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Photoredox Processes in the 254-nm Photochemistry of Chromium(III) Ammine Complexes

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The photochemical reactions of a series of chromium(III) ammine complexes have been studied following excitation at 254 nm in three different supporting electrolytes and in oxygenated and deoxygenated solutions. In addition to ligand substitution reactions, redox processes are observed when O_2 is present or, in NO_3^- media, when O_2 is absent. An ion-pair model is proposed to explain the dependence of the yield for the redox process on ion charge, supporting electrolyte, and nature of the coordinated ligands. At least two excited states are involved in the observed photochemistry.

Introduction

It is well established that the nature and distribution of products in the photochemical reactions of Cr(III) complexes, following excitation into the ligand field bands, depends on the particular state to which the complex was initially excited. These observations, together with a number of other experimental results, have led to the conclusion that a single, common excited state cannot be responsible for the observed photochemistry. For the few Cr(III) systems whose photochemistry has been studied following excitation in the ultraviolet region of the spectrum, the same pattern appears to hold for the ligand substitution, namely that the nature and yield of the various photoproducts are not the same as are found for that compound excited into one of the ligand field bands in the visible region of the spectrum. In the charge-transfer photochemistry of the (μ-hydroxo)bis(pentaamminechromium(III)) ion (the rhodo ion), $[(NH_3)_5CrOHCr(NH_3)_5]^{5+}$, we have previously observed ligand substitution photoproducts that are not seen in the ligand field photochemistry, in this case the formation of mononuclear complexes resulting from photoinduced bridge cleavage.[1] Similar reactions are observed for a variety of other oxy- and hydroxy-bridged complexes of Cr(III) excited at 254 nm.[2]

Excitation at 254 nm leads to production of a charge-transfer state in the complex. In chromium(III) ammine complexes the most reasonable description of this charge-transfer state is that corresponding to a ligand to metal charge transfer. If the photochemical behavior of this state parallels that of the corresponding Co(III) and other related systems, one would expect that the chromium in the photoproduct would have been reduced to the 2+ oxidation state.[3] To date, Cr(II) has not been observed directly in the photochemistry of simple chromium(III) ammine complexes although Cr(II) has been identified in the photochemistry of $Cr(bpy)^{3+}$, where bpy is 2,2′-bipyridyl.[4] Sriram and Endicott have used an indirect technique to study Cr(II) production in the charge-transfer photolysis of $Cr(NH_3)_5Br^{2+}$ and $Cr(NH_3)_5N_3^{2+}$. They detected the presence of Cr(II) by measuring the formation of Co(II) following the reduction of $Co(NH_3)_5F^{2+}$, presumably by Cr(II).[5] In our work on the 254-mm photolysis of a number of Cr(III) complexes, including a variety of chromium(III) ammine complexes, we have frequently observed the formation of small amounts of Cr(VI) species.[6] In this paper we report a quantitative study of the factors that influence the formation of Cr(VI) products in the charge-transfer photolysis of six chromium(III) ammine complexes and discuss the implications of these findings to the overall photochemistry of the charge-transfer state of these systems. In addition we present evidence that the spectroscopically hidden $^4T_1(^4P)$ state is also involved in the 254-nm photolysis.

Table I. Cr(VI) Quantum Yields in Various Supporting Electrolytes with and without O_2[a]

	supporting electrolyte					
	0.1 M HCl		0.1 M $HClO_4$		0.1 M HNO_3	
complex (ϵ(254 nm))	O_2	no O_2	O_2	no O_2	O_2	no O_2
rhodo (61.3)[b]	2.58[c]	0[d]	0.87	0	6.18	6.15
aquo erythro (86.0)	2.03	0	0.53	0	4.70	4.78
chloro erythro (180)	2.09	0	2.09	0	3.81	3.82
chloro pentaammine (25.8)	3.71	0	3.12	0	1.08	1.12
aquo pentaammine (15.3)	1.07	0	0.68	0	1.00	0.97
hexaammine (25.0)	1.88	0	1.24	0	0.94	1.00

[a] All values are at 25 °C and have been multiplied by 10^3. [b] $M^{-1}\,cm^{-1}$. [c] All values are the result of at least three measurements. Standard deviations are in the range 2–12%. [d] A value of O implies $<10^{-6}$.

Experimental Section

The ions studied were the rhodo ion, the *acdeghijk*-nonaammine-*b*-aquo-*f*-(μ-hydroxo)dichromium(III) ion (the aquo erythro ion), $[H_2O(NH_3)_4CrOHCr(NH_3)_5]^{5+}$, the *bcdeghijk*-nonaamine-*a*-chloro-*f*-(μ-hydroxo)dichromium(III) ion (the chloro erythro ion), $[(NH_3)_4ClCrOHCr(NH_3)_5]^{4+}$, the hexaaminechromium(III) ion, $[Cr(NH_3)_6]^{3+}$, and the aquo and chloro pentaammine ions, $[Cr(NH_3)_5H_2O]^{3+}$ and $[Cr(NH_3)_5Cl]^{2+}$. All complexes were prepared as the perchlorate salts by using standard literature techniques.[7]

Deoxygenated samples were prepared by multiple freeze–thaw cycles. Absorption spectra taken before and after such treatment indicate no change in the nature of the complexes.

Solutions were photolyzed at 254 nm in a Rayonet photochemical reactor equipped with 12 254-nm lamps. Solutions were maintained at constant temperature throughout the photolyses in thermostated quartz sample cells.

Photon fluxes, for quantum yield measurements, were determined by ferrioxalate actinometry under the same conditions that the photolyses were performed. When quantum yield calculations were carried out, corrections were made for the cylindrical nature of the sample cells. Absorption and derivative absorption spectra were measured on either a Cary 219 or a Perkin-Elmer Lambda 5 spectrophotometer. Mixtures of photoproducts were analyzed for Cr(VI) by passing the sample through a cation-exchange column containing treated Dowex 50W-X8 resin. This allowed Cr(VI), as $Cr_2O_7^{2-}$, to pass through the column with retention of all other Cr-containing species. The dichromate solutions

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Table II. Cr(VI) Quantum Yields from 254-nm Photolysis of the Rhodo Ion in Mixed Nitrate/Chloride Media

% compn of supporting electrolyte		$10^3\phi$	
NO_3^-	Cl^-	O_2	no O_2
100	0	6.18[a]	6.09
70	30	4.20	4.26
50	50	2.97	2.82
30	70	2.47	1.84
0	100	2.58	0.00

[a] All values are the mean of at least three measurements. Standard deviations are 6–13%.

Table III. Nitrite Quantum Yields for the 254-nm Photolysis of Cr(III) Complexes

complex	$10^3\phi(NO_2^-)$	complex	$10^3\phi(NO_2^-)$
rhodo	9.03[a]	chloro pentaammine	1.93
aquo erythro	7.61	aquo pentaammine	1.73
chloro erythro	6.12	hexaammine	1.61

[a] All values are the average of at least five measurements. Standard deviations average 15%.

thus obtained were converted in base to chromate ion and the concentrations determined from the measured absorbance at 373 nm.

Results

A. Formation of Cr(VI). The quantum yields of Cr(VI) formation for the six complexes studied in three different solvent systems, 0.1 M HCl, 0.1 M $HClO_4$, and 0.1 M HNO_3, oxygenated and deoxygenated, are shown in Table I. In the case of solutions containing chloride or perchlorate ions, all of the light that is absorbed at 254 nm is absorbed by the complex. However, in the case of nitrate ion containing solutions, a significant fraction of the incident light is absorbed by the nitrate ion (the quantum yields in Table I are corrected for the fraction of the light that is absorbed by the sample and hence are defined as moles of Cr(VI)/mole of photons absorbed by the complex). In HCl and $HClO_4$ no Cr(VI) is detected in deoxygenated systems. In 0.1 M HNO_3 dissolved oxygen is not necessary for the formation of Cr(VI). Table II shows the quantum yield for Cr(VI) formation in mixtures of HCl and HNO_3 where the ionic strength of the supporting electrolyte is kept constant at 0.1. When the HNO_3 accounts for more than 50% of the supporting electrolyte, the quantum yield for Cr(VI) formation is independent of dissolved oxygen. In the absorption spectra of the anions eluted from mixtures obtained from photolysis in HNO_3, several small shoulders were noted on the absorption bands of the dichromate ion. When the spectrum of pure dichromate ion is subtracted from this previous spectrum, the difference spectrum is identical with the absorption spectrum of the nitrite ion. The amounts of NO_2^- were quantified by taking the first derivative of the absorption spectrum of $Cr_2O_7^{2-}/NO_2^-$ mixtures. By comparison with a standard set of dichromate/nitrite mixtures, the amplitudes of the first derivative signals were found to be proportional to the nitrite concentration. Table III shows the yield of NO_2^- on photolysis of the six complexes in 0.1 M HNO_3. When solutions of 0.1 M HNO_3 were photolyzed under the conditions of the photolyses reported here, but for 5 times as long as the longest photolysis of a solution containing a Cr(III) complex, there were no detectable photoproducts.

B. Ligand Substitution Products. The ligand substitution products obtained following excitation at 254 nm have been studied quantitatively for the rhodo ion in all three supporting electrolyte systems and for the aquo erythro ion in 0.1 M HCl with and without dissolved oxygen. The results of these studies are shown in Table IV. This table also shows the quantum yields for the photoinduced ligand substitution reactions following excitation into the two lowest excited quartet states, L_1 (502 nm) and L_2 (375 nm), for the rhodo ion.

Discussion

A. Role of Oxygen in the Formation of Cr(VI). From the relatively small values of the extinction coefficients at 254 nm in Table I, it is clear that the systems are being excited into the low-energy end of the very intense charge-transfer transitions. It is also likely that the third ligand field transition, L_3, the $^4T_1$ state that arises, in *O* symmetry, from the ^4P free-ion term, lies in this same region of the spectrum. This state is only seen in Cr(III) complexes when the ligands are as weak or weaker than water in ligand field strength. If we use the spectroscopic parameters obtained from our spectra of the rhodo ion and assume the Racah *B* parameter to be 950–1000 cm^{-1}, the $^4A_2 \rightarrow {}^4T_1(P)$ transition is predicted to occur at 262–257 nm, excluding configuration interaction between the $^4T_1(P)$ state and the lower lying $^4T_1(F)$ (L_2) state. Thus, the L_3 states in these systems can be classified as spectroscopically hidden. The photochemical implications of the L_3 state are discussed later.

Table IV. Quantum Yields for Ligand Substitution Products from the Rhodo Complex

	$10^3\phi$			
	254 nm (0.1 M HCl)		L_1	L_2
product	no O_2	O_2	(502 nm)	(375 nm)
aquo pentaammine	0.07[a]	0.17	0[b]	0
aquo erythro	0.39	0.24	0.37	0.24
chloro erythro	0.22	0.23	0.17	0.17
chloro pentaammine	0	0	0	0

[a] The quantum yields are the average of at least three experiments for each product at each wavelength. Standard deviations average 5%. [b] A value of 0 implies a quantum yield of $<10^{-5}$.

In solutions containing Cl^- and ClO_4^- it is not surprising that no Cr(VI) is obtained in the absence of dissolved oxygen. Given the ligand to metal charge-transfer process expected in these systems, it is unlikely that Cr(VI) would be formed in the absence of a strong oxidizing agent.[8] When oxygen is present, the formation of Cr(VI) must involve excited states of Cr species, since oxygen does not oxidize either Cr(II) or Cr(III) to Cr(VI) under ground-state conditions. Additionally, we have been unable to observe oxygen oxidation of any Cr(III) excited state lying at an energy lower than that of the charge-transfer state. Consequently, we propose that the charge-transfer excited state, which can be viewed as an excited state of Cr(II), is either oxidized directly by oxygen or relaxes to some other excited state of Cr(II), which is then oxidized. Although there is no evidence concerning the detailed mechanism of this oxidation, it seems unlikely that the system involves excited states all the way up to Cr(VI).

Experiments involving varying amounts of dissolved oxygen have shown that the quantum yield for Cr(VI) production does not diminish as the oxygen concentration is reduced to less than one-tenth of its saturation value. In none of our experiments do we consume more than 5% of the dissolved oxygen, and in many experiments oxygen was constantly being bubbled through the reaction vessel. Therefore, we conclude that oxygen is not the limiting reagent in the production of Cr(VI) and that the yield of Cr(VI) can be used as a probe of Cr(II) formation, assuming that the ratio $\phi(Cr(VI))/\phi(Cr(II))$ is constant for a given set of conditions.

B. Role of Supporting Electrolyte (Cl^- or ClO_4^-), Nature of the Complex, and Charge on the Complex. The charge-transfer state that ultimately leads to the formation of Cr(VI) can be further characterized by examining the effects of changing the supporting electrolyte, the nature of the complex, and the charge on the complex. From Table I it is clear that the greatest difference between the quantum yield for Cr(VI) formation between chloride and perchlorate media occurs in the cases of the rhodo and aquo erythro complexes (where the ratio ϕ in Cl^-/ϕ in ClO_4^- is 3.0–3.8). In the aquo pentaamine and hexaammine complexes this ratio is 1.51–1.57, and in the two complexes containing bound

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(8) Work in progress in our laboratory on the charge-transfer photochemistry of the $Cr(CN)_6^{3-}$ ion shows that oxygen is not necessary for the production of oxidation products in any supporting electrolyte, consistent with the metal to ligand nature of the charge-transfer state in this complex.

chloro groups the ratio is 1.19–1.25. Thus, in the most highly charged complexes containing no bound chloride ligands, the chloride ions in the supporting electrolyte stabilize the reacting state to a greater extent, relative to the perchlorate ion, than in the case of the two tripositive ions with no chloride ligands. In the case of complexes containing chloride in the coordination sphere, the stabilization of the reactive state is relatively insensitive to the nature of the supporting electrolyte. The following model appears to be consistent with these observations. In those complexes where there is no chloride in the coordination sphere, there is not an easily oxidizable ligand in the complex. Thus, the efficiency of the charge-transfer process, the precursor to the redox process that gives Cr(II) as an intermediate product and ultimately, when oxygen is present, Cr(VI), is moderately low. The presence of a relatively easily oxidized species, such as Cl^-, helps to facilitate the charge-transfer process and increase the yield of reactions that originate from the charge-transfer state. The interaction with the ions of the supporting electrolyte can be viewed as the formation of an ion pair between the complex of interest and the electrolyte ion. Thus, the strongest ion pairs are expected for the most highly charged ions, the rhodo and aquo erythro ions. In the case of the chloro erythro and chloro pentaammine ions the majority of the stabilization of the charge-transfer state comes from charge transfer involving the bound chloride ligands, and the system is relatively insensitive to the nature of the supporting electrolyte. In the case of the two tripositive mononuclear ions the quantum yield ratio is intermediate between the two cases just discussed. Chloride ion would certainly stabilize the charge transfer to a greater extent, but the lower charge on the ions would weaken the ion-pair interaction. In all of the complexes the charge-transfer process can be said to involve some charge transfer to second coordination sphere nature, but in the chloro-containing complexes this is a small contributor to the state and it is largely an intramolecular ligand to metal charge-transfer process.

C. Reactions in NO_3^- Media. The production of Cr(VI) in the photolysis of nitrate ion containing solutions, independent of oxygen, cannot be attributed to NO_3^- photochemistry. The photochemistry of the nitrate ion has been extensively studied in the region 229–195 nm and in the 300-nm band.[9] Products of these reactions include molecular oxygen and the nitrite ion. We observe no photochemistry of the nitrate ion at 254 nm. In addition to ruling out the possibility that direct photoreaction of the nitrate ion is responsible for the subsequent photooxidation of chromium, this is evidence that the state of the nitrate ion reached on 254-nm excitation relaxes to the ground state without passing through the state responsible for the 300-nm absorption band. This appears to be the first report on the photophysics of the nitrate ion excited at 254 nm.

For all of the systems studied the ratio of $\phi(NO_2^-)/\phi(Cr(VI))$ is 1.4–1.8. These values are consistently lower than the value of 2.0 expected if the only redox process occurring was the oxidation of Cr(II) to Cr(VI) by nitrate ion. There are several possible mechanisms that could lead, qualitatively, to the observed results:

1. The state responsible for the 300-nm band in the nitrate ion could be populated by energy transfer from the excited state of the chromium complex while the nitrate ion was involved in an intimate ion pair with the complex. The oxygen produced as a result of this sensitization could then oxidize the chromium. The most notable disadvantage of this model is that once the energy is transferred to the nitrate the chromium complex is no longer excited and is, to the best of our knowledge, incapable of oxidation to Cr(VI).

2. The NO_3^- ion forms an ion pair with the complex, similar to that proposed above for Cl^- and ClO_4^-. However, in the case of the latter two ions the function of the electrolyte was to stabilize the ion pair for subsequent oxidation by molecular oxygen. Since molecular oxygen is not necessary for the oxidation in nitrate media, the charge-transfer process in the nitrate systems must involve essentially complete metal to second coordination sphere charge-transfer, resulting in the production of Cr(II) and the NO_3 radical, which, prior to escaping from the solvent cage of the complex, reoxidizes the chromium ion. This process is nonproductive in the case of Cl^- and ClO_4^-, since reoxidation by the corresponding radicals leads only to regeneration of Cr(III) and Cl^- or ClO_4^-. However, in the case of nitrate systems, reoxidation, resulting in nitrite or pernitrite formation, can produce chromium oxidation states higher than 3+ and can therefore easily be oxidized up to 6+. The variation of the quantum yield with the charge on the complex measured in nitrate solutions supports this ion-pair proposal.

Table V. Quenching Constants for Cr(III) Complexes

complex	quenching param Q^a	complex	quenching param Q^a
rhodo	0.18	chloro pentaammine	1.00
aquo erythro	0.14	aquo pentaammine	1.00
chloro erythro	0.34	hexaammine	0.83

[a] Values of Q obtained as described in the text.

The observation that the photooxidations in nitrate media proceed by a mechanism different from those in chloride or perchlorate media are further borne out by examining the quantum yields for Cr(VI) formation in mixed nitrate/chloride systems. When data similar to that in Table IV is examined for all six complexes, it is found that linear extrapolation of the quantum yield at high fraction of nitrate to 0% nitrate always leads to a lower yield than that observed at 0% nitrate/100% chloride. (Alternately, it is seen that addition of small amounts of nitrate to a chloride media always lowers the Cr(VI) yield, even for those cases where the yield in 0.1 M HNO_3 is greater than that in 0.1 M HCl.) This phenomenon can be referred to as a quenching of the chloride-dependent path by the presence of small amounts of nitrate ion. When the concentration of nitrate is small, it has the effect of disrupting the chloride-assisted ion pairs, but there are insufficient nitrate ions in the second coordination sphere of a given complex (it must take at least two nitrates per complex to accomplish the net four-electron oxidation) so that the chloride ion path is quenched but the nitrate ion assisted path is not fully established.

A quenching term, Q, can be defined as the ratio between the linear-extrapolated yield of Cr(VI) of 0% nitrate/100% chloride and the actual yield under those conditions. The values of Q obtained in this manner are shown in Table V. The quenching is essentially complete for the 2+ and 3+ ions, very small for the two 5+ ions, and approximately one-third for the 4+ chloro erythro ion. In the two chloro-containing complexes the quenching is also due to the establishment of a new competition in the formation of the charge-transfer state, a competition between the internally bound chloride and the ion-paired, but more easily oxidized nitrate ion. The trend observed in this calculated quenching term is again consistent with the ion-pair mechanism.

D. Ligand Substitution Processes Following Charge-Transfer Excitation. The data in Table III demonstrate excitation into the charge-transfer region results in ligand substitution as well as photoredox processes. In fact, the ligand substitution processes are, at 254 nm, still the dominant processes observed in these systems. These products could arise from relaxation to lower lying ligand field states or from ligand substitution from the "thexi" states resulting from the excited states reached on 254-nm excitation. Relaxation to L_1 and L_2 cannot account for these products, since in the rhodo ion the 254-nm yield of some of the photoproducts is higher than that observed for visible excitation, including the aquo pentaammine photoproduct, which is not observed on L_1 or L_2 excitation. Recent experiments in our laboratory have shown that the solution phosphorescence quantum yield following excitation into the charge-transfer region of several chromium(III) ammine systems is more than 10 times smaller than the yield for the same system excited in the ligand field bands L_1 and L_2.[10] Thus, the charge-transfer states do not communicate

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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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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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