

rane,<sup>10,14</sup> and aminoborane from the corresponding boron-hydrogen compound. However, the reactivities of the boron-nitrogen compound and mercury-containing products are different for the various boron-nitrogen compounds. Aminoboranes react with  $\text{HgX}_2$  at 110 °C to give Hg and HX whereas borazines<sup>9,13</sup> and amine-boranes<sup>10,14</sup> react at 25 °C to give  $\text{Hg}_2\text{X}_2$  and HX as products. As the mercury(II) halides are believed to react with these types of boron-nitrogen compounds by a polar mechanism,<sup>9,10,14</sup> the decreased reactivity of  $[(\text{H}_2\text{BN}(\text{CH}_3)_2)_2]$  compared to that of  $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$  and  $\text{H}_3\text{BN}(\text{CH}_3)_3$  might be related to a smaller partial negative charge on the hydrogen bound to boron<sup>10</sup> due to electronegativity effects and steric effects. At higher temperatures, the reactivities of both  $[(\text{H}_2\text{BN}(\text{CH}_3)_2)_2]$  and  $\text{HgX}_2$  will be enhanced by changes in coordination number. The aminoborane dimer will dissociate into a less sterically hindered monomer and the six-coordinate mercury(II) species of the solid phase<sup>15</sup> will be converted into a linear two-coordinate species.

There is another observation of synthetic utility which is worth noting. The compound  $\text{H}_2\text{ClBN}(\text{CH}_3)_2\text{H}$  readily loses  $\text{H}_2$  to form  $[\text{HClBN}(\text{CH}_3)_2)_2]$ . In our experiments, the reaction was observed at 110 °C. (No attempt was made to determine the lowest temperature necessary for reaction.) Conversely, the compound  $\text{H}_2(\text{CN})\text{BN}(\text{CH}_3)_2\text{H}$  could not be converted to  $[\text{H}(\text{CN})\text{BN}(\text{CH}_3)_2)_2]$  by loss of  $\text{H}_2$ . No reaction was observed at 147 °C and higher temperatures led to decomposition. These cyano-substituted amine-boranes also exhibit unusually high hydrolytic stability.

The  $^1\text{H}$  NMR spectra of  $[\text{HClBN}(\text{CH}_3)_2)_2]$  and  $[\text{HBrBN}(\text{CH}_3)_2)_2]$  suggest some interesting structural properties. The data for both compounds are consistent with a structure involving a four-membered ring and cis-trans isomerism. The multiplicity of CH lines and their temperature dependence suggest that the rings are bent and inverting at room temperature. The  $^{11}\text{B}$  NMR spectra of both compounds, a symmetrical doublet due to B-H coupling, are consistent with only one type of boron atom. Thus, structures involving unsymmetrical substitution, four-membered chains, ionic structures, and monomeric species are eliminated. Molecular weight measurements in solution also confirm the absence of significant concentrations of monomeric species. The room-temperature  $^1\text{H}$  NMR spectrum of  $[\text{HClBN}(\text{CH}_3)_2)_2]$  in  $\text{CDCl}_3$  consists of a broad line at -2.58 ppm and a sharp line at -2.49 ppm. These two lines can be assigned to the N-CH<sub>3</sub> groups of the cis and trans isomers, respectively. The spectrum at lower temperatures confirms the assignments of the lines. Upon cooling, the broad line at -2.58 ppm splits into two lines at -2.62 and -2.56 ppm at -23 °C. The line at -2.49 ppm remains a sharp singlet. These data suggest that the lower field line in the room-temperature spectrum is due to the cis isomer of a bent boron-nitrogen ring. As the temperature is lowered, the two types of methyl groups in the cis isomer, axial and equatorial, are observed. In benzene solution, the lines due to the isomers of  $[\text{HClBN}(\text{CH}_3)_2)_2]$  are not resolved. The situation is exactly the opposite for  $[\text{HBrBN}(\text{CH}_3)_2)_2]$ ; the isomers are resolved in aromatic solvents but not in  $\text{CDCl}_3$ . The  $^1\text{H}$  NMR spectrum of  $[\text{HBrBN}(\text{CH}_3)_2)_2]$  in  $\text{C}_6\text{H}_5\text{Cl}$  exhibits two CH lines (-2.31 and -2.22 ppm) at room temperature and at -40 °C, the lowest temperature we could attain. The data for this compound are also consistent with a bent but flexible boron-nitrogen ring. Apparently, the bromine-substituted molecule is inverting faster than the chlorine derivative. There is also more ring distortion in bromocyclobutanes.<sup>16</sup> For both compounds  $[\text{HClBN}(\text{CH}_3)_2)_2]$  and  $[\text{HBrBN}(\text{CH}_3)_2)_2]$ , this cis isomer is more abundant than the trans isomers. Similar observations have been made for 1,3-dihalocyclobutanes,<sup>16</sup>  $[\text{Cl}(\text{CH}_3)\text{B}$

$\text{N}(\text{CH}_3)_2)_2]$ ,<sup>17</sup> and analogous aluminum-nitrogen compounds.<sup>18</sup> The high cis:trans ratio for group 3-5 compounds may be dependent on the mechanism of dimer formation.

An equilibrium between the dimeric and monomeric species in the gas phase is confirmed by vapor pressure, gas-phase molecular weight measurements, and mass spectral data. The enthalpies for the gas-phase equilibrium (dimer  $\rightleftharpoons$  2(monomer)) for  $[\text{HClBN}(\text{CH}_3)_2)_2]$  and  $[\text{HBrBN}(\text{CH}_3)_2)_2]$  are 30.1 and 42.0 kcal/mol, respectively. The comparison of the thermodynamic data suggest that  $[\text{HBrBN}(\text{CH}_3)_2)_2]$  exhibits the more stable dimer. This conclusion is consistent with the observation that  $\text{BBr}_3$  is a stronger Lewis acid<sup>19</sup> than  $\text{BCl}_3$ . By analogy, there might be more distortion in the bromo derivative than in the chloro to form stronger boron-nitrogen bonds in the dimer. As there is less boron-bromine  $\pi$  bonding than boron-chlorine, increased boron-nitrogen  $\pi$  bonding might be expected to stabilize the monomeric species. However, the monomeric species is certainly not very stable at 25 °C. It is regrettable that there are just too many undetermined variables in the thermodynamic cycle, analogous to that used for the Lewis acidity of boron trihalides, to be able to evaluate the magnitude of boron-nitrogen  $\pi$  bonding in the compounds. There just might be less boron-nitrogen  $\pi$  bonding than we have been led to believe in the past.

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**Registry No.**  $[(\text{H}_2\text{BN}(\text{CH}_3)_2)_2]$ , 23884-11-9;  $\text{HgCl}_2$ , 7487-94-7;  $\text{HgBr}_2$ , 7789-47-1; *cis*- $[\text{HClBN}(\text{CH}_3)_2)_2]$ , 57652-88-7; *trans*- $[\text{HClBN}(\text{CH}_3)_2)_2]$ , 57694-03-8; *cis*- $[\text{HBrBN}(\text{CH}_3)_2)_2]$ , 57652-89-8; *trans*- $[\text{HBrBN}(\text{CH}_3)_2)_2]$ , 57694-04-9.

## References and Notes

- (1) Abstracted in part from the M.A. thesis submitted to the Graduate School of the State University of New York at Buffalo, Buffalo, N.Y., by B. Washburn, June 1973.
- (2) O. T. Beachley, Jr., and G. E. Coates, *J. Chem. Soc.*, 3241 (1965).
- (3) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).
- (4) A. B. Burg and C. L. Randolph, Jr., *J. Am. Chem. Soc.*, 73, 953 (1951).
- (5) A. J. Banister, N. N. Greenwood, B. P. Straughan, and J. Walker, *J. Chem. Soc.*, 995 (1964).
- (6) K. Hess, *Z. Kristallogr., Kristallphys., Kristallchem.*, 118, 361 (1963).
- (7) H. Nöth, *Z. Anorg. Allg. Chem.*, 318, 294 (1962).
- (8) V. Shchukovskaya, *Dokl. Akad. Nauk SSSR*, 143, 887 (1962).
- (9) R. Maruca, O. T. Beachley, Jr., and A. W. Laubengayer, *Inorg. Chem.*, 6, 575 (1967).
- (10) O. T. Beachley, Jr., and B. Washburn, *Inorg. Chem.*, 14, 120 (1975).
- (11) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969, p 63.
- (12) T. Durkin, J. Glorie, and L. DeHayes, *J. Chem. Educ.*, 48, 452 (1971).
- (13) G. A. Anderson and J. J. Lagowski, *Inorg. Chem.*, 10, 1910 (1971).
- (14) J. W. Wiggins and G. E. Ryschewitsch, *Inorg. Chim. Acta*, 4, 33 (1970).
- (15) A. F. Wells, "Structural Inorganic Chemistry", 3rd ed, Oxford University Press, London, 1962, p 357.
- (16) K. B. Wiberg and G. M. Lampman, *J. Am. Chem. Soc.*, 88, 4429 (1966).
- (17) H. Nöth and P. Fritz, *Z. Anorg. Allg. Chem.*, 324, 270 (1963).
- (18) O. T. Beachley, Jr., and K. C. Racette, *Inorg. Chem.*, 14, 2534 (1975).
- (19) B. Swanson, D. F. Shriver, and J. A. Ibers, *Inorg. Chem.*, 8, 2182 (1969).

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## Field Desorption Mass Spectrometry of Inorganic Compounds

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Field desorption mass spectrometry has drawn much interest in recent years as a means to ionize and mass analyze non-volatile and thermolabile organic compounds.<sup>1</sup> This technique may, however, have interesting applications in the field of

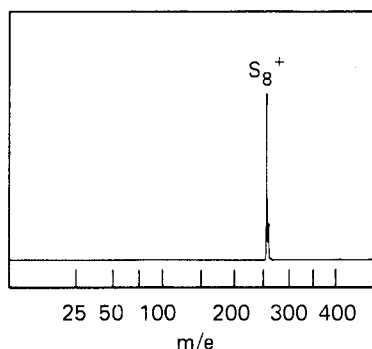


Figure 1. Field ionization spectrum of sulfur (PVA), 105 °C.

inorganic chemistry. First, it is a mild ionizing technique that is applicable at low temperatures (<150 °C), unlike electron impact on inorganic materials evaporated from a Knudsen cell or contact ionization, which are both seldom carried out at temperatures below 1000 °C. Because ionic materials can be mass analyzed at low temperatures, many molecular ionic species can be observed whose existence cannot be directly demonstrated by other means.

We have recently developed a field desorption ionization source based on the structure of one of the Stanford Research Institute multipoint ionization sources.<sup>2</sup> The field desorption or field ionization takes place from a rough surface of a thin (1.6 mm) metal rod (25 mm long) held in a special holder. These rods are generally freshly broken tungsten  $1/16$ -in. rods produced by notching a stock rod. Similar results have been obtained, however, with broken titanium rods as well as with cut iron wire, sharpened to a truncated cone followed by etching in HCl. These field ionizing-field desorbing surfaces are much simpler to produce than the carbonaceous dendrites slowly grown on heated tungsten wire<sup>1</sup> or the multipoint structure formed by vacuum deposition.<sup>3</sup>

This note presents field desorption spectra of inorganic species obtained in a series of preliminary experiments and points out potential applications of this technique to research problems in inorganic chemistry.

### Experimental Section

The ionization source and the sample preparation and insertion techniques have been described elsewhere.<sup>2</sup> The mass analyzer used was a low-resolution 45°, 20-cm radius, sector magnet operated in a manual scanning mode. The detector was an electron multiplier operated in the counting mode, using a count-rate meter to record the spectra as a function of a voltage signal obtained from a Hall-type magnetometer probe.

### Results and Discussion

Ionic materials can be field desorbed in ionic form from microcrystalline deposits on top of highly curved metal surfaces. Ions can also be desorbed from a dissolved state when such a solution is placed on the ionizing surface. We have shown that reproducible spectra are obtained from solution of inorganic species in poly(vinyl alcohol) (PVA).<sup>2</sup> This polar polymer, which may melt or soften at 100–150 °C, acts as a matrix in which the inorganic solute may migrate and field desorb in the regions of highest field strength. This process of field desorption (FD) should be distinguished from field ionization (FI), in which field-induced distortions of the potential surfaces of a given neutral molecule allow its ionization by electron tunneling.<sup>4–6</sup> The latter process results in the formation of unfragmented molecular ions (see, for instance, the FI spectra of sulfur as  $S_8^+$  in Figure 1). Field desorption, on the other hand, desorbs existing ions or ion clusters. Positive or negative<sup>7</sup> ions can be described in this manner. This paper discussed the case of positive ion desorption.

Figure 2 demonstrates this in the cases of potassium fluoride

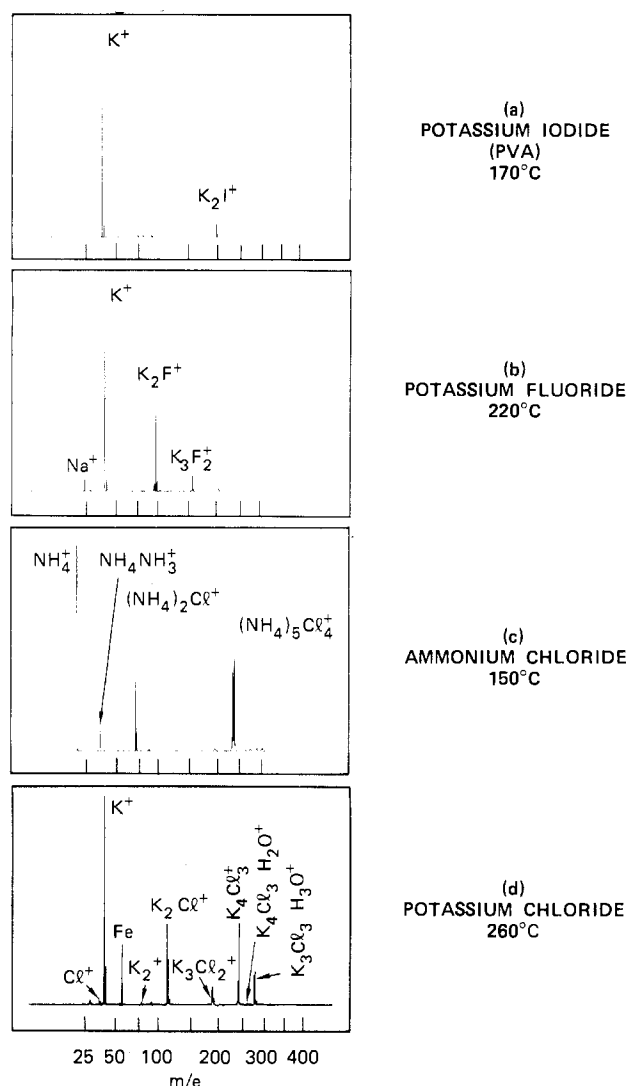


Figure 2. Field desorption spectra: (a) potassium iodide (PVA), 170 °C; (b) potassium fluoride, 220 °C; (c) ammonium chloride, 150 °C; (d) potassium chloride, 260 °C.

and potassium iodide where only  $K^+$ ,  $K_2X^+$ , and  $K_3X_2^+$  are observed. In the case of pure undissolved ammonium chloride in Figure 2(c), we observe  $(NH_4)_5Cl_4^+$  as a predominant species. Similarly,  $KCl(aq)$  in pure form has been shown to form  $K_2Cl^+$ ,  $K_3Cl_2^+$ ,  $K_3Cl_3H_3O^+$ ,  $K_4Cl_3^+$ , and  $K_4Cl_3H_2O^+$ , as shown in Figure 2(d). These spectra are different in character from that of those volatile halides, e.g.,  $HgCl_2$ , which yielded under our conditions solely the  $HgCl_2^+$  ion. The parent ion is evidently produced here by field ionization just like any other volatile compound. Under electron impact, we would observe in this case substantial fragmentation, i.e.,  $HgCl^+$  and  $Cl^+$ .<sup>8</sup> The hydrated ions formed by field desorption should also be distinguished from solvated inorganic ions formed in the gas phase at elevated pressures,<sup>9</sup> since our substrate is maintained at a pressure <math>10^{-6}</math> Torr.

Both FI and FD may take place simultaneously as we can see in the case of the ionization of lithium iodide in Figure 3(a). Here we observe  $I^+$  ions, which probably have been formed by a charge transfer  $I^- \rightarrow I$  followed by field ionization of I atoms. It is also possible that  $I^+$  is formed directly from the field ionization of the  $LiI$  ion pair. The latter process, which took place to some extent in the case of  $KCl$  in Figure 2(d), was predominant for a more concentrated solution of  $KBr$  in PVA, Figure 3(b). For sodium iodide, Figure 3(c), we observe the formation of a high yield of  $Na_2^+$  ions, possibly

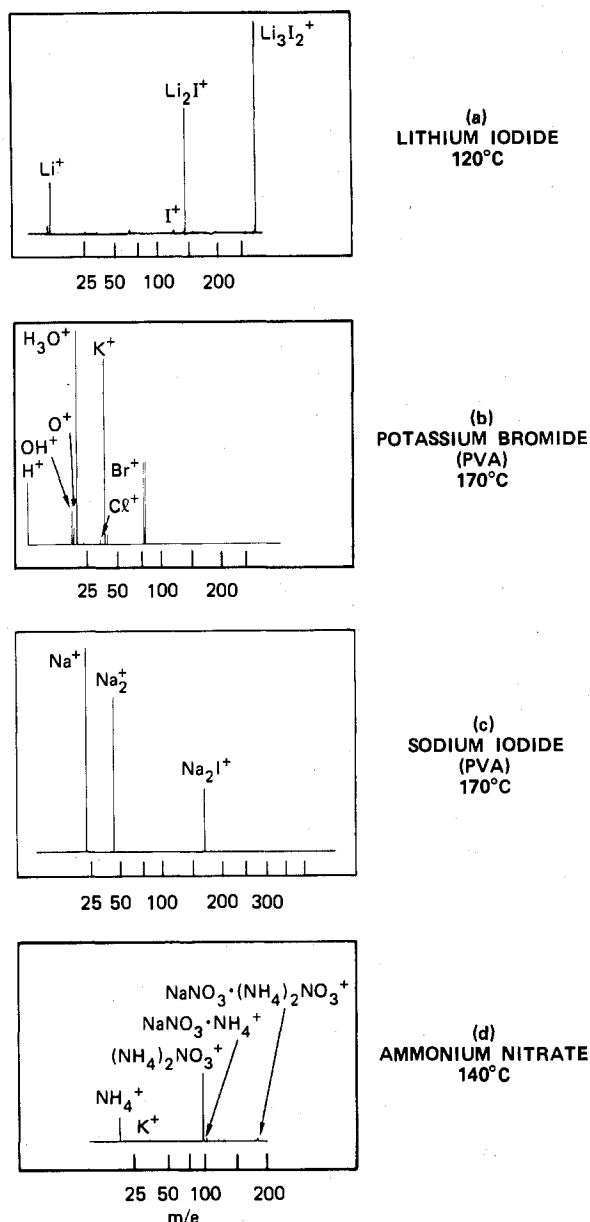


Figure 3. Field desorption spectra: (a) lithium iodide, 120 °C; (b) potassium bromide (PVA), 170 °C; (c) sodium iodide (PVA), 170 °C; (d) ammonium nitrate, 140 °C.

formed by the decomposition of  $\text{Na}_2\text{I}^+$  to  $\text{Na}_2^+$  + I. A small yield of  $\text{K}_2^+$  was also observed for pure KCl, Figure 2(d).

The spectrum of ammonium nitrate, Figure 3(d), shows, in addition to  $(\text{NH}_4)_2\text{NO}_3^+$ , some  $\text{Na}(\text{NH}_4)\text{NO}_3^+$  and  $\text{Na}(\text{NH}_4)_2(\text{NO}_3)_2^+$ . This clustering takes place in the solid phase at low temperatures and should be distinguished from dimeric ionized inorganic species ionized in the gas phase. In a field desorption spectrum of NaOH, not included in the figures, the predominant species was  $\text{Na}_2\text{OH}^+$ , which is also predominant in the vapor-phase electron impact ionization;<sup>11</sup> however, in our case this species was formed at 100 °C as a result of field desorption, since no  $\text{NaOH}^+$  or  $\text{Na}_2(\text{OH})^+$  was observed, and not as a fragmentation product of  $\text{Na}_2(\text{OH})_2$  at elevated temperatures.

These spectra are very preliminary data but are useful to demonstrate the types of species that can be produced under field desorption conditions. No attempt was made to determine quantitatively the relative yields of the ions formed, since the spectra were hand scanned, nor was a systematic study made of the effects of concentration and temperature on the nature

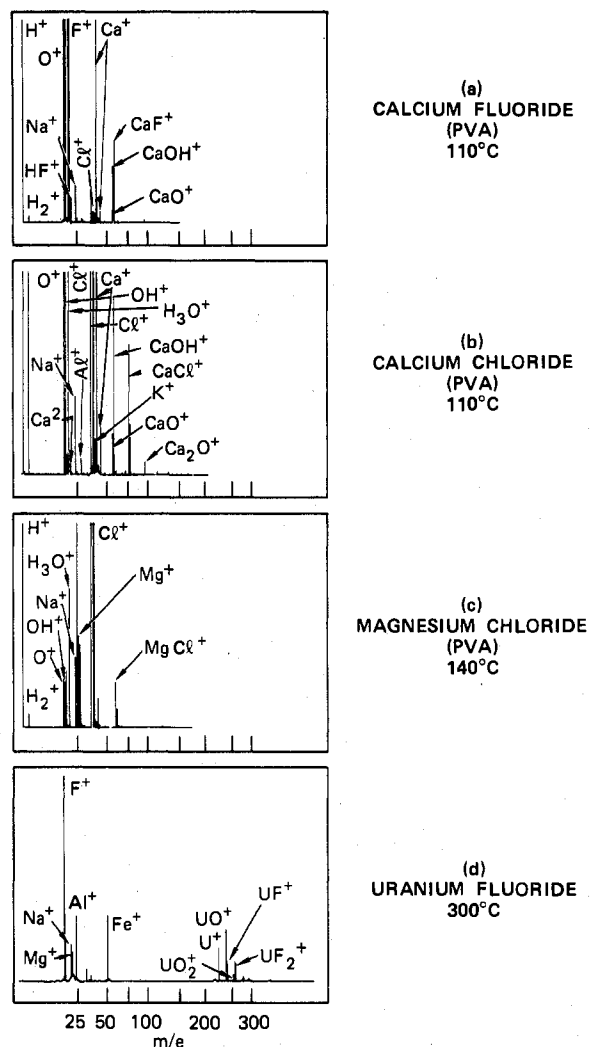


Figure 4. Field desorption: (a) calcium fluoride (PVA), 110 °C; (b) calcium chloride (PVA), 110 °C; (c) magnesium chloride (PVA), 140 °C; (d) uranium fluoride, 300 °C.

of the FD spectrum. The most important conclusion that can be reached even at this early stage is that we can now produce individual ionic species that have previously been merely postulated from the behavior of solution chemistry or derived from x-ray diffraction studies on crystalline materials.

The next group of spectra to be considered are those of polyvalent cations. Figure 4(a), (b), and (c) shows spectra of  $\text{CaF}_2$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$ , respectively. The Ca salts show a relatively high yield of  $\text{Ca}(\text{OH})^+$  and  $\text{CaO}^+$  and even of  $\text{Ca}_2\text{O}^+$  in addition to  $\text{Ca}^+$ ,  $\text{CaF}^+$ , and  $\text{CaCl}^+$ ; there is also a high yield of the halogen cations  $\text{F}^+$  and  $\text{Cl}^+$ , possibly formed by decomposition of  $\text{CaF}^+$  and  $\text{CaCl}^+$ , respectively. The yield of  $\text{Na}^+$  and even  $\text{K}^+$ , present as trace impurities, is relatively high, suggesting a higher relative mobility of the monovalent ions as the cause. The occurrence of reactions of the type  $\text{CaCl}^+ + \text{Na}^+\text{Cl}^- \rightarrow \text{CaCl}_2 + \text{Na}^+$  could be another mechanism for formation of  $\text{Na}^+$ . It should be noted that the FD technique facilitates the mass spectrometry of highly refractory materials like  $\text{CaF}_2$  without difficulty.

The spectrum of uranium tetrafluoride,  $\text{UF}_4$ , deposited in an aqueous slurry onto the field-desorbing surface, Figure 4(d), was obtained at a much higher temperature and at higher field strengths than the previous spectra. We see here substantial reduction of the uranium from the 4+ state ( $\text{UF}_2^+$ ,  $\text{UO}^+$ ,  $\text{UF}^+$ , and  $\text{U}^+$ ) and the appearance of an oxidized  $\text{UO}_2^+$  in a relatively high yield. The field emission and negative ion bombardment from the counterelectrode<sup>2</sup> under the experi-

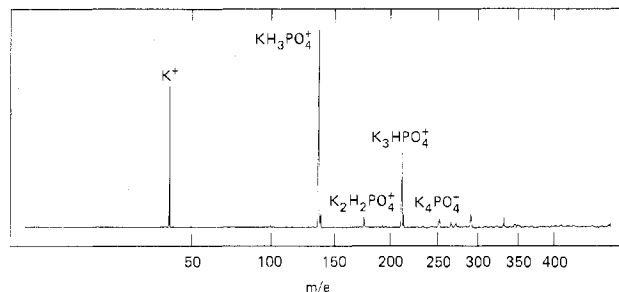


Figure 5. Field desorption spectrum of potassium dihydrogen phosphate, 306 °C.

mental conditions result in the formation of  $\text{Al}^+$  and  $\text{Fe}^+$  ions from the cathode surface, in addition to  $\text{Na}^+$  and  $\text{Mg}^+$  ions present as impurities. This spectrum, obtained at a higher field strength, is therefore not a pure field desorption spectrum but a composite of field desorption and ion bombardment. We may be observing here behavior similar to that observed under secondary ion mass spectrometry (SIMS).<sup>12,13</sup>

An FD spectrum of potassium phosphate, a material containing a polyvalent anion, is shown in Figure 5. Here we can identify, in addition to  $\text{K}^+$  ions,  $\text{KH}_2\text{PO}_4^+$ ,  $\text{K}_2\text{H}_2\text{PO}_4^+$ ,  $\text{K}_3\text{HPO}_4^+$ , and  $\text{K}_4\text{PO}_4^+$ . Analogously, the analysis of  $\text{K}_2\text{CO}_3$  showed only  $\text{K}_3\text{CO}_3^+$  ions in addition to  $\text{K}^+$ . In contrast, under electron impact one might observe a minute yield of  $\text{K}_2\text{CO}_3^+$ <sup>14</sup> but no  $\text{K}_3\text{CO}_3^+$ .

Again it should be emphasized that these are merely rudimentary illustrations of the type of chemistry that can be studied by field desorption mass spectrometry. Unlike classical electron impact mass spectrometry, which is highly useful in the study of the concentration and the structure of inorganic species in the gas phase, and in contrast to SIMS, which is highly useful in determining the elemental composition of thin solid layers, field desorption can teach us about the structure of inorganic solids. This technique could demonstrate nearest neighbor relations in solutions of inorganic materials and provide information on the relative stability of cluster ions. It could also indicate charge-transfer processes in solution, in addition to allowing the assessment of the isotopic composition of oxy anions,  $\text{PO}_4^{3-}$  in particular, using  $^{18}\text{O}$  as a tracer. The great number of possible applications of this technique and its potential as a novel research tool are the main reasons for bringing it this early to the attention of the inorganic chemistry research community.

**Registry No.** Potassium iodide, 7681-11-0; potassium fluoride, 7789-23-3; ammonium chloride, 12125-02-9; potassium chloride, 7447-40-7; lithium iodide, 10377-51-2; potassium bromide, 7758-02-3; sodium iodide, 7681-82-5; ammonium nitrate, 6484-52-2; calcium fluoride, 7789-75-5; calcium chloride, 10043-52-4; magnesium chloride, 7786-30-3; uranium fluoride, 10049-14-6; potassium dihydrogen phosphate, 7778-77-0.

## References and Notes

- H. D. Beckey and H. R. Schulten, *Angew. Chem., Int. Ed. Engl.*, **14**, 403 (1975).
- M. Anbar and G. A. St. John, *Anal. Chem.*, **48**, 198 (1976).
- C. A. Spindt, *J. Appl. Phys.*, **39**, 3504 (1968).
- H. D. Beckey, "Field Ionization Mass Spectrometry", Pergamon Press, Elmsford, N.Y., 1971.
- A. J. Robertson, *J. Phys. E.*, **7**, 321 (1974).
- M. Anbar and W. H. Aberth, *Anal. Chem.*, **46**, 59A (1974).
- M. Anbar and G. A. St. John, *J. Am. Chem. Soc.*, **97**, 7195 (1975).
- R. W. Kiser, J. G. Dillard, and D. L. Dugger, *Adv. Chem. Ser.*, No. **72**, 153 (1968).
- P. Kearnle, *Adv. Chem. Ser.*, No. **72**, 24 (1968).
- I. Lauder, C. Towler, and T. Wuth, *Adv. Mass Spectrom.*, **5**, 379 (1971).
- R. C. Schoonmaker and R. F. Porter, *J. Chem. Phys.*, **28**, 168 (1958).
- R. F. K. Herzog and F. P. Viehblock, *Phys. Rev.*, **76**, 855 (1949).
- C. A. Andersen, *Int. J. Mass Spectrom. Ion Phys.*, **2**, 61 (1969).
- L. N. Gorokhov and G. A. Semenov, *Adv. Mass Spectrom.*, **5**, 349 (1971).

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## Zerovalent Triarylstibine Complexes of Nickel, Palladium, and Platinum

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Although  $\text{Pd}(\text{PPh}_3)_4$ ,<sup>2</sup>  $\text{Pt}(\text{PPh}_3)_4$ ,<sup>3</sup> and  $\text{Ni}(\text{PPh}_3)_4$  have been known for some time, the nature of the species present in solution remained obscure until recently.<sup>5</sup> Tolman examined solutions of the  $\text{ML}_4$  complexes by  $^{31}\text{P}$  and  $^1\text{H}$  NMR and uv-visible spectroscopy. All observations are consistent with complete dissociation of the  $\text{ML}_4$  complexes to  $\text{ML}_3$  and  $\text{L}$  [ $\text{L} = \text{PPh}_3$ ,  $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ ]. Recent studies have reported a relationship between the steric requirements of the phosphine ligands and the degree of dissociation to  $\text{M}(\text{PR}_3)_3$  ( $\text{M} = \text{Ni}$ ,<sup>6,7</sup>  $\text{Pd}$ <sup>8</sup>). The  $\text{Ni}(0)$  complexes were categorized according to the degree of ligand dissociation and the rate of exchange, on the NMR time scale, between free and complexed ligands.

Unlike the triarylphosphine complexes, the zerovalent triarylstibine complexes of Ni, Pd, and Pt have not been extensively studied.  $\text{Ni}(\text{SbPh}_3)_4$  was reported by Wilke.<sup>9</sup>  $\text{Pd}(\text{SbPh}_3)_4$ , the only reported palladium complex, was prepared by the reaction of (acetylacetonato)[8-(acetylacetonyl)cyclooct-4-enyl]palladium with  $\text{Ph}_3\text{Sb}$ .<sup>10</sup> There are no literature references to  $\text{Pt}(\text{SbR}_3)_4$ . The mixed-ligand complexes  $\text{Pd}(\text{PPh}_3)_2(\text{SbPh}_3)_2$  and  $\text{Pt}(\text{PPh}_3)_3(\text{SbPh}_3)$  were formed from the reaction of excess  $\text{SbPh}_3$  with  $\text{Pd}(\text{PPh}_3)_4$  and  $\text{Pt}(\text{PPh}_3)_4$ .<sup>11</sup> All of the reported triarylstibine complexes are insoluble and thus do not lend themselves to solution studies. We therefore undertook the study of soluble zerovalent triarylstibine complexes in order to compare preparations, stabilities, and solution properties with those of the well-known phosphine analogues. This work is a continuation of our studies involving triarylstibine-transition metal complexes.<sup>12,13</sup>

## Experimental Section

All reactions were carried out in Schlenk apparatus. Solvents were dried prior to use. Manipulations of the compounds were carried out in an inert-atmosphere box or in Schlenk apparatus under argon. The complexes  $\text{Ni}(\text{COD})_2$ ,<sup>14</sup> ( $\text{COD} = 1,5\text{-cyclooctadiene}$ ),  $\text{Pd}(\text{PPh}_3)_4$ ,<sup>15</sup>  $\text{Pt}(\text{PPh}_3)_3$ ,<sup>16</sup> and  $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ <sup>17</sup> and the ligands  $\text{Sb}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$ ,<sup>18</sup>  $\text{Sb}(p\text{-CH}_3\text{OC}_6\text{H}_4)_3$ ,<sup>18</sup> and  $\text{Sb}(\text{SPh})_3$ <sup>19</sup> were prepared by literature methods. Analytical data are given in Table I. Preparations are shown in Figure 1.

(a) **Preparation of  $\text{Ni}(\text{SbR}_3)_4$  ( $\text{R} = \text{Ph}$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{OC}_6\text{H}_4$ ), Method I.**  $(\text{CH}_3\text{CH}_2)_3\text{Al}$  (0.50 ml, 0.46 mmol) was added slowly in a Schlenk filtration apparatus to a dried and deaerated diethyl ether solution (30 ml) of  $\text{Ni}(\text{acac})_2$  (0.5 g, 0.19 mmol) and  $\text{SbR}_3$  (0.80 mmol) at 0°C. A yellow crystalline material precipitated ( $\text{R} = \text{Ph}$ ). For the more soluble complexes ( $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{OC}_6\text{H}_4$ ), the solution was reduced in volume to ca. 15 ml and 10 ml of hexane was added, inducing the precipitation of an off-white solid. The complexes were collected by filtration, washed with hexane, and dried under vacuum; yield ca. 75%.

(b) **Preparation of  $\text{Ni}(\text{SbR}_3)_4$  ( $\text{R} = \text{Ph}$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{OC}_6\text{H}_4$ ), Method II.** A solution of  $\text{SbR}_3$  (0.15 mmol) was added slowly to a benzene solution (20 ml) of  $\text{Ni}(\text{COD})_2$  (0.10 g, 0.036 mmol) in a Schlenk filtration apparatus. Further work-up was identical with that described in section a.

(c) **Preparation of  $\text{Pd}(\text{SbR}_3)_4$  ( $\text{R} = \text{Ph}$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ,  $p\text{-CH}_3\text{OC}_6\text{H}_4$ ).**  $(\text{CH}_3\text{CH}_2)_3\text{Al}$  (0.21 ml, 0.20 mmol) was added slowly in a Schlenk filtration apparatus to a dried and deaerated diethyl ether solution (30 ml) of  $\text{Pd}(\text{acac})_2$  ( $\text{acac} = \text{acetylacetonate}$ ) (0.25 g, 0.08 mmol) and  $\text{SbR}_3$  (0.34 mmol) at 0°C. The yellow solution was stirred at 0°C for 1 hr. Further work-up was identical with that described in section a.

(d) **Preparation of  $\text{Pd}(\text{PPh}_3)_2(\text{SbR}_3)_2$  ( $\text{R} = \text{Ph}$ ,  $p\text{-CH}_3\text{C}_6\text{H}_4$ ), Method I.** A benzene solution (10 ml) of  $\text{SbR}_3$  (0.086 mmol) was added dropwise to a suspension of  $\text{Pd}(\text{PPh}_3)_4$  (0.25 g, 0.022 mmol)