THE CHEMISTRY OF ASTATINE

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I. Introduction

Astatine, as the heaviest member of the family of halogens, forms a number of compounds in which the element has different valencies and which do not readily interchange. This means that a fairly large amount of chemical information will eventually become available. However, astatine is one of the most difficult elements to study from a chemical point of view, and our knowledge of its compounds is rather incomplete compared to what we know about other elements. For this there are several reasons.

No stable isotopes of astatine are known and it is evident that none can be expected. Earlier reports on the occurrence* of stable isotopes of element 83 are certainly due either to unreliable experimental techniques or to erronous interpretation of observations. Alleged discoveries of this kind have been reviewed (*24*).

The stability of astatine isotopes can be judged from the information

* Although the isotopes of astatine used for normal purposes are all artificial, it is not correct to say that astatine has no naturally occurring isotopes. Karlik and Bernert discovered At^{218} and At^{215} in side chains of the uranium and the actinium families (*25*, *26*), and Hyde and Ghiorso discovered At^{219} in a similar position in the latter family. A discussion of this group of nuclides is given by Haïssinsky (*16*). The half-lives of these nuclides are, however, so short as to be useless for purposes of chemical research.

available on the masses of nuclei in this region. The recent compilation by Everling *et al.* (*14*) indicates that no isotope of astatine is β-stable with the possible exception of At^{215}, although even here it may well be that the β-stable isobar is Em^{215} and that At^{215} decays to this nuclide by β^- emission. Apart from disintegrations by β emission or by electron capture, all astatine isotopes are α-active. As a matter of fact in the case of the heavier isotopes, the half-life of the α decay is so much shorter than that of the β decay that the latter has not been observed in most cases.

Although it could be suggested that some astatine isotopes might have a half-life sufficiently long to make possible their survival in nature from the time of nucleogenesis of the material in the solar system, all isotopes which might be suspected to have a reasonably long half-life have already been synthesized and observed. This means that for survival of primordial astatine the occurrence of nuclear isomers would be required. Isomers do as a matter of fact exist in the case of At^{208}, but it seems most unlikely that any isomer would have a half-life comparable to 10^9 years. The products of α emission by astatine isotopes have a next-to-magic number of protons, which causes the α-decay energy to be exceptionally high and the α half-life to be correspondingly short. This means that the chances of finding any long-lived "natural" astatine seem from our present state of knowledge to be negligibly small.

Research on the properties of astatine is, moreover, complicated by the fact that the preparation of its isotopes is more difficult than with most elements, as they cannot be prepared by neutron irradiation. This means that a nuclear reactor cannot be used and that an accelerator is required. For ordinary purposes a helium ion accelerator is used and all chemical work on astatine has until now been based on cyclotron irradiations.

A further difficulty is due to the fact that a fairly satisfactory carrier element (comparable to cesium as a carrier for francium) is not available. Although the closest chemical relative, iodine, is often used for the purpose, it does not always fulfill this role in a satisfactory way. Ions or molecules of astatine compounds often do not fit the lattice of the corresponding iodine compound with sufficient accuracy, which means that the astatine may easily be pushed out of the solid phase in the process of recrystallization. Another complication is due to the fact that astatine compounds are often more strongly adsorbed than the corresponding iodine compounds, which may again upset the functioning of iodine as a carrier for astatine.

A final complication in astatine research is the short half-life of even the most suitable isotopes—about 8 hours, making it difficult to work with this element in laboratories which do not themselves produce its isotopes. For this reason it is not surprising that the larger part of our present knowledge concerning astatine and its chemical properties is due to the activities

of only a small number of laboratories. In this connection we may specially mention the work from Berkeley (*2*, *4*, *12*, *22*). Biological work on astatine has been done mainly in Berkeley and in Brookhaven. References to this work will be given later.

Several excellent reviews have been published recently on the properties and behavior of astatine (*1*, *3*, *7*).

II. Isotopes: Production and Measurement

A. Basic Information

A very large number of astatine isotopes are now known (Table I). Their half-lives and decay energies, both for α emission and for electron capture, are of great interest in the study of the influence of magic numbers on nuclear structure, as both magic numbers $Z = 82$ and $N = 126$ make their influence felt in these data. However, it is not reasonable to discuss the nuclear properties of astatine isotopes for this purpose without including the corresponding data concerning other elements in this region.

The isotopes of importance in the chemical study of astatine are At^{211} and At^{210}. Both are prepared by He^{++}-irradiation of bismuth. The cross-sections for these reactions are given in Fig. 1. It is evident that the minimum α energy, which can be used for astatine production, is 20 Mev, but that one cannot conveniently use energies below about 25 Mev.

For many purposes the isotope At^{211} (half-life 7.2 hours) is preferred, mainly because it can be measured by α counting. For every disintegrating nucleus one α particle is emitted, but the energy of the α particles is by no means the same in all cases. As is seen in Fig. 2, about 40% of the α particles have an energy of 5.86 Mev and 60% of 7.44 Mev. The extremely short half-life of Po^{211} (about 1 second) causes the observed α decay to follow exactly the half-life of At^{211}. For the purpose of ordinary α counting the energy is of no importance. If desired, At^{211} can also be determined by X-ray counting, as 60% of the decays give rise to an X-ray in Po^{211}. However, if the astatine is prepared by irradiating bismuth with He^{++} of higher energies, i.e., above about 32 Mev, the quantity of At^{210} prepared will be quite comparable to that of At^{211} and the half-life observed will no longer correspond to the exact value of the latter isotope. In many cases this will not cause a serious inconvenience; even so some laboratories prefer to use He^{++} ions with an energy of only 29 Mev, which gives pure At^{211} (*2*, *21*).

In At^{210} (half-life 8.3 hours) the α emission is negligible, i.e., less than 0.2%. The nuclide can be measured either by its X-rays or by its γ-rays. Every decay process produces a 1.18-Mev γ-ray and about 18% also produces γ-rays in the region 1.44–1.49 Mev. For chemical purposes it does not as a rule matter very much if the astatine activity observed is due

TABLE I
DECAY AND HALF-LIVES OF ASTATINE ISOTOPES[a]

Isotope	Half-life	Decay
At^{219}	0.9 min	97% α
		3% β
At^{218}	1.3 sec	99.9% α
		0.1% β^-
At^{217}	0.018 sec	α
At^{216}	0.3×10^{-3} sec	α
At^{215}	0.1×10^{-3} sec	α
At^{214}	short	α
At^{213}	<2 sec	α
At^{212}	0.22 sec	α
At^{211}	7.2 hr	40.9% α
		59.1% EC
At^{210}	8.3 hr	99.9% EC
		0.1% α
At^{209}	5.5 hr	95% EC
		5% α
At^{208}	1.6 hr	99% EC
		0.5% α
At^{208}	6.2 hr	EC
At^{207}	1.8 hr	α
		EC
At^{206}	30 min	EC
		α
At^{205}	26 min	α
		EC
At^{204}	9.3 min	EC
		α
At^{203}	7.4 min	α
		EC
At^{202}	3.0 min	α
		EC
At^{201}	1.5 min	α
At^{200}	0.9 min	α

[a] It should be kept in mind that all astatine isotopes, with the exception of At^{213}, produce other radioactive nuclides by their decay. In many cases the radiation of the daughter nuclide is observed together with that of the astatine mother, thus occasionally giving rise to complicated decay curves. In astatine isotopes electron capture always produces K-radiation.

partly to At^{210} and partly to At^{211}. An average half-life of about 8 hours will be measured. Interpolation of different measurements and comparison of the activity of different samples will be easy and the precision will be quite satisfactory.

Irradiation of bismuth with He^{++} ions may also produce lighter astatine

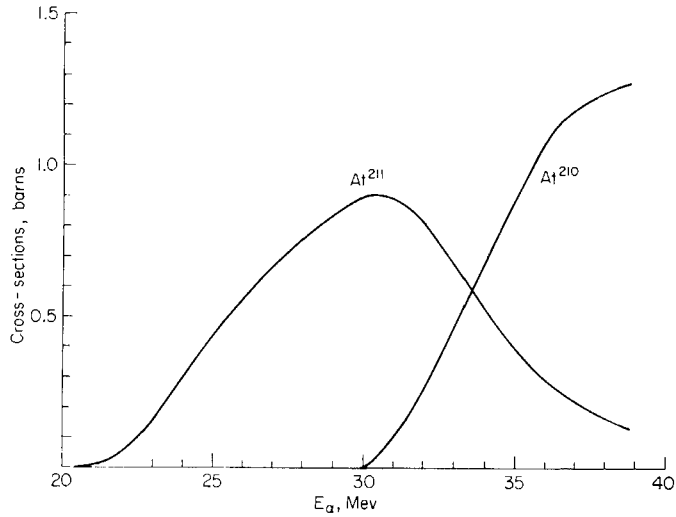

FIG. 1. Cross-sections (in barns) for the formation of the most important astatine isotopes by the reactions $Bi^{209}(\alpha,2n)At^{211}$ and $Bi^{209}(\alpha,3n)At^{210}$ (*27*).

isotopes. Such isotopes are useless as tracers for chemical research, but they may seriously upset the observation of the activities of At^{210} and At^{211}.

At^{209} (half-life 5.5 hours) is formed with a fairly large cross-section by α particles of 60 Mev (*8*). Presumably its formation will be quite important even at lower energies. (The curve drawn by Barton, Ghiorso and Perlman

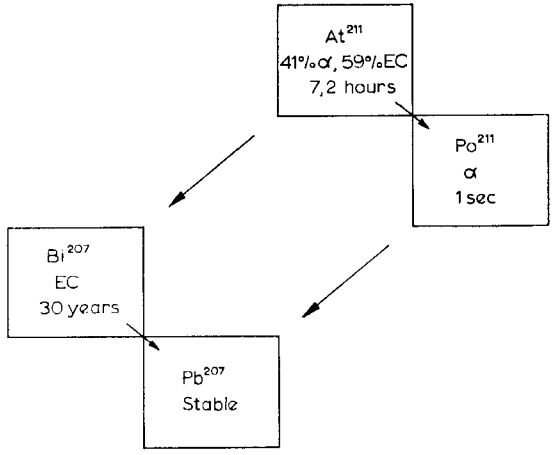

FIG. 2. Decay scheme of At^{211}. For each nucleus of At^{211}, which decays, one α particle will be emitted during the measurement, either by At^{211} or by Po^{211}. The X-rays due to electron capture in At^{211} can also be observed, but those due to capture in Bi^{207} will be lost because of the long half-life of this nuclide. The α-particles from At^{211} have an energy of 5.86 Mev, those from Po^{211} of 7.44 Mev.

through their observed points is hardly convincing, and the actual cross-sections may well be higher than an extrapolation from their curve to lower energies would lead one to expect.) Since only 5% of the decay of this isotope is α emission, At^{209} will hardly disturb measurements of At^{211} made by α counting. (Using α-measurements Barton, Ghiorso, and Perlman could not observe At^{209} in samples of astatine prepared with He^{++} ions having energies of less than 55 Mev.) On the other hand, the presence of At^{209} may well upset measurements of At^{210} and At^{211} by X-ray counting. At^{209} also shows a strong γ-ray emission, but the energies (mainly 0.195 Mev, 0.544 Mev, and 0.780 Mev) are quite different from those of At^{210}. Thus if the γ counting is done with a crystal with good resolution, At^{210} may easily be counted without interference from At^{209}, but if no energy discrimination is made, distinction between At^{210} and At^{209} may be very difficult.

A large number of lighter astatine isotopes are also produced by He^{++}-irradiation of bismuth, but most of them have half-lives of less than 2 hours. This means that in the course of ordinary chemical experiments they will practically disappear and are not likely to upset the measurement of At^{211} and of At^{210}. There is, however, one exception in that At^{208} has two isomers, one of which has a half-life of 6.2 hours. Little is known about it except that it does not seem to emit α particles. It will certainly produce X-rays and its possible occurrence should be taken into consideration if astatine is determined by X-ray counting.

Instruments used for astatine determination are the normal ones. As sufficient activity is usually available, their sensitivity need not be very high nor do backgrounds have to be very low.

Proportional counters and ionization chambers were used for α counting in early investigations, but at present scintillation counters are usually more convenient. It should be kept in mind that in α counting of astatine there is always the danger of the presence of Po^{210}. On the one hand this nuclide is formed by the decay of At^{210}, but the activity produced in this way will usually be fairly small compared to the α activity of At^{211}. A much more serious danger is contamination of the He^{++} beam with D^+ ions, which produce Po directly. It is, of course, possible to separate the polonium from the astatine during the chemical preparation of the latter, but it is always desirable to make sure that this separation has been successful. This is, of course, easily done by following the decay of the α activity of At^{211} over a number of half-lives and preferably by another α measurement after the astatine has disappeared completely.

The α activity of astatine samples may be measured either on an infinitely thin sample or on an infinitely thick one. The former method is more accurate as far as the α counting is concerned, but the preparation

is as a rule more risky. The preparation of thick samples is generally quite simple, but their assay, if done with high degree of efficiency (approximately 2π counter), may produce errors as high as 10%.

Counting of X-rays and of γ-rays is conveniently done by well-type crystal counters. By discrimination these counters make it possible to count γ-rays without X-rays, thus excluding At^{211}, or to count individual γ-rays to distinguish between At^{210} and At^{209}. However, if one wishes to use inexpensive counting equipment, it is generally acceptable to count a mixture of X-rays and γ-rays by means of a GM counter. The counting efficiency of these instruments is low, but the geometry can be made to approximate 4π. (The counters of Philips, Eindhoven, of the type No. 18508 are very satisfactory for this purpose.) If astatine is determined by X-ray counting or γ-ray counting, it should be kept in mind that the decay of At^{209} produces some Bi^{205}, which emits both X-rays and γ-rays with a half-life of 15 days. As a rule, however, this activity will be too low to cause complications.

Autoradiography of astatine has been used successfully in biological work. The activity measured is, of course, the α emission of At^{211}.

B. Experimental Methods

For the production of astatine, bismuth is irradiated either as the metal or as the oxide. The bismuth metal is normally fused onto a metal plate, preferably of gold (*30*) or silver (*21*). Bismuth oxide can easily be pressed into holes drilled in a metal slab (*5*), from which it can be separated after an irradiation by mechanical means. If a high power press is available, the oxide may be pressed into a little boat scooped out of the metal plate. For a synchrocyclotron, which has a very narrow beam, a boat 30 mm long, 1 mm wide, and 1 mm deep is satisfactory. Evidently this boat must be as near as possible to the edge of the metal plate to avoid losing part of the beam. Whatever target construction is used, care should be taken to combine target shape and beam current in such a way that the temperature of the bismuth or the bismuth oxide does not become too high. Overheating may easily cause losses of astatine by evaporation.

Separation of astatine from irradiated bismuth or bismuth oxide is normally done either by distillation or by extraction.

Distillation is done from molten bismuth. It is either performed in a gas which may be stationary air (*8*) or a stream of inert gas (*30*), or it may be carried out in a vacuum (*22*, *27*). The astatine is normally caught on a cold finger. The glass surface may be used to collect the astatine, but it may also be equipped with a platinum disk for the purpose. The astatine is dissolved by immersing the finger or the disk in a suitable solution. If a fairly high temperature is required for the distillation, the astatine will be contaminated with polonium and possibly even with gravimetric quantities

of bismuth. Under these conditions the astatine tends to form radiocolloids (*17*, *30*), which may very seriously interfere with many experiments. (Such disturbances were especially noted with alkaline solutions; in acid solutions this complication will probably be less noticeable.) For these reasons a redistillation of the astatine may sometimes be advisable (*2*, *4*).

The advantage of these distillation methods is that they provide an astatine solution which does not contain weighable quantities of dissolved material. On the other hand, the yields obtained are generally low and irreproducible. This is hardly surprising, since the astatine will probably be present during the distillation in a chemically unstable condition, possibly as astatine atoms. This means that it will easily be lost by adsorption or by chemical reactions on walls or other materials present and that it will be difficult to recover from such parts. Fairly complete recovery (85%) has been reported for the distillation *in vacuo* at 310° from molten bismuth onto a silver foil (*27*), but it seems doubtful whether such quantitative behavior can be relied on to be reproduced in other experimental arrangements. A good adsorption of astatine by silver would be expected from chemical considerations.

Wet methods for the isolation of astatine can be used either for the preparation of carrier-free solutions or for solutions in an excess of iodine.

Extraction from hydrochloric solution into isopropyl ether seems to be satisfactory (*8*, *29*). It has the advantage that after the addition of a suitable quantity of tributylphosphate (TBP), polonium and bismuth can be extracted back into an aqueous phase containing nitric acid and hydrochloric acid.

Astatine iodide in a solution containing an excess of iodine is easily prepared by dissolving irradiated bismuth oxide in aqueous $HClO_4$ (containing I_2) and precipitating the bismuth with phosphate (*5*). For many purposes this liquid can be used as an aqueous solution of AtI. However, it still contains a certain amount of polonium, which in some cases may cause difficulty. A good purification is obtained if the I_2 containing AtI is extracted into CCl_4, from which it may be extracted back into a reducing aqueous phase. If the CCl_4 extraction is used, the phosphate precipitation may be omitted, but no special tests have been made to ensure that the purity in this case is as good as it is in the separation of $BiPO_4$. If an organic solution of AtI is required, the back-extraction is omitted. Chloroform may be used instead of CCl_4 (*6*).

The preparation of astatine for counting is largely dependent on the composition of the solution. If only volatile materials are present in appreciable quantities and if one is dealing with aqueous solutions, the liquid may be evaporated to dryness on silver or platinum. In this case α counting

is indicated. It is advisable to make the solution acidic (3 *M* HCl) before evaporation (*2*, *4*). It might perhaps also be advisable to make sure that the astatine is in the reduced form, e.g., by dissolving some SO_2 gas in the liquid. Quantitative deposition of astatine on evaporation is difficult to obtain from organic systems. It is also possible to precipitate astatine from aqueous solutions onto a silver foil in a way similar to that used for polonium. (It seems uncertain whether such a method would work in the presence of carrier amounts of iodine.) Precipitation on a silver foil is suitable for the collection of astatine from oxidized biological material, if the destruction has been done with a mixture of perchloric and nitric acids. After the oxidation is finished, the nitric acid is distilled off and the perchloric acid diluted to 3 *M*. A silver foil of convenient size is put into the beaker and the solution is stirred for 30 minutes (*15*).

An alternative method is to coprecipitate the astatine with other materials. Tellurium precipitation carries astatine in a satisfactory way, if the element is obtained by reducing tellurous acid with SO_2 in the presence of HCl. There is no objection to the presence of perchloric acid, which makes the method suitable for the analysis of biological samples (*15*). (No information is available to indicate whether this precipitation is reliable if the system contains iodine.)

In the presence of iodine, astatine is best isolated by the precipitation of an iodide from a reducing solution. Silver iodide would seem an attractive choice, but measured activities sometimes tend to be low with this method. This is probably due to losses of astatine from the AgI lattice by recrystallization. It has been suggested that the mixture of AgI and Ag obtained by adding $AgNO_3$ and an excess of sulfite might hold the astatine more efficiently (*5*), but even with this technique occasional losses occur. Precipitation with PdI_2 from a solution containing sulfite and an excess of nitric acid (*6*) is more reliable. This is probably due to the fact that palladium iodide recrystallizes much more slowly than silver iodide, because of the presence of a bivalent ion in the crystal. (Palladium iodide is difficult to filter. It is advisable to centrifuge the liquid containing the precipitate, wash the iodide by centrifugation, and use an organic liquid, like ethanol, either to transfer the liquid to a filter or to dry it in the centrifuge tube.)

Absolute determinations of the activity of astatine can easily be done by α counting. For this purpose liquid scintillation counting has been used (*9*), but probably scintillation counting with a well-defined geometry (*10*, *31*) would be equally satisfactory. This technique requires only a rough vacuum and presumably carrier-free astatine would not evaporate from a silver (or possibly a platinum) backing, though this point would have to be checked. Another possibility would be to rely on X-ray counting, but this

would be feasible only if the astatine did not contain At^{210}. A mixture of At^{210} and At^{211} might be standardized by a combination of X-ray counting and γ-ray counting with a NaI crystal calibrated for both. However, it is evident that α standardization will be far more accurate than other methods.

When thick samples (preferably, of course, samples of infinite thickness) are counted, an absolute calibration can be obtained by precipitating astatine samples, calibrated (in a carrier-free state) beforehand, with a known quantity of PdI_2. However, the counting of the α activity of thick samples is not nearly so reproducible as that of very thin samples.

Although we have mentioned several methods for the quantitative isolation of astatine, no one acquainted with the chemistry of this element will rely on any of these methods without keeping in mind the possibility of its proving to be untrustworthy on occasion. Probably this danger is greatest in those methods which depend on precipitation, but even transferring and dispensing solutions of astatine may possibly cause occasional losses due to adsorption (*22*).

III. Chemical Properties of Astatine

Although study of the chemical properties of astatine began more than 30 years ago (*12*), much of the behavior of this element is still in doubt. As with other tracers, its chemistry has been studied mainly by extraction and by coprecipitation and neither method provides results easy to interpret. It is evident that the chemical similarity between astatine and iodine does not go very far and in many cases the astatine tracer does not follow its iodine carrier in the way one would expect. The situation is complicated by the fact that the chemical properties of the series of halogens do not present a pattern which is easily recognized; in many respects bromine does not interpolate well between chlorine and iodine.

The chemistry of astatine is discussed as a rule under different headings, each one indicating a separate valency state; we shall follow the same scheme in this report.

The general trend in the periodic system suggests that astatine should be more "metallic" than other halogens. This means that it will take up a positive charge more easily than iodine and a negative charge less easily. It will be seen that this is actually the case.

In this connection it may be worth mentioning as an example that strong coprecipitation of astatine has been observed with SnS and with HgS from hydrochloric acid solution and also with several hydroxides (*12*, *22*). These experiments are, however, difficult to interpret owing to lack of knowledge of the valency of the astatine.

A. At^-

The astatide ion presents the best known chemical state of astatine and its similarity to the iodide ion is very striking. Even so astatide is not retained very well by some iodide precipitates like AgI, though initially it coprecipitates quite efficiently.

Astatide ion is normally prepared by reduction of some chemical state of astatine (usually and preferably AtI or At^0) with SO_2. The resulting solution coprecipitates entirely—at least initially—with iodide, and no astatine is extracted by CCl_4 (*2*, *4*, *22*). Reduction to astatide is also possible by means of ferrocyanide or by arsenite in acid solution. However, in these cases reduction seems to be somewhat incomplete. [Almost all of the activity coprecipitates with TlI; only a small but observable fraction—of the order of one or a few percent—is still extracted by CCl_4 (*2*, *4*).]

Measurements have been made of the mobility of astatide ions (*23*). The diffusion of a mixture of I^{131} and At ions was determined through the wall of Visking sausage-casing bags in solutions containing I^- and SO_3^{2-}. The ratio of the diffusion coefficient was found to be:

$$D_{I^-}/D_{At^-} = 1.41.$$

If the ratio of the mobilities in the plastic is equal to the ratio in pure water, this result is of the highest interest; it clearly demonstrates the maximum in the mobility of the halide ions as a function of the atomic number, as shown in Fig. 3.

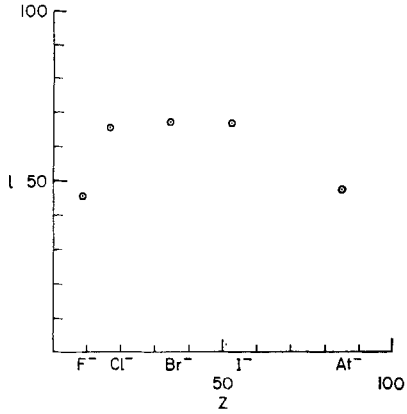

FIG. 3. Equivalent conductivity of halogen ions in water at 18°C. Equivalent conductivities (= 1) in $cm^{-1}\Omega^{-1}$ for a solution containing 1 gm ion/cm^3. Values for F^-, Cl^-, Br^-, and I^- from (*28*); the value for At^- was calculated as $1(I^-)/1.41$.

The negative charge on astatide ions was demonstrated by means of migration experiments (*22*).

B. At^0 AND AtI

Elementary astatine, unless diluted with a carrier amount of iodine, shows a most irreproducible behavior. This is by no means astonishing, as similar observations have been made on carrier-free radioactive iodine (*24*). It has occasionally been suggested that pure astatine in aqueous solutions should consist of At_2, but this seems rather doubtful in view of the very low concentration of the element. It is generally assumed that astatine in solution reacts with a number of impurities. This means that a "pure" solution of astatine has a composition which is unknown and irreproducible. It is hardly surprising that attempts to observe the chemical behavior of At^0 have not given satisfactory results. Appelman observed distribution ratios of 1–10 of At^0 between organic liquids, such as benzene or CCl_4, and water.

The assumption that carrier-free At^0 reacts with a number of impurities is supported by the observation that this activity can only partially be back-extracted from an organic solution into an aqueous phase. Another alarming fact is that a large but very irreproducible percentage of At^0 is absorbed onto glass wool from I_2-free aqueous solutions. Part of this activity can again be leached off the glass wool, but part always gets lost in experiments of this kind (*2*).

However, if a large excess of iodine is present, the behavior of astatine becomes much more reasonable. In this case the zero-valent element is present entirely as AtI molecules and a large excess of I_2 molecules protects the astatine against adsorption. Under these circumstances Appelman was able to obtain a fairly accurate and reliable value for the distribution ratio between CCl_4 and water:

$$[AtI]_{CCl_4}/[AtI]_{H_2O} = 5.5.$$

Extraction experiments of this kind have been used, together with coprecipitation tests, to study the formation of the zero oxidation state of At.

AtI is easily obtained by reduction of more oxidized forms of astatine with Fe^{++} ions, or with VO^{++} ions, in the presence of iodine. It is, however, essential that the reaction be carried out in the dark (*2*, *4*). The same reduction with Fe^{++} ions may be used to produce At^0, at least under favorable circumstances. Dilute nitric acid easily oxidizes At^- to At^0 (*22*). At^- is changed to AtI by the action of I_2 (*4*) (which evidently requires that no I^- or only very little be present, as otherwise AtI_2^- will be formed. This is discussed in Section III,G.)

The coprecipitation of AtI with I_2 from chloroform solutions has also been studied (*6*). The uptake of AtI by iodine crystals was found to follow the logarithmic distribution law of Doerner and Hoskins (*38*) with an initial distribution coefficient:

$$\lambda = \frac{\log\{(\text{AtI in solution})/(\text{AtI in solution} + \text{solid})\}}{\log\{(I_2 \text{ in solution})/(I_2 \text{ in solution} + \text{solid})\}} = 4.$$

C. At^+

In a solid or in an organic solvent iodine can easily be obtained as a monovalent positive ion, especially if it is stabilized by complex formation, e.g., with two molecules of pyridine. It is to be expected that the formation of such positive ions will be as easy or easier in the case of astatine. Both iodinedipyridineperchlorate—$I(C_5H_5N)_2ClO_4$—and the corresponding nitrate are easily prepared. It is not surprising that the ratio of astatine to iodine is higher in the perchlorate and in the nitrate than in the I_2 used for the synthesis (*33*).

D. At(X)

In aqueous solutions there also seems to exist an intermediate oxidation state between At^0 and AtO_3^-. Presumably this is either AtO^- or AtO_2^-, but no convincing evidence is available on this subject. In the case of iodine the ion IO^- seems to occur, although it has not been isolated. On the other hand, the existence of IO_2^- does not seem to have been established (*34*). The analogy here, however, between astatine and iodine does not seem to be very good, since this state of astatine seems to be much more stable than either of the two iodine states mentioned.

At(X) can be produced from astatine in a higher oxidation state by reduction with chloride. It can also be obtained from At^0 by oxidation with VO_2^+ or with Fe_3^+. Both oxidations are photochemical processes and both can take place in the absence or in the presence of excess iodine.

Conclusions concerning the occurrence of At(X) are based in general on negative evidence. Astatine in aqueous solution, which does not coprecipitate with insoluble iodides or iodates and which does not extract into CCl_4, is considered to be At(X).

E. AtO_3^-

Astatate ions seem to be fairly stable and are easily recognized by their coprecipitation with insoluble iodates. Appelman (*2*) has used coprecipitation with both $Pb(IO_3)_2$ and $Ba(IO_3)_2$.* Several means exist for oxidizing

* A very curious fact has been pointed out by Appelman (*2*). In many oxidizing systems astatine coprecipitates well with $Pb(IO_3)_2$, but a large part of this activity may be washed off this precipitate by means of acetone.

astatine quantitatively—or almost so—to astatate. Persulfate, ceric ion, or periodate all seem to be satisfactory. An acid solution of elementary chlorine or chromate oxidizes part of the astatine to astatate, but as a rule the oxidation does not seem to be quite complete (*2*).

The negative charge on astatate ions was demonstrated by means of migration experiments (*22*).

F. AtO_4^-

Appelman considers that perastatate has not been prepared and probably does not exist. He treated astatine with very strong oxidants, and by using a much higher concentration of iodate than of periodate was able to obtain a precipitate of $Ba(IO_3)_2$ containing very little periodate. From similar solutions he could precipitate periodate as KIO_4 (*2*). The activity in the periodate precipitate was negligible compared to that of the iodate. (The actual observations indicated that less than 10% of the total activity precipitated with KIO_4. If one takes into consideration the contamination, which is always observed in astatine chemistry, one will not consider such a small percentage coprecipitation as proof of the formation of perastatate.)

G. At IN POLYHALIDES

The fact that iodine forms a large number of polyhalides suggests a similar behavior on the part of astatine. The formation of such compounds has been studied by means of solvent distribution experiments by Neumann (*29*) and Appelman (*2*). The basic assumption is that charged complexes are extracted into polar organic solvents like isopropyl ether, but not into apolar liquids like CCl_4 or C_6H_6. (The extraction is done from acid solutions and it is not suggested that the polyhalide is present in the organic phase in an ionized state.) Strong evidence was obtained for a chloroastatide, but it was not possible to decide whether this ion should be formulated as $AtCl_2^-$ or $AtCl_4^-$ (*29*). Appelman has determined distribution coefficients between water and CCl_4 in systems containing different halogens, and from this has derived a number of equilibrium constants for the formation of various complexes of At, I, Br, and Cl. It is interesting to note that astatine is always complexed a little more strongly than iodine in the corresponding position, the differences in the equilibrium constant amounting to a factor of 2.5–8 (*2*). Another general rule is that halogen molecules consisting of two identical atoms are extracted more strongly into CCl_4 than molecules containing two different halogen atoms, due to the fact that the former type of molecule is entirely apolar, whereas the latter type represents a dipole. The distribution coefficient for iodine between CCl_4 and water is 86 and for AtI is 5.5.

An alternative way to investigate polyhalides is by obtaining them in a solid. CsI_3 containing $CsAtI_2$ is easily prepared from an aqueous solution of CsI, which is first used to extract I_2 containing AtI from chloroform and to which a suitable quantity of solid I_2 is added afterwards. Heating and cooling produces CsI_3 containing astatine.

A general rule in the chemistry of polyhalides says that in the decomposition of a polyhalide the lightest halide remains behind to form the monohalide (*35*). Evidently this rule has been observed with pure polyhalides, whereas in the case of astatine we are dealing with a mixed lattice containing a tracer quantity of AtI_2^- in a carrier of I_3^-. Even so it is gratifying to observe that the same rule holds in this case and that during the decomposition of $CsAtI_2$ in CsI_3 the AtI follows the iodine vapor (*11*).

H. At in Organic Compounds

The difficulties encountered in the work on inorganic astatine are even more upsetting in the study of its organic chemistry. Irregular extraction and coprecipitation combined with the instability of many astatine compounds often make the interpretation of observations quite uncertain. If, for instance, iodoform is synthesized from iodine containing AtI (*36*), the first precipitate of CHI_3 shows a very appreciable At activity, which disappears rapidly in the course of a series of recrystallizations (*32*). It is hardly possible to say for certain whether this means that the lattice did not contain $CHAtI_2$ at all, or whether this compound was formed initially but decomposed very easily. However, the first explanation seems to be the more reasonable. This situation probably explains the rather conflicting remarks repeatedly made about the synthesis of organic compounds of astatine. Thus one laboratory reported the preparation of phenyl astatide (*21*), whereas the preparation of this compound was not successful in another institute (*18*). In some cases attempts to synthesize organic astatine compounds give negative results (*32*), e.g., in the case of *p*-iodoaniline (*37*). In other cases successful synthesis has been reported, e.g., for *p*-astatobenzoic acid and *p*-astatobenzenesulfonic acid. The latter compound provides a means for incorporating astatine into different proteins (*20, 21*). This can also be done by means of a diazo coupling of benzidine to protein (*21*).

A general consideration of the chemical properties of astatine suggests that the best chance for the incorporation of astatine into organic molecules exists in those cases where the astatine atom carries a partial positive charge, both in the final product and in any intermediate stage through which it passes during the reaction. Workers interested in the synthesis of organic astatine compounds may find it useful to give this point serious attention.

I. Biochemical Compounds of At

Astatine in the living organism is taken up rapidly by the thyroid gland, due to its similarity to iodine. It is not clear whether the astatine is carried by the blood as At^- or as At^0. For some time its chemical condition in the thyroid gland was also in doubt, but, recently it has been shown that a large fraction of the astatine in the thyroid follows the protein fraction as it is precipitated by trichloroacetic acid or by concentrated ammonium sulfate (*19*). This suggests that astatine can take up positions in the thyroid protein similar to those normally occupied by iodine.

IV. Biological Behavior

The fate of astatine in living organisms is very similar to that of iodine, as is to be expected. Much work has been done on the absorption and distribution of the element; it has been observed that if astatine is administered as a radiocolloid, it tends to accumulate in the liver (*17*, *30*), a tendency common to most radiocolloids. If administered as a true solution, astatine is concentrated strongly in the thyroid. A large number of publications on this subject are listed in a recent paper by Hamilton *et al.* (*13*). The distribution of astatine can be observed very easily in autoradiograms, in which At^{211} is recognized by its α tracks (*23*). The uptake of astatine by the thyroid gland is reduced by the administration of thiocyanide, a behavior quite analogous to that of iodine. However, the influence of propylthiouracil enhances the uptake of astatine, but reduces that of iodine (*19*).

Because of its α emission, most of the decay energy of At^{211} is strictly localized in the region where the element is concentrated, i.e., the thyroid. For this reason astatine has been suggested as a "thyroidectomizing" agent (*19*).

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Referenced

1. Anders, E., *Ann. Rev. Nucl. Sci.* **9**, 203 (1959).
2. Appelman, E. H., "Chemical Properties of Astatine." UCRL-9025, Ph.D. Thesis, University of California (1960).
3. Appelman, E. H., *U. S. At. Energy Comm. NAS-NS* No. 3012 (1960).
4. Appelman, E. H., *J. Am. Chem. Soc.* **83**, 805 (1961).
5. Aten, A. H. W., Jr., Doorgeest, T., Hollstein, U., and Moeken, P. H., *Analyst* **77**, 774 (1952).
6. Aten, A. H. W., Jr., van Raaphorst, J. G., Nooteboom, G., and Blasse, G., *J. Inorg. Nucl. Chem.* **15**, 198 (1960).

7. Bagnall, K. W., "Chemistry of the Rare Radioelements." Butterworths, London, 1957.
8. Barton, G., Ghiorso, A., and Perlman, I., *Phys. Rev.* **82,** 13 (1952).
9. Basson, J. K., *Anal. Chem.* **28,** 1472 (1956).
10. Brinkman, G. A., "Standardization of Radioisotopes," p. 60. Ph.D. Thesis, University of Amsterdam (1961).
11. Brinkman, G. A., Veenboer, J. T., and Aten, A. H. W., Jr., *Radiochim. Acta* **2,** 48 (1963).
12. Corson, D. R., Mackenzie, K. R., and Segrè, E., *Phys. Rev.* **57,** 1087 (1940).
13. Durbin, P. W., Asling, C. W., Johnston, M. E., Parrot, M. W., Jeung, N., Williams, M. H., and Hamilton, J. G., *Radiation Res.* **9,** 378 (1958).
14. Everling, F., König, L. A., Mattauch, J. H. E., and Wapstra, A. A. W., *Nucl. Phys.* **18,** 529 (1960).
15. Garrison, W. M., Gile, J. D., Maxwell, R. D., and Hamilton, J. G., *Anal. Chem.* **23,** 204 (1951).
16. Haïssinsky, M., "La Chimie Nucléaire et ses Applications," p. 176. Masson, Paris, 1957.
17. Hamilton, J. G., Parrot, M., Johnston, M., and Durbin, P., University of California Radiation Laboratory, UCRL-2418, p. 11 (1953).
18. Hamilton, J. G., Wallace-Durbin, P., and Parrot, M. W., "Harwell Radioisotopes Conference," p. 230. Butterworths, London, 1954 (remark in discussion).
19. Hamilton, J. G., Durbin, P. W., Asling, C. W., and Johnston, M. E., *Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva 1955* Vol. *10,* 175 (1956).
20. Hughes, W. L., and Klinenberg, J., *Brookhaven Natl. Lab.* **BNL-367,** 42 (1955).
21. Hughes, W. L., Smith, E., and Klinenberg, J., *Brookhaven Natl. Lab.* **BNL-406,** 44 (1956).
22. Johnson, G. L., Leininger, R. F., and Segrè, E., *J. Chem. Phys.* **17,** 1 (1949).
23. Johnston, M., Asling, C. W., Durbin, P. W., and Hamilton, J. G., University of California Radiation Laboratory, UCRL-3013, pp. 35, 36 (1955).
24. Kahn, M., and Wahl, A., *J. Chem. Phys.* **21,** 1185 (1953).
25. Karlik, B., and Bernert, T., *Naturwissenschaften* **31,** 298 (1943).
26. Karlik, B., and Bernert, T., *Naturwissenschaften* **32,** 44 (1944).
27. Kelly, E., and Segrè, E., *Phys. Rev.* **75,** 999 (1949).
28. Kohbrausch, F., "Praktische Physik," 18th ed., p. 543, Table 59. Teubner, Leipzig, 1943.
29. Neumann, H. M., *J. Inorg. Nucl. Chem.* **4,** 349 (1957).
30. Parrot, M., Garrison, W., Durbin, P., Johnston, M., Powell, H., and Hamilton, J., University of California Radiation Laboratory, UCRL-3065, p. 3 (1955).
31. Robinson, H. P., *U. S. At. Energy Comm. NAS-NS* No. 573, 2 (1958).
32. Samson, G., and Aten, A. H. W., Jr., Unpublished observations (1963).
33. Schats, J. J. C., and Aten, A. H. W., Jr., *J. Inorg. Nucl. Chem.* **15,** 197 (1960).
34. Sidgwick, N. V., "The Chemical Elements and their Compounds," Vol. II, p. 1225. Clarendon, Oxford, 1950.
35. Sidgwick, N. V., "The Chemical Elements and their Compounds, Vol. II, p. 1195. Clarendon, Oxford, 1950.
36. Prepared as described by Vogel, A. I., "A Textbook of Practical Organic Chemistry," p. 299. Longmans, Green, New York, 1959.
37. Prepared as described by Vogel, A. I., "A Textbook of Practical Organic Chemistry," p. 647. Longmans, Green, New York, 1959.
38. Wahl, A. C., and Bonner, N. A., "Radioactivity Applied to Chemistry," p. 106. Wiley, New York, 1951.