result of loose nomenclature, as discussed in Section 1.

(a) **Kinetic Evidence.**—In the Reviewers' opinion the thermodynamic calculations of Bell and Gelles,[6] even when allowance is made for such effects as increased solvation energy of the halogen cations arising from their incompleted outer shell[9] [see Section 2(a)], make the participation of chlorine cations in reactions in aqueous media appear extremely improbable.

Nevertheless, the kinetic evidence in favour of chlorination by the chlorine cation in certain reactions of hypochlorous acid is so strong[9] that many workers simply assume that this ion is the usual agent in aqueous acidic media.[34]

This evidence has been summarised by de la Mare and Ridd,[9] and rests on the significant observation that, for relatively unreactive aromatic compounds, the rate of chlorination is of the form

$$-d[HOCl]/dt = k_1[HOCl] + k_2[HOCl]\,[H^+]$$

This is interpreted in terms of a rate-determining heterolysis of the oxygen–chlorine bond, followed by a rapid attack of the resulting chlorine cations upon the aromatic compound. In accord with this is the observation that when deuterium oxide is used as solvent there is a large increase in rate.[35] This has been accepted as good evidence for the transient formation of chlorine cations in these solutions. However, we think it is significant that, in order to suppress reactions such as (19) a large excess of

$$Cl^- + H_2OCl^+ \rightleftharpoons Cl_2 + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (19)$$

silver perchlorate was present in the solutions under consideration.[35,36] However, reaction rates were insensitive to small changes in the concentra-

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[33] Vonk and Wiebenga, *Acta Cryst.*, 1959, **12**, 867.
[34] Harvey and Norman, *J.*, 1961, 3604.
[35] Swain and Ketley, *J. Amer. Chem. Soc.*, 1955, **77**, 3410.
[36] de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

tion of silver perchlorate and thus it was concluded that silver ions were not involved in the reaction whose rate was measured.[36]

There is strong evidence that the complex AgI_2^+ has considerable stability [Section 3(b)] and that it is a powerful iodinating agent.[21] There is also evidence from spectrophotometric, solubility, and conductometric studies for the formation of $AgBr_2^+$ and $AgCl_2^+$,[28] and hence the possible participation of $AgCl_2^+$ in the halogenations studied by de la Mare and his co-workers[36] should be considered. Thus an alternative mechanism for chlorination in acidified aqueous solution of hypochlorous acid containing a large excess of silver perchlorate and some solid silver chloride is:

$$AgCl(solid) + H_2OCl^+ \overset{k_{20}}{\rightleftharpoons} AgCl_2^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (20)$$

$$AgCl_2^+ + ArH \xrightarrow{k_{21}} ArCl + AgCl(solid) + H^+ \quad . \; . \; . \quad (21)$$

This will be in accord with the kinetic data if k_{21} is larger than k_{20}, and the concentration of $AgCl_2^+$ is large compared with that of Cl_2. This would make the forward part of reaction (20) rate-determining, and hence the overall rate would be independent of the concentration of silver ions in solution and of the aromatic substrate. We suspect that several other mechanisms could be found for these complex systems which would adequately accommodate the kinetic data.

(b) **Molten Iodine and Iodine Monochloride.**—Molten iodine is a moderately good conductor of electricity[4] and this has been explained by the equilibrium

$$2I_2 \rightleftharpoons I^+ + I_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (22)$$

It is inconceivable that, in the presence of a large excess of iodine, the free cation would not be completely converted into I_3^+, and hence the equilibrium

$$3I_2 \rightleftharpoons I_3^+ + I_3^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (23)$$

is surely a better description of the self-ionisation of iodine. Similarly, the electrical conductivity of molten iodine monochloride[37] which has been attributed to the equilibrium

$$2ICl \rightleftharpoons I^+ + ICl_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (24)$$

is better depicted as

$$3ICl \rightleftharpoons I_2Cl^+ + ICl_2^- \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (25)$$

(c) **Reaction of Iodine with Ethyl Alcohol.**—Iodine dissolves in ethyl alcohol to give brown solutions which have a small electrical conductivity.[2] These solutions are diamagnetic, and the diamagnetism increases linearly with added iodine;[38] this indicates that appreciable concentrations of

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[37] Emeléus, and Greenwood, *J.*, 1950, 987.

[38] Couty, *Bull. Soc. chim. France*, 1938, 5, 84.

iodine cations are not formed in these solutions. The addition of an alcoholic solution of silver nitrate to one of iodine results in the deposition of 69—74% of the iodine as silver iodide.[39] This was interpreted as being indicative of the formation of the free iodine cation together with a species containing iodine in the +3 oxidation state.[39] Solutions of silver perchlorate[40] or silver nitrate[41] with iodine in phenol remain unchanged, but the addition of ethyl alcohol results in the immediate formation of tri-iodophenol and silver iodide.[40,41]

Solutions of iodine and silver nitrate in ethyl alcohol, cooled to 2° to prevent oxidation of the alcohol, when treated with the required amount of iodine to bring the overall oxidation state to +1, were found to displace hydrogen ions from a cation-exchange resin, the iodine being absorbed. 70% could be recovered as the element, from the resin, on treatment with aqueous potassium iodide. This was interpreted in terms of the reaction

$$H_2O + \text{Resin-}I^+ + I^- \rightleftharpoons I_2 + \text{Resin-}H^+ + OH^- \quad . \quad . \quad . \quad . \quad (26)$$

and quoted as evidence for the existence of free iodine cations in the original solutions.[12]

In view of the chemical evidence given earlier, and the thermodynamic considerations of Section 2(a), it appears most unlikely that free iodine cations are present in these solutions. A possible explanation of the results is that the species containing iodine in the +1 oxidation state in these solutions is ethyl hypoiodite or its conjugate acid. All the reactions described above can be accommodated in terms of this postulate, although others are possible.

These arguments illustrate the danger of relying on purely chemical evidence to establish the presence of free halogen cations in a system.

(d) Solutions of Iodine Monochloride in Acetonitrile.—The electrical conductance of solutions of iodine monochloride in acetonitrile is consistent with the fact that some ions are formed in these solutions. Reaction (24) was postulated in explanation.[42] Acetonitrile is, like ethanol, a basic solvent, and is readily protonated by acids dissolved in it.[43] Nitrogen-containing compounds readily bond to iodine in the +1 oxidation state to form stable species such as the *N*-iodopyridinium ions. We consider it much more likely that the electrical conductivity of these solutions is due to the equilibrium

$$MeCN + 2ICl \rightleftharpoons MeCNI^+ + ICl_2^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

particularly since no optical absorption attributable to the positively-charged iodine species was detected.[42]

[39] Ushakov, *J. Gen. Chem.* (*U.S.S.R.*), 1931, **1**, 1258.
[40] Birkenbach and Goubeau, *Ber.*, 1932, **65**, 395.
[41] Fiakov and Gengrinovitch, *Inst. Khim. Akad. Nauk.* (*U.S.S.R.*), 1940, **7**, 125.
[42] Popov and Deskin, *J. Amer. Chem. Soc.*, 1958, **80**, 2049; Popov and Geske, *ibid.*, p. 2976.
[43] Kolthoff, Bruckenstein, and Chantooni, *J. Amer. Chem. Soc.*, 1961, **83**, 3927.

(e) **Iodine Cations as Catalysts in Polymerisation Reactions.**—Cationic vinyl polymerisation can be induced by iodine,[44] and equilibrium (5) has been suggested as an explanation. In view of the arguments given above this seems unlikely, one alternative being that I_3^+ ions are the active species.

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[44] Eley and Pepper, *Trans. Faraday Soc.*, 1947, **43**, 112.