very well with the lower ligand field states and it seems unlikely that relaxation to those states could account for the observed ligand substitution products. Focusing on the ligand substitution products from the rhodo ion in chloride-containing solutions, both with and without oxygen, it is interesting to note that the yield of the aquo pentaammine and aquo erythro ions varies from oxygenated to deoxygenated solutions, whereas the yield of the chloro erythro ion is independent of oxygen.

Due to the lability of Cr(II) systems it is reasonable to suggest that the increase in the yield of the bridge cleavage product in oxygenated systems is in some way related to the charge-transfer process. The fact that some aquo pentaammine is formed in the absence of oxygen supports the suggestion made above that the Cr(II) that is formed in the charge-transfer process is quickly reoxidized to Cr(III) by geminate recombination with the chloride radical in the ion pair. The invariance of the chloro erythro yield suggests that it arises from a state whose reactivity is unaffected by the presence or absence of oxygen. We propose that at least two states, the charge-transfer state and the L_3 state, are involved in the 254-nm photolysis and that the chloro erythro product arises solely from the L_3 state, while the aquo pentaammine and aquo erythro products arise at least from the charge-transfer state and perhaps from both states. Given that no bridge cleavage is observed in L_1 and L_2, it is tempting to suggest that all of the aquo pentaammine arises from the charge-transfer state but that some of the aquo erythro arises from the L_3 state.

The general conclusions reached here about the nature of the states involved in the photochemistry following 254-nm excitation are further supported by recent preliminary experiments on the rhodo ion following excitation at 249 and 195 nm using KrF and ArF rare-gas-halide lasers. Although it has proven difficult to determine quantum yields from these experiments, due to problems with measuring the intensities of the very intense laser pulses, we have measured relative amounts of photoproducts in several experiments. The following trends have been observed:

1. The photochemistry observed at 249 nm is similar to that observed at 254 nm except that the yield of Cr(VI), relative to that of the other products, has increased by 20–30% and the ratio of aquo pentaammine to aquo erythro has also increased.

2. At 195 nm, where, in nitrate media, photochemistry of the nitrate ion is expected to be important, the ratio of nitrite formed to Cr(VI) is greater than 20/1.

These results are consistent with preparation of a state at 249 nm that is more charge transfer and less L_3 in character than that prepared at 254 nm and with reactions at 254 nm in which nitrate photochemistry is of minimal importance.

Conclusion

The production of Cr(VI) species from the charge-transfer photolysis has been quantified and an ion-pair model proposed to explain the observations. The yield of Cr(VI) should parallel the yield of Cr(II) formed in the charge-transfer process and can be used as a probe of the charge-transfer-state reactivities. This technique would appear to probe the same phenomenon that Sriram and Endicott investigated using the $Co(NH_3)_5F^{2+}$ reduction.[5] We have not yet studied the same systems that they did so we cannot comment on how the two methods agree. Those workers did observe some Co(II) production following states that would not be classified as charge transfer in nature but that may reflect the greater ease of oxidation of the ligands and a corresponding mixing of the natures of ligand field and charge-transfer states.

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(10) Coleman, W. F. Unpublished results.

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Stabilization of Homopolyatomic Cations of Iodine in Anhydrous Hydrogen Fluoride

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Sodium fluoride and the Lewis acids NbF_5, TaF_5, and SbF_5 have been used to fix precisely the levels of basicity and acidity in the solvent anhydrous HF in order to establish the acidity thresholds above which the cations I_5^+, I_3^+, and I_2^+ can be generated in solution. Addition of an excess of the base F^- causes disproportionation of each of the cations to I_2 and IF_5. When these disproportionation products are dissolved in HF and the acidity level is adjusted appropriately, the individual cations can be generated. It is shown that the level of acidity is the principal determinant of the nature of the iodine cations generated in HF.

For well over a century it has been known that when I_2 is dissolved in H_2SO_4 and oleums, highly colored solutions are formed. These were thought to contain oxo compounds of I_2. In 1938 Masson postulated the existence of I_3^+ and I_5^+ in explaining iodination of aromatic compounds in H_2SO_4. The most characteristic solution, which was deep blue, was thought for many years to contain I^+. Gillespie and co-workers showed this blue species to be I_2^+, and they also positively identified I_3^+ and I_5^+ in solution. They used stoichiometric amounts of the strong oxidant $S_2O_6F_2$ to oxidize elemental I_2 in the superacidic solvent HSO_3F. By cryoscopy they determined the number of moles of particles produced when 1 mol of I_2 was oxidized by $S_2O_6F_2$, and they used conductance studies to determine the number of moles of SO_3F^-, the product of reduction of $S_2O_6F_2$ and also the base of the solvent system, that was produced in the oxidation of 1 mol of I_2. From these two types of physicochemical measurement they were able to deduce the complexity and numbers of the iodine cations produced for different I_2–$S_2O_6F_2$ stoichiometries and they recorded the UV-visible spectra in HSO_3F of the individual cations I_2^+, I_3^+, and I_5^+. The background to this work, the methodology involved, and the spectra recorded for I_5^+, I_3^+, and I_2^+ (and for I_4^{2+}, the cation stable in HSO_3F at low temperatures) are given in a review by Gillespie and Morton.[1]

The implicit assumption in most of Gillespie's work was that HSO_3F would be sufficiently acidic as a medium to sustain each of the cations as a stable entity when the appropriate I_2–$S_2O_6F_2$ ratio was used to generate a particular cation. A recent review[2] demonstrates that progressive increase of the acidity of the medium is necessary to produce stable cations of a nonmetallic element with increasing charge-to-element ratios; i.e., I_2^+ requires a more acidic medium that I_3^+, which in turn requires higher acidity than

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(1) Gillespie, R. J.; Morton, M. J. *Q. Rev., Chem. Soc.* **1971**, *25*, 553.
(2) O'Donnell, T. A. *Chem. Soc. Rev.* **1987**, *16*, 1.

0020-1669/89/1328-1669$01.50/0

I_5^+. It is then highly significant in the light of this review that, whereas I_5^+ and I_3^+ were stable in HSO_3F made slightly basic by the SO_3F^- produced by reduction of $S_2O_6F_2$, I_2^+ decomposed slowly by disproportionation in such a medium but was stable when the HSO_3F was made more acidic by the addition of SbF_5. It should be noted that Gillespie and Morton[1] recognized the importance of the level of acidity in the instance in which they showed that, for the generation of Br_2^+, it was necessary to use the highly acidic solvent HSO_3F–SbF_5–SO_3 whereas Br_3^+ could be obtained in a less acidic medium.

That review[2] systematizes a large body of earlier work on the stabilities of the cations of iodine and of many other nonmetallic and metallic elements in a range of protonic superacids (oleums, HSO_3F, and HF) and in chloroaluminate melts. Regardless of the chemical nature or temperature domain of the medium, I_2^+ is stable in solutions of highest acidity but disproportionates in turn to I_3^+, I_5^+, and I_2 with increasing availability of the base of the solvent system as the acidity of the medium is decreased, the other product of disproportionation in each case being a covalent compound of the base of the solvent system and of iodine in a higher oxidation state than the formal oxidation state of iodine in the parent cation.

This paper gives a detailed description of the dependence of the stabilities of the iodine cations on the level of acidity of the solvent anhydrous hydrogen fluoride (AHF). It is the obverse of the pioneering work by Gillespie, who generated particular cations by fixing oxidant–reductant stoichiometry in media of high acidity. This work shows that, almost regardless of the oxidant–reductant stoichiometry, the level of acidity of the solvent is the principal determinant of cation speciation. The study does not purport to be an investigation of equilibria existing between iodine cations of the general formula I_n^+, the reductant I_2, and an oxidant such as IF_5. It establishes the acidity threshold in HF below which iodine cations are not stable—they would disproportionate in reacting with the available base—and those thresholds above which I_5^+, I_3^+, and I_2^+ are, in turn, stabilized.

It is now possible to adjust the acidity or basicity of HF to within very narrow limits as a result of the measurements by Gillespie and Liang[3] of the values of the Hammett acidity function (H_0) for HF solutions to which have been added various concentrations of the base F^- or of Lewis acids, such as the group V pentafluorides. We have demonstrated that when a mixture of I_2 and F_2 is maintained in HF of controlled acidity, there is a lower limit of acidity ($H_0 \approx -10.9$) below which no iodine cation can exist in solution in HF. Above that limit I_5^+ can be generated and, as the acidity of the solvent is increased, I_3^+ and I_2^+ gradually become the dominant species as I_5^+ disappears. Above $H_0 \approx -16.2$, the only cationic species is I_2^+. We have no evidence to suggest that cations of higher charge-to-element ratio, e.g. I^+, can be generated in SbF_5–HF solutions for which H_0 is more negative then −21. Gillespie's recording of the UV–visible spectra[1] for the cations generated individually in HSO_3F by fixed oxidant–reductant stoichiometry provided the basis for our identification of mixtures of cations at particular HF acidities, peak positions being shifted by less than 15 nm between the two solvents.

It was stated above that I_5^+, I_3^+, and I_2^+ are progressively stabilized as the acidity of the solvent HF is increased. A more fundamental generalization, a necessary consequence of the foregoing one, is that, as the base F^- is added progressively to a solution of I_2^+ in HF, the cationic species present undergo disproportionation to cations of lower charge-to-element ratio and ultimately to I_2. The other product of disproportionation can be considered to be IF_5. We have shown IF_5 to be the predominant fluoride in disproportionated systems by Raman spectroscopy. I_2 can be identified in such solutions by a characteristic peak at 508 nm in UV–visible spectra.

In a further series of experiments we took the typical cationic disproportionation products I_2 and IF_5 in HF and gradually increased the acidity of the solvent. Again, we found the same acidity thresholds for individual cation generation, regardless of the fact that, in the I_2–F_2 reactions, the reductant I_2 was in great excess whereas, in the I_2–IF_5 reactions, the oxidant IF_5 was in great excess.

Experimental Section

Reagents. Commercially available SbF_5 (Ozark-Mahoning) was redistilled in a carefully dried greaseless glass system. NbF_5 and TaF_5 were also commercial products (Ozark Mahoning) and were handled in a nitrogen-filled glovebox. Commercially available HF (Matheson) was purified by "trap-to-trap" distillations in Kel-F containers, "heads and tails" being discarded. IF_5 was prepared by reacting I_2 with an excess of the amount of F_2 required to produce IF_5 and removing the more volatile IF_7 by controlled distillation.

Caution! Hydrogen fluoride and molecular fluorides such as IF_5, which can be hydrolyzed to HF, can cause very serious skin, eye, and respiratory tract damage and must be manipulated in closed vacuum systems.

Preparation of Solutions. F_2, HF, and volatile pentafluorides were admitted directly or distilled *individually* into reaction tubes with use of a stainless steel vacuum line based on Hoke valves and Swagelok fittings. Simultaneous distillation of HF and a Lewis acid leads to rapid dissolution of the passivating fluoride layer adhering to the metal components and consequent contamination of solutions.

Weighed amounts of involatile reagents were loaded in the glovebox into "synthetic sapphire" (fused alumina) tubes supplied by Tyco Saphikon. These tubes (8 × 0.5 in.) are supplied with one end plugged with fused alumina and can be connected to the vacuum system through a Kel-F head machined to provide a vacuum seal to the alumina tube by means of a tapered Teflon gasket. A Kel-F valve is self-sealed to the Kel-F head and is connected to the metal vacuum line by means of $^1/_4$ in. o.d. Kel-F tubing "flare-sealed" to the valve and connected to the line through a Swagelok union. The details of these heads and connections have been reported previously.[4] HF was distilled into sapphire tubes containing a Lewis acid, and solution molalities were determined by weighing the tube containing the solvent after previously weighing the evacuated tube with and without solute. Very dilute solutions of NaF in HF were prepared by adding to sapphire tubes aliquots of dilute solutions of NaCl of known concentration in H_2O, removing H_2O by distillation, adding AHF, pumping off HCl, adding AHF as solvent, and weighing.

Recording of Spectra. Solutions were transferred directly from the sapphire reaction tubes to spectral cells through a Kel-F crosspiece. The very small "dead space" of the crosspiece minimizes the possibility of change in solution conditions between the reaction tube and the spectral cell. Pairs of spectral cells, one for the solution and one for the solvent HF, have synthetic sapphire windows directly sealed to Kel-F bodies and have been described previously.[5] Spectra were recorded on a Cary 14 spectrometer.

Results and Discussion

Two series of experimental runs were conducted in order to establish the levels of acidity or basicity of AHF at which the cations I_5^+, I_3^+, and I_2^+ can be stabilized in HF solutions. The reductant was well in excess of stoichiometric proportions in the first series, excess oxidant being used in the second.

In each experiment in the first series, elemental I_2 was oxidized by an amount of elemental F_2 less than that required to convert all of the I_2 to cations, and the acidity of the AHF was varied from basic (0.1 *m* NaF) to acidic (0.2 *m* SbF_5). In a typical experiment, 0.1 mmol of I_2 would be reacted with 0.05 mmol of F_2 in about 10 mL of HF solution of fixed acidity or basicity and the system would be allowed to equilibrate for several hours. The results are summarized in Table I.

In moderately basic solutions (0.1 and 0.01 *m* NaF, for which H_0 values are −9.95 and −10.8, respectively[3]) the species in solution after fluorination were shown to be elemental I_2, which has a small but significant solubility in HF and absorbs at 508 nm, and IF_5, as characterized by a typical Raman spectrum from this work

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(3) Gillespie, R. J.; Liang, J. *J. Am. Chem. Soc.* **1988**, *110*, 6053.

(4) Canterford, J. H.; O'Donnell, T. A. In *Technique of Inorganic Chemistry*; Jonassen, H. B., Weissberger, A., Eds.; Interscience: New York, 1968; Vol. VII, p 273.

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(6) Beattie, I. R.; Ozin, G. A.; Perry, R. O. *J. Chem. Soc. A* **1970**, *12*, 2071.

(7) Naumann, D.; Renk, E.; Lehmann, E. *J. Fluorine Chem.* **1977**, *10*, 395.

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Table I. Dependence of the Formation of Iodine Cations on the Level of Acidity of Hydrogen Fluoride[a]

HF acidity/basicity (solute concn, *m*)	$-H_0$[b]	signif I-containing species at equil[c]
NaF (0.1)	9.95[d]	$I_2 + IF_5$
NaF (0.01)	10.80[d]	$I_2 + IF_5$
NaF (0.0075)	10.95[e]	$I_3^+ + I_5^+$
NaF (0.001)	11.80[e]	$I_3^+ + I_5^+$
NbF_5 (0.05)	15.65[d]	I_3^+ + trace I_2^+
NbF_5 (0.075)	15.90[d]	$I_3^+ + I_2^+$
NbF_5 (0.091)	16.05[f]	$I_3^+ + I_2^+$
NbF_5 (0.11)	16.20[f]	I_2^+
TaF_5 (0.4)	19.20[d]	I_2^+
SbF_5 (0.2)	20.65[d]	I_2^+

[a] Excess I_2 reacted with controlled amounts of F_2 under the conditions listed. [b] Values rounded to 0.05 unit. [c] Excess elemental I_2 would be present in all solutions. [d] Experimentally determined values.[3] [e] Calculated from experimental values from ref 3, an autoprotolysis constant of 5×10^{-13}, and a value of −15.10 for H_0 for pure HF.[3] [f] Obtained by interpolation between experimental values.[3]

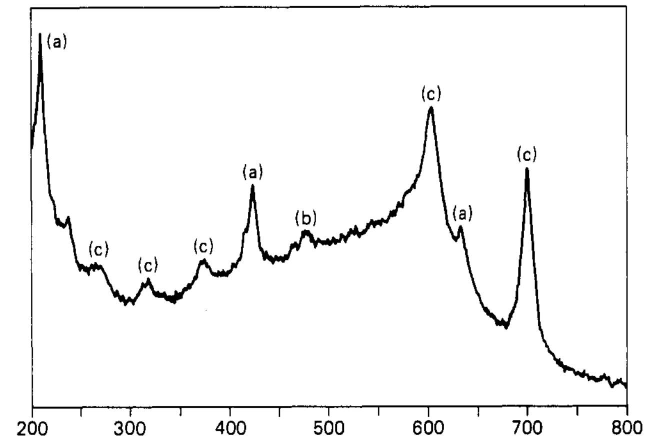

Figure 1. Typical Raman spectrum after disproportionation of iodine cations in HF. Peak assignments: (a) I_2;[6] (b) IF_3;[7] (c) IF_5.[8]

reproduced as Figure 1. There is some weak Raman evidence for a small amount of IF_3, but the dominant high-oxidation-state fluoride of iodine is IF_5. For this reason all equilibria between I_2, F_2, iodine fluorides, and iodine cations will be discussed as though IF_5 were the only covalent fluoride of iodine present. The validity of the discussions below on disproportionation of iodine cations is not affected in any way if there is a small amount of IF_3 in equilibrium with IF_5 in these HF solutions.

Although IF_5 could be viewed simply as the oxidation product resulting from the partial reaction of I_2 with F_2, it, together with I_2 in basic HF solutions, is better seen in the context of the present work as one of the disproportionation products of an iodine cation as discussed below.

When the basicity of the HF was reduced to the level set by 0.0075 *m* NaF ($H_0 = -10.95$), the UV–visible spectrum showed peaks at 237, 303, and 457 nm (Figure 2). The first two peaks, as well as the other features of the observed spectra in HF, are diagnostic for I_5^+ and I_3^+. Figure 3 gives superimposed spectra for I_5^+, I_3^+, and I_2^+ in HSO_3F as reported by Gillespie and Morton.[1] As indicated earlier, these spectra were recorded separately in HSO_3F under conditions of reactant stoichiometry such that, in each case, only one cation had spectroscopic significance. We have established that peak positions for spectra of each of the cations in HSO_3F and in HF shift by less than 15 nm on moving from the solvent HSO_3F to HF. Well-defined peaks at 237, 303, and 626 nm in HF are diagnostic for I_5^+, I_3^+, and I_2^+, respectively. The spectral region between about 350 and 550 nm, where bands for all species overlap, need not be used.

Table I shows that the acidity threshold above which iodine cations can be generated and observed spectroscopically in HF is very well defined in terms of concentration of added F^-, cations not forming at $[F^-] = 0.01$ *m* but being detectable at $[F^-] = 0.0075$ *m*. As shown immediately below, this corresponds with a threshold of −10.8 to −10.95 in terms of H_0 values. Excess solid I_2 was present in these solutions, with a small equilibrium amount of I_2 in solution.

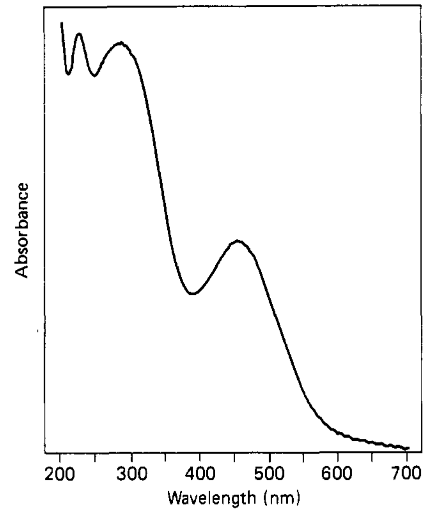

Figure 2. UV–visible spectrum showing I_5^+ and I_3^+ in weakly basic HF ($H_0 = -10.95$).

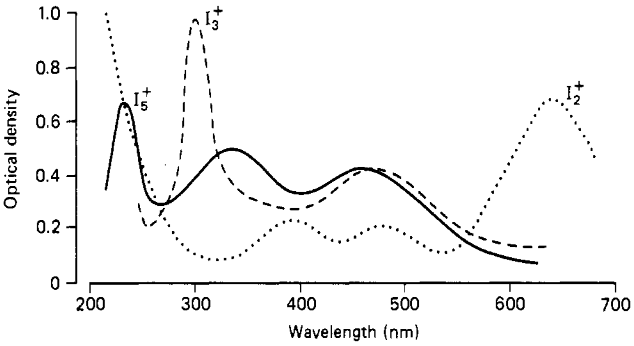

Figure 3. UV–visible spectra of iodine cations in HSO_3F (adapted from ref 1).

Although Gillespie and Liang[3] did not measure experimental values of H_0 for NaF concentrations below 0.01 *m*, a fairly reliable estimate of H_0 at 0.0075 *m* F^- and at 0.001 *m* can be made on the basis of H_0 values measured by them in the most dilute basic solution and in the most dilute acidic solution. From these the approximate autoprotolysis constant K_{ap} can be calculated for HF. Their H_0 values of −10.8 for 0.01 *m* (0.02 mol %) KF, a source of the strong base F^-, and −20.15 for 0.025 *m* (0.05 mol %) SbF_5, assumed to be a very strong Lewis acid in HF, suggest a value for K_{ap} of about $10^{-12.3}$. If we take the Gillespie and Liang value of −15.1 as H_0 for pure HF, H_0 values can be calculated for 0.0075 and 0.001 *m* F^- as −10.95 and −11.80 relative to Gillespie and Liang's experimental value of −10.8 for 0.01 *m* (0.02 mol %) F^-.

In 0.001 *m* F^- in HF ($H_0 = -11.80$) I_3^+ and I_5^+ still coexist. As stated above, Gillespie and Liang give a value of −15.10 for H_0 for pure, neutral HF. Figure 4 is the spectrum for excess I_2 oxidized by F_2 in very weakly acidic HF solution, i.e. 0.075 *m* with respect to NbF_5 ($H_0 = -15.90$). Reference to Figure 3 shows that in this acidity region I_3^+ and I_2^+ coexist in equilibrium. When the solution is made slightly more acidic ($H_0 = -16.20$), I_2^+ is the only cationic species able to be detected spectroscopically. Even though solutions 5 *m* in SbF_5 ($H_0 = -22$) were investigated, there was no evidence for any cationic species other than I_2^+. Specifically, there was no indication of the formation of I^+. It is significant that, in these acidic solutions, elemental I_2 was always present in excess. That is, even though a potential reductant was present, I_2^+, the iodine cation with the highest ratio of charge to iodine atom, was stabilized because of the acidity of the medium.

When excess NaF solution in HF was added to HF solutions of these cations, the characteristic colors of the solutions disap-

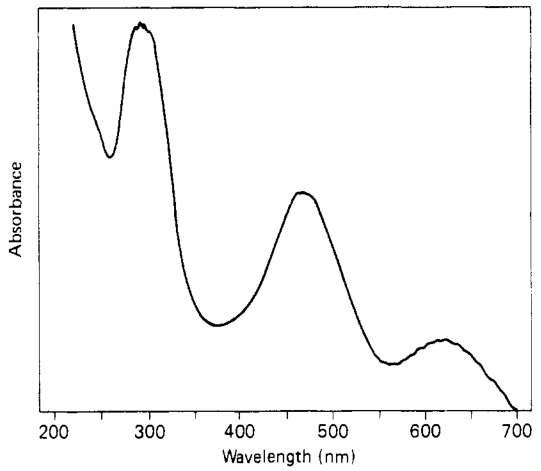

Figure 4. Spectrum showing I_3^+ and I_2^+ in weakly acidic HF (H_0 = −15.90).

Table II. Formation of Iodine Cations in Hydrogen Fluoride[a]

concn of Sb(V)[b] after SbF_5 additions, *m*	signif I-containing species at equil[c]	concn of Sb(V)[b] after SbF_5 additions, *m*	signif I-containing species at equil[c]
0–0.007	I_2	0.013	I_2^+ + trace I_3^+
0.009	$I_3^+ + I_5^+$	0.02	I_2^+
0.010	$I_3^+ + I_2^+$		

[a] A 10-fold excess of IF_5 (0.011 M) was added to solid I_2 in HF. Dilute SbF_5/HF was added progressively to the reaction mixture. [b] As discussed in the text, these concentrations would be somewhat smaller than listed because of progressive dilution of the solutions. [c] Excess IF_5, as the molecular entity or as IF_4^+ depending on the level of acidity, would be present in all solutions.

peared and it was shown that disproportionation had occured, by identifying I_2 in solution from UV–visible spectroscopy and IF_5 by Raman spectroscopy. The stepwise disproportionations may be represented as

$$14I_2^+ + 5F^- \rightarrow 9I_3^+ + IF_5$$

$$12I_3^+ + 5F^- \rightarrow 7I_5^+ + IF_5$$

$$5I_5^+ + 5F^- \rightarrow 12I_2 + IF_5$$

Relative to the amount of I_2^+ in HF solution, only small amounts of the base F^- are required to cause disproportionation of the cation. Progressive addition of base produces in turn I_3^+, I_5^+, and iodine in addition to IF_5.

It was stated earlier that there was some Raman spectroscopic evidence for a very small amount of IF_3, possibly in equilibrium with IF_5. The presence of some IF_3 would not invalidate the general proposition that base-induced disproportionation of iodine cations leads to the formation of elemental iodine and of a covalent fluoride containing the iodine in a higher oxidation state than the formal oxidation states of iodine in the parent cations.

In the second series of experiments on the dependence of the generation of iodine cations on acidity or basicity of the solution, summarized in Table II, the formal disproportionation products I_2 and IF_5 were dissolved in HF and a dilute solution of SbF_5 in HF was added accurately and gradually to the initial solution. Whereas the reductant (I_2) was in excess in the first series of experiments, the oxidant IF_5, initially 0.011 *m* in solution, was present in 10-fold excess over the reductant I_2. For the SbF_5 additions up to 0.007 *m* elemental I_2 was the only species observed in UV–visible spectra. SbF_5 would be interacting with IF_5 to produce IF_4^+ and SbF_6^- in solution; however, IF_5, itself a weak base, would be in excess and so the resultant solution would be weakly basic. After adjustment of the SbF_5 concentration to 0.009 *m* IF_5 would still be in very slight excess with Sb(V) present as SbF_6^- and the resulting solution would be very weakly basic, probably not very different from that of the "natural" solvent. Cationic species I_5^+ and I_3^+ were observed under these conditions.

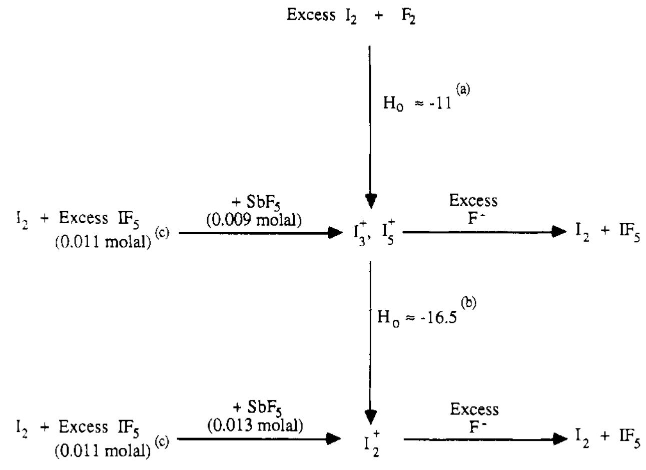

Figure 5. Formation and disproportionation of iodine cations in hydrogen fluoride. Legend: (a) H_0 value for NaF/HF;[3] (b) H_0 value for NbF_5/HF;[3] (c) amount of solid elemental I_2 such that IF_5 was in a 10-fold excess relative to I_2 in the experimental volume of HF solution, which was 0.011 *m* in IF_5 initially.

The real level of acidity of "natural" HF calls for some comment. Most textbook and other authors quote a very old value of about −11 for H_0 for "pure" or "natural" HF.[9] Using the methodology they adopted for estimation of H_0 for pure H_2SO_4 and for pure HSO_3F, Gillespie and Liang[3] cite a value for H_0 of −15.10 for pure HF. Natural HF will be less acidic than is indicated by this H_0 value, regardless of the care taken in distilling and storing the solvent. All likely impurities will act as bases in distilled HF. The one most commonly quoted is residual water, which will be protonated in HF, thus increasing the concentration of the base F^- over that of the solvated proton, when self-ionization of HF is considered. However, even if H_2O is removed in the distillation process, the solvent will be more basic than the theoretically pure solvent particularly, as is usual, if the solvent has been stored in Kel-F containers. It has been shown experimentally[10] that unsaturated material can be leached from Kel-F by HF solutions. Protonation of these impurities leads to enhanced basicity. The best distilled and stored HF will always have a value of −11 to −12 for H_0 rather than that of −15.10 given from the self-ionization equation. In this present work we have shown that natural HF supports generation of I_3^+ and I_5^+, indicating the range −11 to −12 for H_0 for our solvent. The position regarding pure HF is not different in principle from that for pure H_2O, where, after the most rigorous distillation, the pH of the solvent is always less than 7.

When the acidity deficiency was further halved, by adjustment of the SbF_5 concentration to 0.010 *m*, I_5^+ was replaced by I_2^+ with I_3^+ the dominant species. Beyond neutrality, when the SbF_5 concentration had been adjusted to 0.013 *m* and was in excess of the amount of IF_5, the solution would have been weakly acidic, IF_4^+, H_2F^+, and SbF_6^- all being in equilibrium in the solution, and I_2^+ was the dominant species with a trace of I_3^+. This I_3^+ disappeared when the SbF_5 concentration (adjusted to 0.02 *m*) was well in excess of IF_5. All acid or base concentrations would be somewhat less than as given by the stoichiometric difference between IF_5 and SbF_5 concentrations because of the progressive dilution factor, but the argument put forward above would still hold because of the buffering effect of excess base or excess acid.

It should be noted that, in this second series of experiments, the potential oxidant iodine(V) is always present in large excess, either as free IF_5 or as IF_4^+. However, the "low oxidation state" cations I_5^+ and I_3^+ are stable in slightly basic solution. More specifically, I_2^+, if formed, would disproportionate to these cations under these conditions.

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(9) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley: New York, 1980; p 238. (b) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: New York, 1985; p 7.

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Therefore, the important point emerging from this work is that, within wide limits, the level of acidity of the medium is the principal determinant of cation speciation, regardless of whether oxidant or reductant is in excess. This certainly holds when the disproportionation reactions are reversed. The generalization would not be valid if F_2 were to be in excess. Its extreme power as an oxidant would override solution acidity/basicity effects.

A further indication of the prime importance of acidity control in generating individual cations was that conproportionation reactions similar to those described above for IF_5 and I_2 were carried out within the present study with IO_3^- and I_2 in HF solutions of controlled acidity. SbF_5 gave I_2^+, and GeF_4, potentially a Lewis acid of the system but one that is almost vanishingly weak, gave I_5^+ and I_3^+. This, however, is an untidy way of producing cations by comparison with the reaction of IF_5 and I_2, because each of the oxo ligands of IO_3^- would be triply protonated in HF on release from the oxidant, generating much of the unnecessary base F^-. However, this approach could be used for convenience in the synthesis of iodine cations. We have shown this to be a general synthetic approach by generating sulfur cations by reaction of S_8 with SO_3^{2-} and with SO_4^{2-} in HF, the acidity of which has been adjusted appropriately.

The overall program on generation of individual cations by control of the HF acidity is summarized briefly in the flow sheet in Figure 5. Excess reductant, I_2, with F_2 gives I_5^+ and I_3^+ for H_0 values between −11 and −16.2 and I_2^+ in more acidic solutions. Each cation disproportionates to I_2 and IF_5 when treated in solution with excess base. With the disproportionation products in solution and, now, the oxidant in excess, appropriate acidity control leads to generation in solution of I_5^+, I_3^+, or I_2^+.

This scheme is presented to highlight the proposition developed in this paper that the principal determinant of the nature of cations of iodine stabilized in AHF is the level of acidity or basicity of the solution.

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Registry No. SbF_5, 7783-70-2; NbF_5, 7783-68-8; TaF_5, 7783-71-3; HF, 7664-39-3; F_2, 7782-41-4; NaF, 7681-49-4; NaCl, 7647-14-5; I_2, 7553-56-2; IF_5, 7783-66-6; I_3^+, 12596-32-6; I_5^+, 44222-71-1; I_2^+, 28712-14-3.

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ESR Study of the Solution Thermochromism Resulting from Low-Temperature Isomerization of Pyrazolato-Bridged Dirhodium Complexes Generated via Electrochemical Oxidation

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Paramagnetic complexes of the type $[Rh_2(\mu\text{-EE}')_2(t\text{-BuNC})_2(\mu\text{-Z})](PF_6)_2$ (EE′ = bis(diphenylphosphino)methane (dppm), (diphenylarsino)(diphenylphosphino)methane (dapm), bis(diphenylarsino)methane (dpam); Z = pyrazolate (pz), 4-methylpyrazolate (4mpz), 3,5-dimethylpyrazolate (35mpz), 4-bromo-3,5-dimethylpyrazolate (4B35mpz), 3,4,5-tribromopyrazolate (345Bpz)) containing the Rh_2^{3+} core have been prepared via controlled-potential electrolysis of the parent Rh_2^{2+} species $[Rh_2(\mu\text{-EE}')_2(t\text{-BuNC})_2(\mu\text{-Z})](PF_6)$. The Rh_2^{2+} diisocyanide complexes and analogous dicarbonyl complexes have cyclic voltammograms that exhibit a quasi-reversible wave followed by an irreversible or a second quasi-reversible wave. The $E_{1/2}$ values for the couple at less positive potentials are in the order dppm < dapm < dpam for analogous diisocyanide and dicarbonyl complexes; thus, the stabilities of the Rh_2^{3+} paramagnetic complexes toward reduction are in the order dpam < dapm < dppm. UV-vis spectroscopy has been used to demonstrate that electron transfer occurs between Rh_2^{2+} and Rh_2^{3+} species containing different EE′ ligands when the initial Rh_2^{3+} species is the less stable one of the two possible Rh_2^{3+} species. Solutions of the Rh_2^{3+} diisocyanide species in 4:1 CH_2Cl_2/toluene at room-temperature are green and give room-temperature ESR spectra that exhibit a single isotropic signal near $g = 2.15$. The frozen solutions exhibit anisotropic ESR spectra with resonances between g values of 1.99 and 2.22. Frozen solutions of the Rh_2^{3+} diisocyanide species at −196 °C are red, except for $[Rh_2(\mu\text{-dppm})_2(t\text{-BuNC})_2(\mu\text{-345Bpz})](PF_6)_2$, which remains green. Frozen-solution spectra at temperatures above −196 °C for $[Rh_2(\mu\text{-dapm})_2(t\text{-BuNC})_2(\mu\text{-345Bpz})](PF_6)_2$ clearly indicate the existence of two forms of the complex, a green α form and a red β form. The temperatures at which the α to β isomerization occurs are in the order dppm < dapm < dpam for a given pyrazolate. The possible nature of this isomerization is discussed.

Introduction

In recent years a very rich chemistry has been discovered for dirhodium complexes containing bis(diphenylphosphino)methane (dppm)[1] and, to a lesser extent, (diphenylarsino)(diphenylphosphino)methane (dapm) and bis(diphenylarsino)methane (dpam) as transoid bridging ligands. Unlike the dirhodium tetracarboxylate complexes $Rh_2(O_2CR)_4$ and analogous complexes that contain the Rh_2^{4+} core and four anionic bridging ligands,[2,3] the majority of the known dirhodium complexes with transoid dppm, dapm, and dpam ligands contain the Rh_2^{2+} core. A few dirhodium(II) complexes containing the transoid dppm, dapm, and dpam ligands have been prepared by either chemical or electrochemical oxidative addition.[4–7]

Many of the Rh_2^{4+} complexes with four anionic ligands have been shown to undergo electrochemical oxidation to form Rh_2^{5+}

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