

Contribution from the Department of Chemistry,
New Mexico State University, Las Cruces, New Mexico 88003**Photolysis of Europium(II) Perchlorate in Aqueous Acidic Solution**DENNIS D. DAVIS,* KENNETH L. STEVENSON,¹ and GARY K. KING

Received June 10, 1976

AIC604308

A kinetic study of the photochemical oxidation of europium(II) ions in aqueous perchloric acid solutions over the range of acid concentrations 8.7×10^{-3} to 3.74 M HClO_4 showed the quantum yield for the reaction $\text{Eu}^{2+} + \text{H}^+ \rightarrow \text{Eu}^{3+} + \frac{1}{2}\text{H}_2$ to be of the form $\Phi = \Phi_0 + k[\text{H}^+]^{1/2}$. The quantum yield for hydrogen production increases with decreasing wavelength varying from 0.053 at 405 nm to 0.20 at 254 nm in 1 M perchloric acid solutions at 296 K. Trapping experiments with the H atom scavenger 2-propanol indicated the presence of H atoms in the bulk solution. A mechanism is proposed which involves the scavenging of geminate ($\text{Eu}^{\text{III}}\text{H}\cdot$) radical pairs by H^+ preventing secondary recombination. The acid-independent yield may arise from water acting as a scavenger.

The photochemical oxidation of aquometal ions to produce hydrogen by reduction of H^+ has been considered in possible solar energy conversion schemes² and the photochemistry of Fe(II),³ Cr(II),⁴ Ce(III),⁵ and Eu(II)⁶ has been investigated with this in mind. Except for Fe(II) and Ce(III) these are not capable of storing solar energy since their E° values for proton reduction are positive, and some of them, notably Cr^{2+} and Fe^{2+} , produce oxidized ions which are stronger absorbers of light causing a quenching of the photoreaction by an internal filter effect. The europous ion, Eu^{2+} , $E^\circ_{\text{ox}} = +0.35$ V,⁷ photolyzes in aqueous acidic solutions with reasonable efficiency in the near-UV range to produce the colorless europic ion, Eu^{3+} ,^{6a} and H_2 , and although the potential of this reaction is positive, the absence of the internal filter effect makes it a convenient model system for a study of the kinetics and mechanism of the photooxidation reaction.

Experimental Section

The light source was an Osram HBO 200-W mercury short-arc lamp with 10-nm half-width interference filters (Corion). Irradiations were carried out under an argon atmosphere in a 1-cm quartz cuvette held in a thermostated block at 23 °C or in a 50-ml Pyrex round-bottom flask in a thermostated bath. The rate of H_2 formation was determined volumetrically using a recording microvolumeter described elsewhere.⁸ Quantum yields were determined for the reaction using the ferrioxalate actinometer⁹ for light intensity measurements and the rate of H_2 evolution. Hydrogen was identified both by mass spectrometry (Perkin-Elmer RMU-6) and by gas chromatography (Molecular Sieve 4A column with both He and Ar carrier gases). Europous perchlorate was prepared by reduction of europic perchlorate with Zn(Hg) and determined both by spectrophotometry¹⁰ (ϵ 602 at 320 nm) on a Cary 14 and by cerate titrimetry of the ferrous ion formed by quenching an aliquot of europous ion in excess ferric chloride. All titrations were carried out under an inert atmosphere of CO_2 . Typically the initial Eu(II) concentrations were 0.03–0.04 at the start of a photolysis and the reactions were followed to completion. In 1 M HClO_4 and with unfiltered radiation from the 200-W lamp a 0.029 M Eu(II) solution photolyzes to completion in 18 min. Solutions of $\text{Eu}(\text{ClO}_4)_3$ in water were prepared by dissolving Eu_2O_3 (Moly Corp) in 1 M HClO_4 (Baker). Solutions of various acidities containing Eu(II) were prepared by diluting a stock solution of europous perchlorate with concentrated perchloric acid. Final acid concentrations were determined by potentiometric titration with NaOH.

The determination of relative quantum yields as a function of acid concentration was carried out with Pyrex-filtered light ($\lambda > 290$ nm) since the quantum yields at low acid concentration are small and the increased intensity due to several Hg lines gave more reproducible results.

Results

The major features of the absorption spectrum of europous perchlorate in acidic media include maxima at 320 nm (ϵ 602) and 250 nm (ϵ 1778) as shown in Figure 1. The 320-nm maximum shows no significant change in intensity or position over the range of perchloric acid concentrations from 0.1 to 5 M as determined by difference spectra. Photolysis of such solutions rapidly evolves hydrogen gas with a bleaching of the

characteristic faint yellow color of Eu(II) and the spectrum of the final solution shows several very weak absorptions and is identical with that of europic perchlorate.^{6b} The stoichiometry of the reaction was determined by measuring the volume of hydrogen formed and determining the decrease in europous concentration by cerate titrimetry, and it agrees very satisfactorily, over a wide range of acid concentrations, with the equation



The kinetics of hydrogen formation were followed by means of a recording microvolumeter, which is, in essence, a constant-pressure gas buret (with a sensitivity of $\pm 1\%$ of a 1-ml volume change) whose output is monitored on a strip chart recorder.¹¹ The photolysis of stirred 0.038 M europous perchlorate solutions under conditions of total light absorption and a 10-fold excess of acid gave a volume vs. time curve as shown in Figure 2. A small saturation effect is noted in some runs at the very start of the reaction, but once the solution is saturated, hydrogen is evolved linearly (pseudo zero order) until nearly 90–95% reaction and the total-light absorption assumption no longer holds. This assumption is valid at all wavelengths at which the reaction occurs except 405 nm where the initial absorbances were in the range 0.5–0.8. Since the intensity at 405 nm is a small fraction of the total incident radiation, nonlinearity in the rate plots due to partial light absorption at 405 nm is not apparent. No significant reaction could be detected at 436 nm.

The dependence of product formation rate on illumination intensity was determined using neutral density filters in conjunction with a 4-mm Pyrex filter. Neutral density filters (Oriel) with optical densities of 0.26 and 0.51 attenuated the rate of hydrogen formation from a 0.02 M Eu(II) solution (0.5 M HClO_4) by factors of 0.55 and 0.34 compared to the calculated values of 0.54 and 0.31 assuming direct proportionality to intensity. The quantum yields then are light intensity independent ruling out major effects due to secondary photolysis of the initial photoproducts.

The quantum yield, Φ , is defined by

$$d(\text{H}_2)/dt = \Phi_{\text{H}_2} J \quad (2)$$

where the rate of H_2 formation is the slope of a run as shown in Figure 2, in mol s^{-1} , and J is the light absorption rate, in Einstein s^{-1} . There are several advantages to using H_2 -formation rates followed volumetrically for studying the photokinetics. (1) A continuous monitoring of gas volumes eliminates tedious point-by-point measurements, as would be the case for spectrophotometric determination of product formation. (2) Concentrations of reactant do not have to be restricted to allow for a measurable range of absorbance values during a run. (3) The stoichiometry of the reaction is easily obtained from ΔV values. (4) This method allows a total precision of 5–10% in quantum yield determination.

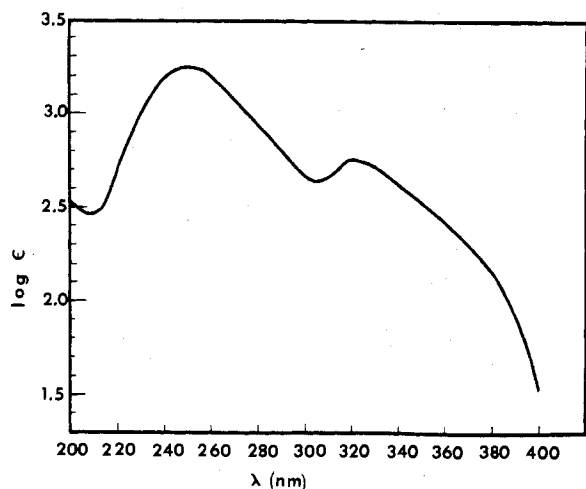


Figure 1. Electronic spectrum of europus perchlorate in perchloric acid.

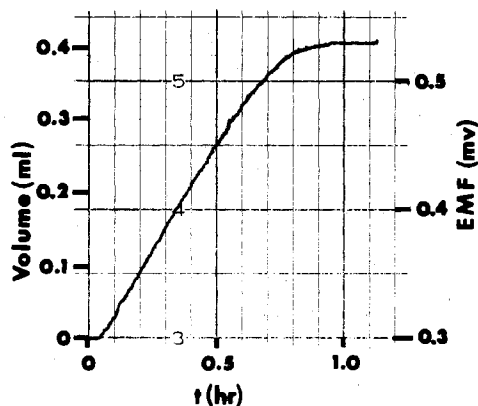


Figure 2. Typical pseudo-zero-order reaction curve for Eu^{2+} photolysis at 365 nm.

Table I. Wavelength Dependence of Quantum Yield (1 M HClO_4)

λ , ^a nm	Rate of H_2 formn $\times 10^6$, mM s^{-1}	$J \times 10^5$, ^b mEinstein s^{-1}	Φ_{H_2}
405	3.63 ± 0.10	6.86 ± 0.21	0.053 ± 0.002
365	7.45 ± 0.10	11.4 ± 0.2	0.065 ± 0.002
334	0.898 ± 0.05	1.25 ± 0.04	0.072 ± 0.004
313	1.19 ± 0.08	1.50 ± 0.04	0.079 ± 0.005
254	0.61 ± 0.05	0.298 ± 0.020	0.20 ± 0.02

^a 10-nm band-pass interference filters. ^b Light absorption rate by ferrioxalate actinometry.⁹

Quantum yields at various Hg lines and 1 M HClO_4 are listed in Table I, and they agree well with the reported value of 0.15 ± 0.02 (0.5 M HCl , $\mu = 1.0$) for $\Phi_{\text{Eu}^{3+}}$ at 366 nm.^{6a} From the stoichiometry of eq 1, $\Phi_{\text{Eu}^{3+}} = 2\Phi_{\text{H}_2}$. The quantum yield increases with decreasing wavelength, and, surprisingly, it is still appreciable at 405 nm on the long-wavelength absorption edge. The light absorption rate measurement at 405 nm includes a correction for partial absorption.

The efficiency of hydrogen production is dependent upon the acidity of the medium. The quantum yield increases by a factor of 14 for a 430-fold increase in acid concentration suggesting fractional order dependence. Indeed the quantum yield relative to that at 1 M HClO_4 follows the equation

$$\Phi_{\text{rel}} = \Phi_0 + k[\text{H}^+]^{1/2} \quad (3)$$

over the range of perchloric acid concentrations 8.7×10^{-3} to 3.74 M, with $\Phi_0 = 0.15$ and $k = 0.85$ as shown in Figure 3. It was anticipated that the acid dependence might follow the

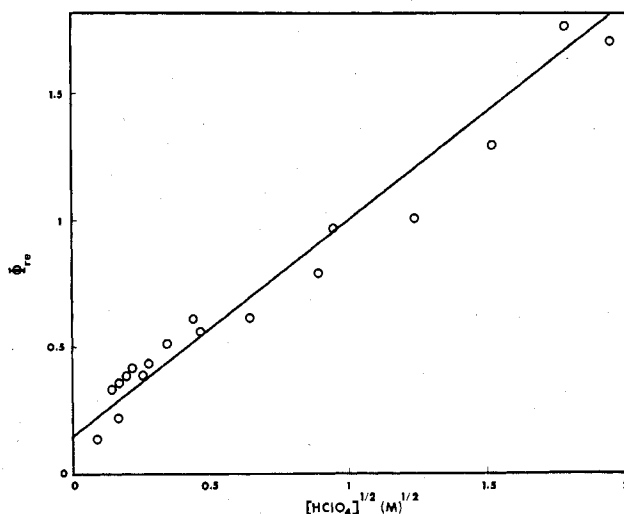


Figure 3. Half-order dependence of Φ_{rel} on perchloric acid concentration. The line is that calculated from a least-squares fit of the data.

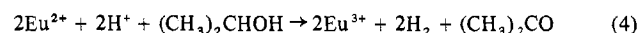
Table II. Effect of Ionic Strength on Quantum Yield

NaCl added		NaClO ₄ added	
Φ_{rel}	μ , ^a M	Φ_{rel}	μ , ^b M
1.0	1.0	1.0	1.09
1.20	2.0	0.98	1.19
1.33	3.0	0.95	1.29
		0.79	2.09
		0.67	2.59

^a Reference 6a; $[\text{HCl}] = 0.5 \text{ M}$. ^b This work; $[\text{HClO}_4] = 0.56 \text{ M}$.

Hammitt acidity function, H_0 , and hence no effort was made to control the ionic strength in this series of runs. However, increasing the ionic strength from $\mu = 1.09$ to $\mu = 2.09$ by the addition of NaClO_4 to a solution 0.56 M in HClO_4 gave a 20% decrease in quantum yield as shown in Table II. Douglas and Yost^{6a} noted a 20% increase for the same ionic strength change in 0.50 M HCl by NaCl addition. These small changes are not indicative of a primary salt effect and are most probably due to slight changes in activity coefficients. Over the very limited ranges in these studies the logarithms of the relative quantum yields are linear with ionic strength but with slopes opposite to those of Douglas and Yost. Long, Dunkle, and McDevitt¹² noted similar effects of NaCl and NaClO_4 on the hydrolysis of butyrolactone up to $\mu = 4$.

The addition of an H atom scavenger, 2-propanol, leads to an increased yield of H_2 but has little effect on the rate of H_2 evolution. For example, the photolysis of solutions containing 0.0366 M Eu(II) , 0.0366 M 2-propanol, and 0.1 M HClO_4 gave a $30 \pm 3\%$ increase in hydrogen yield and a rate of reaction 1.07 ± 0.07 times that of the same solution without 2-propanol. The 30% increase in yield represents 15% of the reaction proceeding according to eq 4.



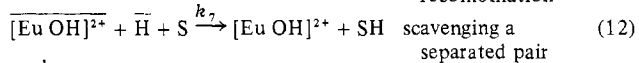
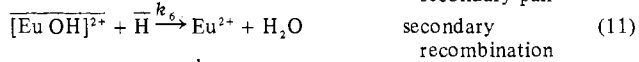
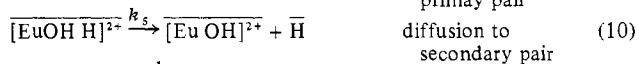
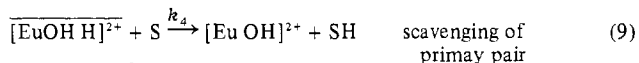
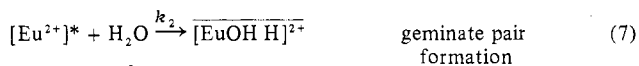
Discussion

The absorption spectrum of $\text{Eu}^{2+}(\text{aq})$ consists of a long-wavelength band, λ_{max} at 320 nm, with a barely discernible "staircase structure" on the high-energy side and an overlapping band in the UV centered at 250 nm. These bands have been characterized as $4f \rightarrow 5d$ transitions,¹³ the two bands being due to the ligand-field splitting of the d orbitals in a cubic field. Since the 5d orbitals are strongly mixed with ligand orbitals, this amounts to appreciable charge transfer to ligand (CTTL),^{13b} giving rise to the observed photooxidation of Eu(II) .

Irradiation of the 250-nm band results in appreciably greater product formation, $\Phi_{254} = 0.2$, than in the longer wavelength region, for example, $\Phi_{405} = 0.053$. Overlap of the absorption bands results in intermediate yields at intermediate wavelengths. The two transitions have similar character as evidenced by the same chemistry, H atom formation; however reaction out of the upper electronic level appears to occur with a larger dissociative rate constant and hence a higher quantum yield.

The acid dependence of this reaction is most notable and the functional form of this dependence, i.e., half order, is consistent with the theoretical treatment by Noyes¹⁴ of the process referred to as geminate recombination. The pair of reactive fragments initially produced in the primary photoprocess may undergo recombination while still in the solvent cage in which they were formed, i.e., primary recombination; or they may undergo diffusive displacements and recombine as a result of a reencounter, secondary recombination. The theoretical treatment by Noyes of the effect of scavengers on the secondary recombination process gives the result that secondary recombination should decrease as a function of the square root of scavenger concentration and this effect should be operative at relatively low (10^{-2} M) concentrations of scavenger. The observed product quantum yield for hydrogen production from the photolysis of europous perchlorate increases linearly with $[H^+]^{1/2}$ over the range 8.7×10^{-3} to 3.7 M perchloric acid concentration in complete accord with these theoretical predictions.

Thus, a possible mechanism for the photoprocess would be eq 5–13.¹⁵ For the situation in which H^+ is the scavenger,



i.e., eq 14–18, the formation of H_2^+ and its reduction by



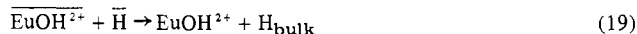
another equivalent of europous ion as required by the stoichiometry lead to the observed product formation. If Eu^{3+} was acting as a scavenger under these conditions, one would have expected to see significant deviations from pseudo-zero-order kinetics as the photolysis proceeds and the concentration of $Eu(III)$ is rapidly changing.

Waits and Hammond¹⁶ have suggested that the effect of scavengers on geminate recombination can be described by a simple model which considers the probability of a geminate pair being born with a scavenger as a nearest neighbor. At low concentrations of scavenger the fraction of newly formed

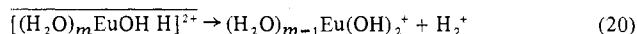
pairs that have scavengers as nearest neighbors will be proportional to the concentration of scavenger, and depending on the parameterization of the Waits–Hammond model, a nearly linear dependence of geminate pair trapping on scavenger concentration is predicted.

The distinctly better agreement of our data with the Noyes model may be due to the fact that both the geminate pair and scavenger (H^+) are charged and repulsive forces may prevent the close approach inherent in the nearest-neighbor model.

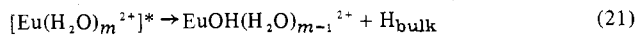
The nonzero intercept shown in Figure 3 may be due to diffusion of the secondary pair into the bulk solution, eq 19,



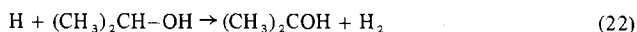
or to coordinated water on the Eu ion interfering with primary recombination, eq 20. A third process not involving geminate



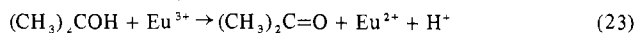
pairs at all, the direct decomposition to $Eu(III)$ and H atoms in the bulk, eq 21, would also be scavenger concentration



independent. The Noyes model for geminate recombinations suggests that primary pairs can be captured only if the scavenger is extremely reactive and/or present in very high concentrations. Coordinated water is present in very high local concentration around the metal ion, and although water is a poor scavenger compared to hydronium, the local concentration effect may become important at low hydronium concentrations. The addition of a neutral scavenger, 2-propanol, affects the rate of reaction slightly and acts as a scavenger for H atoms (eq 22) as shown by the increased yield of H_2 due to the



recycling of $Eu(III)$ to $Eu(II)$ as shown in eq 23.

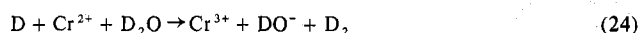


At 0.1 M $HClO_4$ and 0.036 M 2-propanol 15% of the hydrogen is formed according to eq 22. The fraction of H_2 formed independent of scavenger concentration is 36% of the total and it is conceivable that 2-propanol is scavenging only H atoms injected into the bulk of solution via a primary dissociation.

Although a relationship between solution acidity and the efficiency of hydrogen formation in the photooxidation of low-valent metal ions has been noted by several groups of workers, no general explanation for the phenomenon has been forthcoming. Heidt et al.^{3b} found that Φ_{H_2} increased from 0.155 at 0.15 M to 0.33 at 2 M and to 0.74 at 6 M H_2SO_4 in the 254-nm photolysis of $Fe(II)$. However, Jortner and Stein^{3a} reported that the photolysis of $Fe(II)$ in the pH range 0–3 shows half-order dependence on $[H^+]$ similar to that noted for $Eu(II)$ in this study. A direct quantitative comparison of these two sets of data is not possible because Heidt et al. reported at only three acidities so that the acidity responses could be mutually compatible except at very high acidities. Both reports indicate a finite quantum yield when extrapolated to zero acid concentration. The mechanism proposed by Jortner and Stein is based upon the Noyes model for geminate recombination and our proposal for $Eu(II)$ photolysis is very similar. At high acid concentrations the formation of ferrous sulfate contact ion pairs has been proposed to account for the large increase in quantum yields.^{3b}

Chromous salts photolyze in the near-ultraviolet region in a manner similar to that for ferrous and europous salts and with similar efficiencies.⁴ Although it is not possible to accurately quantify the graphical data presented by Collinson et al.⁴ the changes in quantum yield for H_2 formation are very much like those of $Eu(II)$ from 10^{-2} to 4 M, but with the added feature of a very large increase in efficiency at high acid concentrations (>6 M HCl or $HClO_4$). This increase may

be due to the incursion of the spontaneous thermal reduction of hydronium by Cr(II). A dark reaction was noted in some Eu(II) solutions at 5–6 M HClO₄ in this study which would have given spuriously high quantum yields. For the data reported here, up to 3.7 M HClO₄, no dark reaction of Eu(II) was noted under the experimental conditions. Raphael and Malati¹⁷ have determined an isotope effect on CrCl₂ photolysis in D₂O. By use of the data in ref 4 for the light system, the ratio Φ_{H_2}/Φ_{D_2} was found to be 1.4 at pH 1. They have proposed that the acid dependence is due to the reaction



This reaction, we feel, is very unlikely to account for the acidity data.

A third form of acid dependence of Φ_{H_2} appears in the photolysis of V(ClO₄)₂.¹⁸ V(II) photolyzes similarly to Cr(II) and is half-order in [H⁺] at lower acidities; however Φ_{H_2} reaches a maximum at 2 M HClO₄ and decreases slightly in more concentrated perchloric acid solutions.

A common feature of the photooxidation of Fe(II), Eu(II), Cr(II), and V(II) aquo ions is the half-order dependence from the pH range up to approximately 2 M solutions of strong acids. At this point bulk solution phenomena such as ion-pair formation as for Fe(II), spontaneous thermal reductions of solvent (standard reduction potential for both Cr(III) and Eu(III) is -0.4 V), or possible dehydration-polymerization reactions become important in determining Φ_{H_2} .

We are continuing the investigation of the effect of neutral scavengers such as 2-propanol on the efficiency of hydrogen formation, as well as the investigation of anionic metal complexes.

Acknowledgment. We wish to thank the New Mexico Energy Resources Board for support of this work.

Registry No. Eu²⁺, 16910-54-6; H⁺, 12408-02-5.

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Electronic Spectra of Some Transition Metal and Lanthanide Ions in Anhydrous Hydrogen Fluoride

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Received June 24, 1976

AIC60454E

Electronic spectra have been recorded in solution in anhydrous hydrogen fluoride of the cations nickel(II), cobalt(II), praseodymium(III), and neodymium(III). The fluorides of these cations are not sufficiently soluble for spectra to be observed by conventional procedures. Solutions of sufficient concentration have been prepared by treatment of suspensions of the fluorides with boron trifluoride. The spectra so obtained show a general resemblance to the corresponding spectra in aqueous solution, although the detailed numerical values are almost exactly equal to those for coordinated fluoride anions. This suggests that under these conditions the metals are present in solution as simple solvated cations with coordination similar to that in water in each case.

Introduction

Techniques based on the use of cells with Kel-F bodies and sapphire windows have been available for investigation of solutions in anhydrous hydrogen fluoride (AHF) in the ultraviolet and visible spectral regions for over 20 years. However very little work has been done and, for the most part, organic systems have been studied. The present situation is little different from that given in a review¹ by Kilpatrick and Jones in 1967.

To date almost no spectroscopy has been possible for metal ions dissolved in AHF because of the lack of availability of suitably soluble species. The fluorides of the metals of group 1 and of thallium(I) have quite high solubilities.² As the charges on the cation increase, the solubilities of the ionic fluorides decrease markedly² so that even the fluorides of group 2 with the exception of SrF₂ and BaF₂ have limited solubilities. However as the oxidation state of the metal in a fluoride

becomes high and the molecular nature of the fluoride becomes predominant, solubility again becomes relatively high as has been shown for the highest fluorides of metals such as vanadium,³ molybdenum, tungsten, uranium,⁴ and rhenium;⁵ but spectroscopic studies on solutions such as these present little of interest in the visible and ultraviolet regions.

Another limitation on the ability to study spectra of transition metal ions and of lanthanide and actinide ions in anhydrous hydrogen fluoride is that relatively few anions other than fluoride can exist as such in hydrogen fluoride. If chlorides, bromides, or iodides of heavy metals are treated with AHF, the halide ions are protonated and expelled from the solution as the gaseous hydrogen halides,⁶ leaving effectively a very dilute solution of the heavy-metal fluoride, most of the metal being precipitated as fluoride. The common inorganic oxo anions undergo complete or extensive and complex solvolysis⁶ while anions such as carboxylates are completely