in determining the relative stabilities of the MCl_2 phases, but the sublimation enthalpy changes available to them were much poorer, 10 to 15 kcal too low in the critical cases of Sc,[31] Pr, Dy, and Er for example. Estimates of some I_1 and I_2 values led to a number of significant errors, especially in the heavier half, where $I_1 + I_2$ was taken as constant at 18.9 ev, up to 1.4 ev higher than now reported.[24] Since borderline stabilities are very dependent on small differences in a quantitative calculation, errors resulted in the prediction of a regular trend in the second half of the lanthanides analogous to that in the first, particularly for Dy, Er, (Lu?), and Sc. Correction with present data would put the calculations largely in agreement with experiment.

Topol[36] has treated relative metal solubilities in a somewhat different manner, one which essentially used the logarithm of the Henry's law constant $[C_M(g)/C_M(melt)]$ at constant temperature to describe an "interaction energy" or standard free energy of metal dissolution. These were observed to group roughly according to charge type and position in the periodic table. The few energies determinable at that time for rare earth metal systems were in the range of -62 ± 3 kcal/mole, which, with again erroneous vapor pressure data, led to predictions of generally large metal solubilities ($>10\%$) for the heavy elements Tb to Er and "even complete miscibilities" for Sm, Eu, Tm, Yb, and Lu(!) with their molten chlorides. Although the

(36) L. E. Topol, *J. Phys. Chem.*, **69**, 11 (1965).

literal attainment of the last condition does not seem likely,[37] the procedure would probably predict results comparable to those known with better vapor pressure data now available. Although different standard states and dimensions (and philosophy) are involved in Topol's procedure, it actually parallels that found suitable here in that, for constant interaction energy, $-\Delta F^\circ_{subl}$ was taken as proportional to log N_M, which is in turn proportional to log K_{assoc} for small N_M. The other terms in the cycle used here are then included in the "interaction energy" range considered as constant. General applicability to other groups of systems involving chemical equilibria then depends on $\Delta F^\circ_{subl\ M}$ being of major importance relative to other quantities, particularly on the absence of disproportionate ionization energies not reflected in ΔF°_{subl}. Of course, the more physical nature of the treatment does not consider or interpret the chemistry involved, but, on the other hand, the prime importance of the sublimation energy found in the present work supports a chemical model largely in its continuity with known dihalides, in small but significant ionization factors, and in any explanation of trends in the metals themselves.

(37) The interaction energy of M with MCl_2 would be considerably less than with MCl_3 to form MCl_2—compare Tl with $TlCl_3$ and $TlCl$.[36]

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Observation of Astatine Compounds by Time-of-Flight Mass Spectrometry[1]

BY E. H. APPELMAN, E. N. SLOTH, AND M. H. STUDIER

Astatine compounds were prepared and were identified in a time-of-flight mass spectrometer. The compounds observed were HAt, CH_3At, AtI, AtBr, and AtCl. No evidence was found for the existence of At_2. An attempt to identify astatine fluorides was unsuccessful.

Introduction

Astatine is a synthetic halogen element with no long-lived nuclides. As a result, all investigations of astatine chemistry to date have been carried out at extremely low concentrations, and the astatine has been detected only by its radioactivity. Such investigations can never unambiguously establish the identity of astatine species, and some sort of independent verification of the conclusions of these studies is therefore desirable.

In the case of volatile astatine compounds, such verification can be obtained through the use of a mass spectrometer to measure directly the masses, and hence the

probable identities of the principal molecular species present. The Bendix time-of-flight mass spectrometer, with its source modified for continuous duty,[2] has an ultimate sensitivity of about 40 atoms/cc and is thus quite suitable for the examination of astatine species. We have therefore set out to prepare and to identify with this instrument a number of astatine compounds, particularly those that we would expect astatine to form with other members of the halogen family.

Experimental Section

Preparation and Isolation of Astatine.—Astatine-211 was synthesized by bombardment of bismuth with 29-Mev α particles in the 60-in. cyclotron at Argonne National Laboratory. The

(2) M. H. Studier, *Rev. Sci. Instr.*, **34**, 12 (1963).

targets were prepared by fusing bismuth into a 10 mil deep well milled in a piece of 0.032-in. 2S aluminum and then fly-cutting the surface down to leave an inlay of bismuth 0.004–0.005 in. thick. The target was cooled from behind by water and in front by a static 0.5 atm of helium. The beam energy was reduced to 29 Mev with aluminum foils to avoid production of At^{210}, which would leave a radioactive residue of Po^{210}. Targets were bombarded for about 8–10 hr at an average current of 30–40 μa. Using published yield data,[3] we may calculate that we had at the end of each bombardment around 0.05 μg of At^{211}, corresponding to about 3×10^{11} dpm.

The bombarded target was heated to 250° in air to drive off volatile contaminants. The astatine was then distilled from the bismuth in air at 800° and collected on a water-cooled platinum plate, using an apparatus similar to that of Barton, Ghiorso, and Perlman.[4]

Monitoring.—The location of the astatine could readily be determined by detecting its X-rays with an ionization-chamber-type survey meter.

Sample Handling.—Satisfactory results were obtained when the astatine was distilled in an all-glass or silica vacuum system prior to its introduction into the mass spectrometer source. When a metal system was tried, on the other hand, the astatine adhered to the walls and could not be moved into the spectrometer. In later experiments an all-silica system was used to permit higher baking temperatures. Iron bars used to open break-seals and lift check-valves were also enclosed in silica. In the rest of this paper the term "glass" may refer either to Pyrex or to vitreous silica. Before use, the glass apparatus was always baked at 540° or higher in air or oxygen to destroy organic impurities.

The platinum plate containing the astatine was placed in the glass apparatus, which was then sealed off and evacuated. There was no appreciable loss of the astatine, for it did not distil from the plate until temperatures well above 100° were reached. In a few experiments the astatine was distilled directly from the plate into the mass spectrometer, but in most cases an auxiliary pumping system was used to pump out the glass apparatus and distil the astatine into a U tube cooled with Dry Ice or liquid nitrogen. In early experiments we used a conventional glass-and-grease pumping system, but in later experiments a metal system was used, with a Kel-F section between the metal and the glass. The Kel-F was joined vacuum-tight to the glass by forcing a Kel-F tube over a warm, tapered glass tube. In all cases cold traps were employed to protect the glass line against any contamination from the pumping system.

To reduce further the level of organic impurities, we found it useful to ignite the astatine-bearing plate in oxygen, and the following procedure was adopted in our later experiments. The glass tube into which the plate was put was isolated from the rest of the apparatus by a break-seal. This tube was evacuated by a separate pump and filled with 1 atm of oxygen before being sealed off. It was then heated with a torch to bright red heat. Then the astatine and oxygen were condensed in a solid–liquid nitrogen slush, the break-seal was broken, and the oxygen was pumped away. This left the astatine again fixed on the platinum, and we could warm the tube to room temperature and thoroughly pump it out before distilling the astatine.

After the astatine was distilled into the U tube and any desired macro halogen was introduced, the apparatus was sealed off first from the platinum plate and then from the auxiliary pumping system. The seals were made in such a way that a side arm remained attached to one side of the U tube. The astatine could be warmed up, equilibrated with the other halogen if one was present, and distilled back and forth between the U tube and the side arm.

The astatine was introduced into the mass spectrometer through a glass tube run through a hole in the stainless steel

bottom flange of the ion source and protruding about 2 in. into the source region. The entry point of the tube was sealed with Apiezon W wax, but the geometry was such that compounds entering the instrument were ionized and accelerated before having a chance to contact either the wax or the metal walls of the spectrometer. The glass tube contained a break-seal to isolate the spectrometer from the glass apparatus, to which the tube was connected at a point between the U tube and the side arm.

In experiments with Br_2, Cl_2, and ClF_3 we separated the astatine compound from the bulk halogen through the use of ball-and-socket check-valves with iron cores. One of these valves was placed below the break-seal in the tube leading to the mass spectrometer; the other was placed at the top of the side arm. Both were oriented so that the plugs moved down to seat. These valves could be operated either manually with a bar magnet or automatically with a solenoid. Using them we could, for example, distil the contents of the U tube into the liquid nitrogen cooled side arm and observe the distilling species by periodically opening the valve to the spectrometer. The less volatile astatine compound always distilled after the bulk halogen.

Introduction of Other Halogens.—Small, but indeterminate, amounts of iodine were introduced in the following manner. A crystal of iodine was wrapped in a piece of platinum and heated to about 200° on a hot plate until no more fumes were observed. The platinum was then placed in the glass apparatus along with the astatine-bearing plate, and the two were subjected to the same treatment. This led to something of the order of 10 μg of iodine accompanying the astatine into the U tube.

Bromine and chlorine were introduced by putting *ca.* 200-μg portions of $PtBr_2$ or $PtCl_4$ into a special side arm on the apparatus. The compound was decomposed by heating, and the halogen was condensed in the U tube. The side arm was then sealed off.

Chlorine trifluoride was introduced in the following manner. The astatine was transferred to the U tube cooled in Dry Ice. Then the glass sytem was opened through the auxiliary line to a can of ClF_3 cooled in an ethanol slush ($-117°$). The ClF_3 can was closed off with a valve, liquid nitrogen was placed on the U tube to condense the ClF_3 vapor out of the line, and the glass system was sealed off from the auxiliary line. In this way about 50 μg of ClF_3 was introduced into the system.

The Mass Spectrometer.—We used a Bendix Model 12 time-of-flight mass spectrometer with a 100-cm flight tube. The instrument had been modified to give its source a continuous duty cycle.[2] The mass spectra were displayed on an oscilloscope and recorded with a Polaroid camera. A "blanking" circuit was used which suppressed the response of the detector to unwanted portions of the spectrum. This greatly reduced the loss of gain that would ordinarily result from saturation of the detector by large extraneous peaks.

Even though scrupulously clean, the spectrometer generally had a small hydrocarbon peak at every mass from 12 to over 400. Hence, it was usually possible to identify an unknown peak simply by counting from a known one. When this was not satisfactory, a calibration curve of flight time *vs.* square root of mass was plotted using known peaks. The mercury spectrum was always present from the mercury-diffusion pump of the spectrometer, and it provided a convenient reference.

Results

When the astatine was distilled directly from the platinum plate into the spectrometer, a large At^+ peak appeared suddenly. It built up and died away rapidly, and when it was at its maximum, nothing else in the spectrum above Hg^+ was as much as a tenth of its magnitude.

When the astatine was transferred to the glass U tube first, it distilled into the spectrometer gradually as the glass was heated. A typical spectrum is shown in Figure 1. The CH_3At^+ peak was observed even

(3) G. L. Johnson, R. F. Leininger, and E. Segrè, *J. Chem. Phys.*, **17**, 1 (1949).

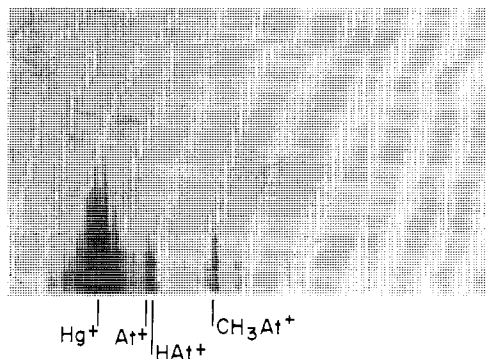(4) G. W. Barton, Jr., A. Ghiorso, and I. Perlman, *Phys. Rev.*, **82**, 13 (1951).

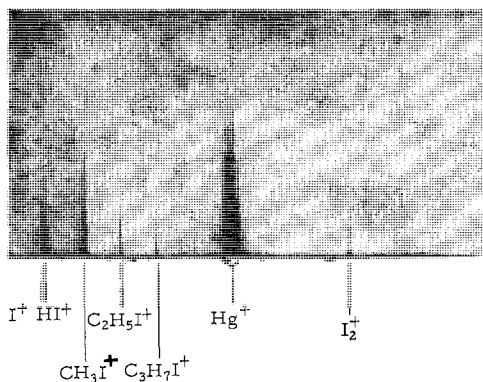Figure 1.—Mass spectrum of astatine in the absence of macro amounts of other reagents.

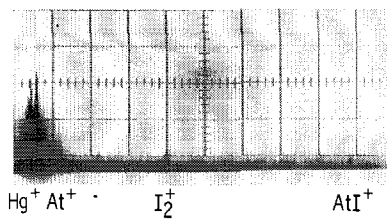Figure 2.—Mass spectrum obtained with very small amounts of iodine.

Figure 3.—Mass spectrum obtained from a mixture of astatine and iodine.
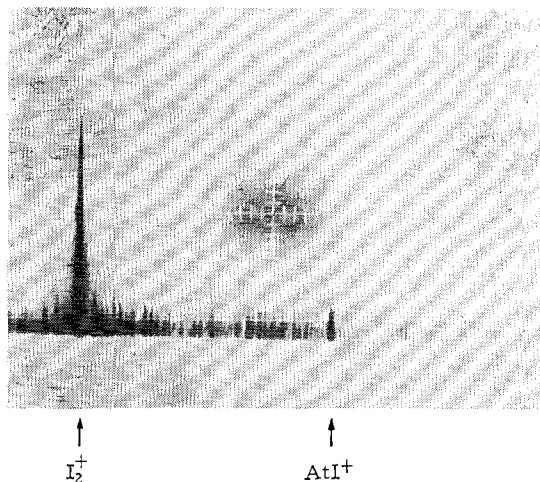

Figure 4.—Expanded portion of a mass spectrum obtained from a mixture of astatine and iodine.
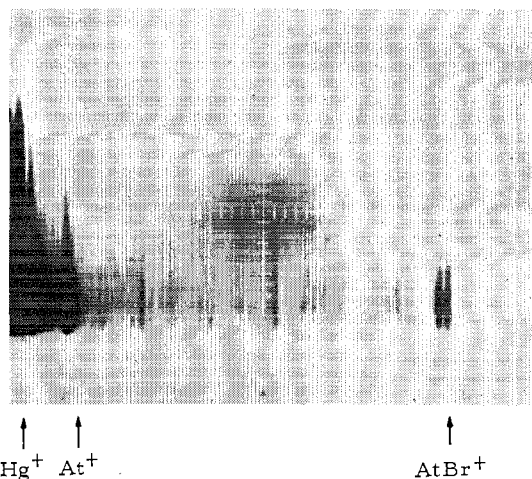

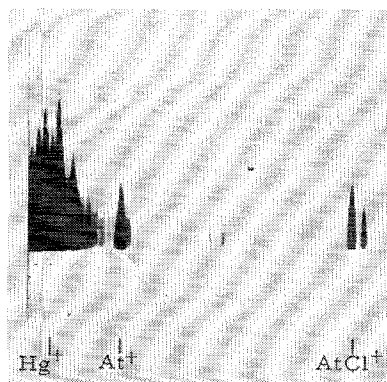Figure 5.—Mass spectrum of astatine after reaction with bromine, showing the $AtBr^{79}$–$AtBr^{81}$ doublet.

Figure 6.—Mass spectrum of astatine after reaction with chlorine, showing the $AtCl^{35}$–$AtCl^{37}$ doublet.

when the platinum plate with the astatine had been baked in oxygen.

For comparison we treated a platinum plate with iodine as described in the Experimental Section. After pumping on it exhaustively, we heated it and allowed the iodine to distil directly into the spectrometer. The result appears in Figure 2.

Figures 3 and 4 show the results obtained with a mixture of astatine and iodine. The iodine and astatine entered the spectrometer together when the walls of the glass apparatus were heated quite strongly. In addition to the ions shown in the figures, I^+, HI^+, and organoiodine fragments were observed. Much of the background "hash" in these figures came from the α radiation of astatine adsorbed on the elements of the electron-multiplier detector of the spectrometer.

When astatine and bromine were mixed, the bromine could be readily distilled away from the astatine compound somewhat below room temperature. The latter distilled slowly at room temperature and more rapidly upon gentle heating. Similar results were obtained with astatine and chlorine, except that the chlorine distilled away at considerably lower temperatures than the bromine. The resulting spectra appear in Figures 5 and 6. In addition to the major species, traces of CH_3At^+ can be seen in both figures.

When mixed with ClF_3, the astatine adhered so strongly to the glass walls that it could not be moved into the spectrometer. Considerable amounts of ClF, Cl_2, and SiF_4 were formed.

Discussion

Previous investigations of astatine chemistry have shown that its behavior is not too different from that of other halogens.[3,5,6] These studies have characterized a "zero oxidation state" of astatine that is volatile, is soluble in organic solvents, and has a tendency to adsorb on surfaces. Unfortunately, another characteristic of this state has been severe irreproducibility of behavior. Much the same situation is found with very small amounts of iodine,[7-11] and it seems reasonable to attribute the difficulties to the fact that some or all of the halogen is tied up in the form of compounds with organic impurities.[6,7,11] On the other hand, when "zero-state" astatine is mixed with other halogens, it is often possible to obtain reproducible behavior characteristic of interhalogen compounds.[12-14]

On the whole, the results of the present study confirm these observations. Figure 1 indicates that in the absence of macro amounts of another halogen a substantial part of the astatine is present in something other than the elemental form, and comparison with Figure 2 shows that small amounts of iodine behave in a remark-

ably similar fashion. The HI^+ and HAt^+ appearing in these figures may result either from hydrolysis with traces of water or from substitution reactions with organic hydrogen.

Our failure to observe At_2 does not allow us to draw any definite conclusions about the equilibrium $2At \rightleftharpoons At_2$. When the astatine was distilled directly from the platinum into the spectrometer a platinum astatide may have been decomposing, and the At atoms formed may not have had time to combine to At_2 molecules. In the other experiments, most or all of the At^+ observed may have arisen from fragmentation of vapor-phase compounds.

As we might have expected, addition of excess iodine, bromine, or chlorine converts a large part of the astatine into the corresponding monohalide. Although higher astatine bromides and chlorides might be expected to exist, they would probably not form under the rather mild halogenating conditions that we have employed.

The low volatility observed for the astatine compounds probably means that we are dealing with surface adsorption effects bearing little relation to bulk vapor pressure. However, the nearly complete loss of volatility in the presence of ClF_3 is puzzling since under such conditions we might have expected the formation of a relatively volatile astatine fluoride.

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(11) M. H. Studier, C. Postmus, Jr., J. Mech, R. R. Walters, and E. N. Sloth, *J. Inorg. Nucl. Chem.*, **24**, 755 (1962).
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(13) E. H. Appelman, *J. Phys. Chem.*, **65**, 325 (1961).
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Mössbauer Spectra of SnH₄ and Related Compounds

BY R. H. HERBER[1a] AND G. I. PARISI[1b]

The Mössbauer spectra of SnH₄ and a number of related organotin hydrides, organotin halides, and other compounds have been determined at 77°K. The isomer shifts (with respect to SnO₂) noted for the hydrides fall into two groups: 1.24 ± 0.03 mm/sec for compounds with at least one CH₃–Sn bond, and 1.42 ± 0.04 mm/sec for molecules not having a CH₃–Sn bond. The R_nSnH_{4-n} spectra show the absence of a quadrupole interaction between the Sn^{119m} nuclei and the electric field gradient tensor, consistent with an effect first noted by Greenwood. The relationship between this observation and the bonding in organotin compounds is examined in detail. The decomposition of SnH₄ at 0° to give white (β) tin has been confirmed. The infrared spectrum of n-butyltin trihydride is presented.

Introduction

In a recent study[2] of the Mössbauer spectra of a number of organotin compounds, three observations

relating to the systematic substitution of ligands bonded to the metal atom were noted: (1) Substitution of sp^2 hybridized (aromatic) C atoms for sp^3 hybridized (aliphatic) C atoms has only a very small effect on the isomer-shift parameter. (2) In binuclear compounds with tin–tin linkages of the type $R_3Sn–SnR_3$, no quadrupole splitting could be resolved from the resonance