

Path a is the non-symmetrical withdrawal from the transition state; path b is the disilane + potassium hydride formation previously diagnosed and path c is the normal reaction of potassium hydride and a disilane derivative. In addition to bridge bond formation dipole orientation can contribute to determining the structures of particular transition states. Formation and withdrawal along path a from a transition state such as (I) can constitute a route for direct isotopic exchange in experiments 13 and 14 a,b, while along path b the same transi-

tion state can give exchange *via* potassium hydride formation.

As a base silyl anion should form a 1:1 adduct with borane, BH_3 , acting as a generalized acid. The proportions observed were 1:1.16, but the adduct anion was unstable, undergoing disproportionation with respect to boron to produce borohydride anion and with respect to silicon to produce silane. The other product appears to be one or more probably condensed species, which will be characterized later.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LAWRENCE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA]

The Oxidation States of Astatine in Aqueous Solution¹

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The redox equilibria among the oxidation states of astatine have been studied in acidic solution. Reversible couples have been used and equilibria have been approached from both sides. The -1 , 0 , $+1$ (?) and $+5$ states have been characterized, but no evidence has been found for a $+7$ state. The following potential scheme has been determined at $\text{pH } 1$:

$$\text{At}^- \xrightarrow{-0.3} \text{At}(0) \xrightarrow{-1.0} \text{HOAt}(\text{?}) \xrightarrow{-1.5} \text{AtO}_3^- \xrightarrow{<-1.6} \text{H}_5\text{AtO}_6(\text{?})$$

It has been shown that in the absence of I_2 the predominant $\text{At}(0)$ species are neither At_2 nor $\text{At}\cdot$ but may well be compounds formed between astatine and organic impurities in the solutions. Whenever possible, I_2 has been introduced to try to convert the $\text{At}(0)$ to AtI . The photochemical oxidation of $\text{At}(0)$ by VO_2^+ and by Fe^{+++} has also been investigated.

Introduction

The halogen family constitutes a fertile field for the study of periodic behavior within a series of elements. To complete this series it is necessary to have knowledge of the chemistry of its heaviest member, astatine. However, astatine is an unstable synthetic element which can be worked with only at very low concentrations—concentrations much less than the impurity levels commonly present in an experimental system. Hence the desired knowledge is not easily obtained.

The oxidation potential scheme given for astatine by Latimer³ is derived from the exploratory work of Johnson, *et al.*⁴ In their work the potentials of the systems studied were not usually controlled by the presence of both halves of a reversible redox couple, and equilibria were not approached from both sides. In the present investigation we have attempted to correct these faults.

A more subtle obstacle to the interpretation of the results of Johnson, *et al.*,⁴ is the uncertain nature of the "zero" oxidation state of astatine. This state is generally identified either with molecular astatine, At_2 , or with the free radical $\text{At}\cdot$. However, the latter seems unlikely in aqueous solution, and the expected reactivity of the former makes it probable that at least some of the "zero" state species commonly encountered are actually compounds of astatine with the various organic

impurities unavoidably present in aqueous solutions. The erratic solvent extraction behavior displayed by $\text{At}(0)$ lends support to this notion.⁴ Elemental astatine should react rapidly and quantitatively with iodine to form the interhalogen AtI , and we have therefore attempted to fix the identity of $\text{At}(0)$ by keeping aqueous solutions about 10^{-4} M in I_2 whenever possible.

Experimental

Preparation of Astatine.—The isotope At^{211} , which has a 7.2 hr. half-life, was prepared by bombardment of bismuth with alpha particles of energy less than 29 Mev. in the University of California's 60" cyclotron. The astatine was distilled from the bismuth in air at about 750° and was collected on a water-cooled platinum plate.⁵ The plate was then heated to 500° in an all-glass high-vacuum system, and the astatine was distilled into a u-tube cooled to Dry Ice temperature. The only lubricant used on joints in the path of the astatine was a completely fluorinated fluorocarbon fraction—Hooker Chemical Co.'s Fluorolube HG 1200. The astatine was washed from the u-tube with an appropriate aqueous solution, giving one ml. of concentrated stock solution about 10^{-8} M in astatine.

Analysis for Astatine.—Astatine analyses were made by counting in a scintillation counter the X-rays accompanying the electron-capture decay of the At^{211} .⁶ Aliquots of solutions were counted directly, using a thallium-activated sodium iodide crystal with a built-in well, made by the Harshaw Chemical Co. Precipitates were counted as slurries in propanol. The counter was set to respond only to radiation of energy in the vicinity of the *ca.* 90 kev. k-X-ray peak, thus reducing the high background normally associated with scintillation counters.

Decay corrections were made on the basis of a carefully determined At^{211} half-life. Related assays were counted at so nearly the same time that these corrections never exceeded about 20%.

The long-lived, electron-capture isotope Bi^{207} grows into an At^{211} sample,⁶ the residual bismuth X-ray activity being

(5) G. Barton, A. Ghiorso and I. Perlman, *Phys. Rev.*, **82**, 13 (1951).

(6) D. Strominger, J. Hollander and G. Seaborg, *Revs. Modern Phys.*, **30**, 585 (1958).

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Abstracted from the Ph.D. thesis of the author, University of California (Berkeley), June 1960 (UCRL-9025). Author's present address: Argonne National Laboratory, Argonne, Illinois.

(3) Wendell M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, New York, N. Y., 1952.

(4) G. Johnson, R. Leininger and E. Segré, *J. Chem. Phys.*, **17**, 1 (1949).

about 10^{-6} the initial astatine X-ray activity. Therefore samples assayed after a number of astatine half-lives were reassayed after all of the astatine had decayed, the residual count being subtracted from the original.

Solvents and Reagents.—All reagents were prepared from commercial products of C.P. or "reagent" grade. Distilled water was redistilled from alkaline permanganate for use in these experiments. Mallinckrodt "low-sulfur" carbon tetrachloride was used.

Ferrous perchlorate solutions were prepared by dissolution of iron wire in perchloric acid. Ferric perchlorate solutions were made by exhaustively fuming ferrous solutions in perchloric acid. Solutions of lead, barium and thallous perchlorates were made by dissolving the carbonates or hydroxides in slight excesses of perchloric acid. A pervanadyl perchlorate solution was prepared by dissolving ammonium metavanadate in hot, dilute sodium hydroxide and rapidly adding a large excess of perchloric acid.

Chlorine solutions were prepared from Matheson chlorine passed only through glass and Teflon tubing.

Identification of Astatine Species.—The (-1) state of astatine, the astatide ion At^- , was identified by its coprecipitation with AgI , TlI and PbI_2 . The "zero" or elemental state was identified as the only form of astatine displaying appreciable extractability into CCl_4 . A positive oxidation state (or states) of unknown valence between zero and +5, which we shall designate $\text{At}(+X)$, was characterized by its unextractability into CCl_4 and its failure to coprecipitate with either insoluble iodides or iodates. The (+5) state, the astatate ion AtO_3^- , was indicated by its coprecipitation with AgIO_3 , $\text{Ba}(\text{IO}_3)_2$ and $\text{Pb}(\text{IO}_3)_2$, the last being most frequently used.

General Procedure.—Portions of solutions of astatine in a previously identified state were treated with various redox couples. Aliquots of the reaction mixtures were withdrawn periodically, and the extraction and coprecipitation behavior of the astatine was determined. Intermediate astatine states were approached from both sides to assure that equilibrium had been attained. Unless otherwise indicated, reactions were carried out at about $\text{pH } 1$. Perchlorate was usually the only non-reacting anion present, but vanadyl ion was introduced as VOSO_4 and silver as AgNO_3 , while acetate and phosphate buffers were used in low acidity experiments with the $\text{As}(\text{III})$ - $\text{As}(\text{V})$ couple. Astatine concentrations generally ranged from 10^{-13} to $10^{-15} M$. Variation of the astatine concentration was without effect on any reaction, indicating that radiation damage to the solutions was probably unimportant.

All reactions were tested for photosensitivity. Reactions were carried out at room temperature (21 - 23°), and no materials other than glass and Teflon were allowed to contact the astatine solutions.

Special Procedure for Differentiating between $\text{At}(\text{V})$ and $\text{At}(\text{VII})$.—Since the foregoing procedure may not unambiguously distinguish astatate from perastatate, a special scheme was devised to seek the latter. It is known that addition of Ba^{++} to a weakly acidic solution containing a small amount of periodate mixed with a much greater amount of iodate precipitates nearly all of the iodate but little of the periodate.⁷ Therefore, in our procedure aliquots of vigorously oxidized astatine solutions were added to solutions $0.05 M$ in IO_3^- and $0.01 M$ in H_5IO_6 at $\text{pH } 2$, from which $\text{Ba}(\text{IO}_3)_2$ was subsequently precipitated. We assumed that $\text{At}(\text{V})$ would coprecipitate but $\text{At}(\text{VII})$ would not.

In these experiments, the astatine was oxidized at 100° with H_5IO_6 , with $\text{Ce}(\text{IV})$ in $6 M$ HClO_4 and with $\text{K}_2\text{S}_2\text{O}_8$ with and without added Ag^+ catalyst. When $\text{Ce}(\text{IV})$ was used as oxidant, it was necessary to remove the cerium as the hydroxide before introducing iodate. Otherwise ceric iodate would precipitate and might carry both $\text{At}(\text{V})$ and $\text{At}(\text{VII})$. Very little of the astatine coprecipitated with the ceric hydroxide.

Estimation of Potentials.—The potentials of the reaction mixtures are referred to the standard hydrogen electrode and have been estimated from the standard potentials and activity coefficients given by Latimer for the redox couples employed.⁸

(7) H. H. Willard and J. J. Thompson, *THIS JOURNAL*, **56**, 1827 (1934).

Results

The Search for $\text{At}(\text{VII})$.—After the most vigorous oxidation the astatine appeared to be entirely in the form of AtO_3^- , and no evidence for a higher state was ever obtained.

The $\text{At}(+X)$ - AtO_3^- Couple.—The iodate-periodate couple (e.m.f. ca. -1.6 v.) oxidizes $\text{At}(+X)$ to AtO_3^- , although the reaction is sometimes slow and incomplete at room temperature, possibly due to the presence of reducing impurities. Astatate is reduced to $\text{At}(+X)$ by the chloride-chlorine couple (e.m.f. -1.40 v.). However, when the only chloride present is that resulting from hydrolysis of the chlorine (e.m.f., -1.46 v.), the reduction is incomplete, and $\text{At}(+X)$ is partially oxidized to AtO_3^- .

The $\text{At}(0)$ - $\text{At}(+X)$ Couple.—Even at very low bromine concentrations (e.m.f., -1.04 v.) the bromide-bromine couple oxidizes $\text{At}(0)$ to $\text{At}(+X)$, regardless of whether or not the $\text{At}(0)$ solution contains iodine. The $\text{At}(+X)$ is reduced to $\text{At}(0)$ in the dark by the VO^{++} - VO_2^+ couple (e.m.f., -0.95 v.) and by the ferrous-ferric couple, even at very high ferric/ferrous ratios (e.m.f., -0.89 v.). These dark reactions are qualitatively independent of the presence or absence of I_2 .

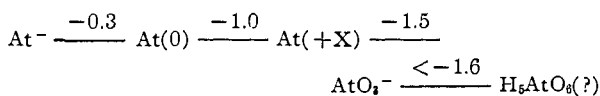
In light, however, the vanadium couple oxidizes $\text{At}(0)$ to $\text{At}(+X)$. Only a fraction of the astatine is oxidized in the absence of iodine, but if the I_2 concentration is $10^{-8} M$, the photochemical oxidation is complete! The reaction of astatine with the ferrous-ferric couple is not sensitive to light unless the ferric/ferrous ratio exceeds 100 (e.m.f. < -0.87 v.). When the ratio is greater than this the astatine is nearly completely photo-oxidized to $\text{At}(+X)$ whether or not I_2 is present.

The At^- - $\text{At}(0)$ Couple.—Astatide is oxidized to $\text{At}(0)$ by the iodide-iodine couple (e.m.f., -0.60 v.), by a 1:1 ferrocyanide-ferricyanide mixture at $\text{pH} < 3$ (e.m.f. < -0.4 v.)^{8,9} and by the $\text{As}(\text{III})$ - $\text{As}(\text{V})$ couple at $\text{pH} < 4$ (e.m.f. < -0.3 v.).

The ferrocyanide-ferricyanide couple reduces $\text{At}(0)$ to At^- at low acidity and ionic strength if the concentration of ferrocyanide is several times that of ferricyanide (e.m.f. > -0.4 v.)⁸⁻¹⁰ and the $\text{As}(\text{III})$ - $\text{As}(\text{V})$ couple does likewise at $\text{pH} > 4$ (e.m.f. > -0.3 v.).

Discussion

From the foregoing results we may construct the potential scheme in $0.1 M$ acid



Although oxidants with potentials less than -2 v. were used in the search for perastatate, any perastatate formed at such potentials could have been reduced by the iodate-periodate precipita-

(8) I. M. Kolthoff and W. J. Tomsicek, *J. Phys. Chem.*, **39**, 945, 955 (1935).

(9) Since $\text{HFe}(\text{CN})_6^{4-}$ is a weak acid and since its salts tend to be weakly dissociated, the e.m.f. of the ferrocyanide-ferricyanide couple is sensitive both to acidity and to electrolyte concentration.

(10) After reduction with ferrocyanide the astatine is unextractable into CCl_4 and is completely coprecipitated with TlI but is only partially coprecipitated with AgI or PbI_2 . This may be due to a disturbance of the equilibrium by precipitation of lead and silver ferrocyanides.

tion mixture. Hence the potential of the latter must be taken as our limit.

The identity of "At(+X)" remains undetermined. HAtO is the most likely species, though HAtO₂ is also a reasonable possibility. It should be borne in mind that "At(+X)" need not represent a single species or even a single oxidation state. Indeed, the nature of the state may vary with the mode of preparation. Under appropriate conditions an interhalogen compound such as AtCl₃ may be present,¹¹ and we can never exclude the possibility of compounds with impurities.

The At(0)-At(+X) potential is about the same whether or not I₂ is present. Both the At₂-At(+X) and the At-At(+X) potentials should be much more positive than the AtI-At(+X) potential, since under our conditions both At₂ and At should be highly unstable with respect to AtI. Hence neither At₂ nor At· can be the predominant At(0) species in the absence of I₂. It seems not at all unlikely that when I₂ is absent, most of the At(0) reacts with impurities to form organic astatine compounds.

The photochemical reactions of astatine with the iron and vanadium couples appear quite remarkable, since they involve a gross shift of a chemical equilibrium under the influence of light. Such an effect is likely only if the reaction under investigation involves a species present at trace concentrations, but the primary photochemical process involves only species present at macro concentrations. Our information on these astatine reactions, however, is insufficient to permit meaningful speculation as to their mechanisms. Nonetheless, these reactions make it clear that serious misinterpretation may result from neglect of photochemical effects on tracer-level studies. Thus Latimer set the At(0)-At(+X) potential at *ca.* -0.7 v.³ on the basis of Johnson, *et al.*'s, report that ferric ion oxidized At(0).⁴ This oxidation is almost certainly the photochemical reaction

(11) H. M. Neumann, *J. Inorg. Nuclear Chem.*, **4**, 349 (1957).

we have examined, and Latimer's potential is therefore not sufficiently negative.

In studying the reduction of At(0), one cannot avoid ambiguity as to the nature of the At(0) species, since any iodine in the system is reduced before the astatine. A discrepancy exists between the results with the As(III)-As(V) couple, which indicate the At-At(0) potential to be about -0.3 v., and the ferrocyanide-ferricyanide results, which suggest -0.4 v. We have favored the former, since there seem yet to be some unanswered questions regarding the ferrocyanide-ferricyanide couple.¹²

In Table I the astatine potentials are compared with those of the other halogens. The astatine values are in general agreement with the trends exhibited by the lighter members of the series, although astatate might seem to be an unduly strong oxidant. This, however, could have been anticipated by analogy with the nitrogen group, in which bismuthate is a much more powerful oxidant than any other +5 state. This discontinuity makes astatine the only halogen with a state between zero and +5 which is stable to disproportionation and is consistent with the tendency among all the main group elements for increasing molecular weight to be accompanied by increasing stabilization of intermediate positive states.

TABLE I

	X ⁻ -X ₂ (aq.)	X ₂ (aq.)-HOX	HOX-HXO ₂	HXO ₂ -HXO ₃
Cl	-1.40	-1.53	-1.35	-1.13
Br	-1.09	-1.51	-1.42
I	-0.62	-1.31	-1.07	(-1.6)
At	(-0.3)	(-1.0)	(-1.5)	<-1.6

Acknowledgments.—I wish to express my gratitude to Professor I. Perlman for his direction of this study and to Professor Robert E. Connick for many helpful discussions.

(12) W. L. Reynolds, *THIS JOURNAL*, **80**, 1830 (1958).

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Acid Hydrolysis of [PtCl₄]⁻ and [PtCl₃(H₂O)]⁻¹

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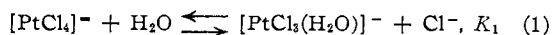
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The equilibrium constant for the acid hydrolysis of [PtCl₄]⁻ at 25° is 3.0 × 10⁻³ at μ = 0 and 1.5 × 10⁻² at μ = 0.318. The equilibrium constant for the acid hydrolysis of [PtCl₃(H₂O)]⁻ at 25° is 1.0 × 10⁻³ at μ = 0 and 5.4 × 10⁻⁴ at μ = 0.318. A tentative value of 7.0 is reported for pK'₁₁ where K'₁₁ is the acid dissociation constant of [PtCl₃(H₂O)]⁻. Tentative values are pK'₂₁ = 5.2 and pK'₂₂ = 8.3, where K'₂₁ and K'₂₂ are the first and second acid dissociation constants for [PtCl₄(H₂O)₂].

Introduction

From earlier isotopic exchange experiments it was reported^{2a} that the acid hydrolysis of [PtCl₄]⁻ was conveniently measurable by a titration with

standard base of the acid formed, which was considered to be the [PtCl₃(H₂O)]⁻ ion. The hydrolysis reaction was written as



The titration of aged 0.0166 molar solutions of K₂-

(1) (a) Presented at the Symposium on Aqueous Solutions, Division of Inorganic Chemistry, American Chemical Society Meeting at Atlantic City, Sept. 17, 1959. (b) Contribution No. 895. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) (a) L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., *THIS JOURNAL*, **77**, 2965 (1955). (b) W. W. Dunning and D. S. Martin, Jr., *ibid.*, **81**, 5566 (1959).