Adducts of Dimethylselenium Dichloride and Trimethylamine

By Kenneth J. Wynne and John W. George

Interest in the Lewis acid–base characteristics of dimethylselenium dichloride, $(CH_3)_2SeCl_2$[1] (I), has prompted the examination of the behavior of I toward the strong base trimethylamine, $N(CH_3)_3$.

Experimental

Materials.—Dimethyl selenide, prepared according to the method of Bird and Challenger,[2] was treated with gaseous Cl_2 in CCl_4 solution. Recrystallization of the product of this reaction from CCl_4 gave a solid, m.p. $61.0 \pm 0.5°$. *Anal.* Calcd. for $(CH_3)_2SeCl_2$: Se, 43.8; Cl, 39.4. Found: Se, 42.8; Cl, 39.2. Trimethylamine, Eastman White Label, was dried over sodium prior to use.

Methods.—Standard vacuum line procedures were used. Unreacted $N(CH_3)_3$ was removed from reaction systems containing an excess of this material by volatilization from the reaction site and condensation in a liquid N_2 cooled trap. Sufficient time was allowed in the removal of excess $N(CH_3)_3$ to bring the sample to constant weight. In a typical observation 5.5 mmoles of I was mixed with 20.9 mmoles of $N(CH_3)_3$ at $-85°$ and the mixture equilibrated for 30 hr.; 18.2 mmoles of unreacted $N(CH_3)_3$ was removed by opening the reaction system to a trap at $-195°$; adduct composition was then calculated. Contact of the adduct with excess $N(CH_3)_3$ for longer periods gave no further significant uptake of $N(CH_3)_3$ at $-85°$ (see Figure 1).
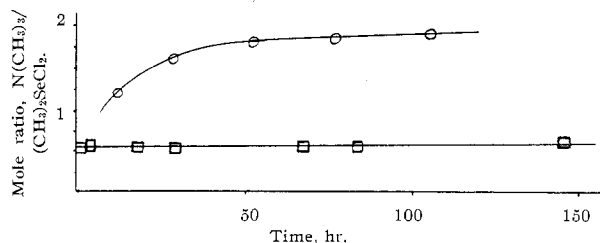

Figure 1.—Moles of trimethylamine reacted per mole of dimethylselenium dichloride as a function of time: —□—, $-85°$; —○—, $-45°$.

Decomposition products were identified by infrared spectroscopy techniques and by general physical properties. Dissociation pressure measurements were made using a Gaertner M911 cathetometer.

Results

At $-85°$ the condensation of excess $N(CH_3)_3$ with a known amount of I yields an adduct of composition $2(CH_3)_2SeCl_2 \cdot N(CH_3)_3$ (II). By careful warming and continuous collection of evolved $N(CH_3)_3$ in a trap at $-195°$ II may be reversibly decomposed to the starting materials. When II is warmed above $-10°$ without continuous removal of $N(CH_3)_3$ the products are tetramethylammonium chloride, methyl chloride, elementary selenium, and small amounts of a yellow oil having the characteristic odor of dimethyl diselenide. That

$N(CH_3)_3$ plays an important role in this decomposition is indicated by the observation that I alone is stable to its melting point $(61°)$, above which it decomposes slowly to elementary Se and CH_3Cl. Dissociation pressures, 3.9 mm. at $-63.5°$, 16.3 mm. at $-49.8°$, and 26.3 mm. at $-45.2°$, enable the calculation of a ΔH of $+9.7 \pm 1$ kcal. for the process

$$2(CH_3)_2SeCl_2 \cdot N(CH_3)_3(s) \rightleftharpoons 2(CH_3)_2SeCl_2(s) + N(CH_3)_3(g)$$
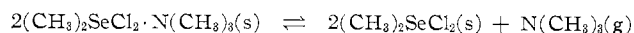
At $-45°$, however, the reaction of $N(CH_3)_3$ and I proceeds extremely slowly. A plot of the mole ratio of reacted $N(CH_3)_3$ to $(CH_3)_2SeCl_2$ *vs.* time (Figure 1) suggests an adduct having a limiting composition of $(CH_3)_2SeCl_2 \cdot 2N(CH_3)_3$ (III) at $-45°$. This species has an immeasurably small dissociation pressure at $-45°$ (the dissociation pressure of II at $-45°$ is 26 mm.) and begins to decompose irreversibly and slowly at $-23°$ as evidenced by the presence of a 1 mm. pressure of CH_3Cl over the solid. When III is allowed to decompose completely above $-10°$, the products are the same as those formed in the decomposition of II, plus $N(CH_3)_3$. When II was held at $-35°$ for 30 hr. the dissociation pressure was observed to undergo a pronounced decrease.

Discussion

The dissociation pressure data for II and III at $-45°$ indicate II to be metastable with respect to III at this temperature; thus, a slow conversion of II into the more stable III is expected. The decline in dissociation pressure of II on standing at $-35°$ is consistent with an over-all reaction represented by

$$2[2(CH_3)_2SeCl_2 \cdot N(CH_3)_3] \rightarrow$$
$$(CH_3)_2SeCl_2 \cdot 2N(CH_3)_3 + 3(CH_3)_2SeCl_2$$
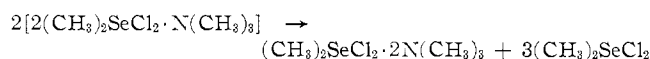
The possible existence of other metastable adduct composition at temperatures intermediate between -85 and $-45°$ cannot be excluded.

The thermal instability of these adducts and our failure to find suitable solvents for them at low temperatures have prevented the acquisition of data appropriate to the formulation of structures for these materials. However, the recent proposal[3] of di(pyridine)trichloroselenium(IV) chloride, $[SeCl_3py_2]^+Cl^-$, for the $SeCl_4 \cdot 2py$ adduct prompts for III a corresponding ionic formulation, $\{SeCl(CH_3)_2[N(CH_3)_3]_2\}^+Cl^-$.

Speculation regarding the structure of II leads to two possibilities. The results of X-ray crystallographic examination of dimethyltellurium dichloride,[4] $(CH_3)_2TeCl_2$, indicate a very weak polymerization of molecules of this substance *via* halogen bridges. Assuming a similar crystalline arrangement holds for I, the bonding of a trimethylamine molecule to a selenium atom could lead to the observed stoichiometry of the adduct if a second molecule of I were joined to the first by a single chlorine bridge. The resulting species would be similar

(1) C. L. Jackson, *Ann.*, **179**, 1 (1875).
(2) M. L. Bird and F. Challenger, *J. Chem. Soc.*, 570 (1942).
(3) A. W. Cordes and T. V. Hughes, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.
(4) G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *Acta Cryst.*, **11**, 782 (1958).

to those proposed for such 1:2 adducts as py·2BF₃ and (C₂H₅)₃N·2BF₃.[5]

A second, perhaps less attractive, formulation involves the possible utilization of the unshared electron pair on one selenium atom in bonding to the selenium atom of an adjacent molecule. The formation of an N→Se bond by interaction of trimethylamine with I would aid in making the unshared pair associated with the selenium atom more available for coordinate bond formation. Such an arrangement would present the rather unusual situation of simultaneous Lewis acid and Lewis base behavior by the same species in an addition compound.

In any of the formulations suggested here a total of six electron pairs, bonding plus nonbonding, are disposed about each selenium atom. In light of the existence of ions such as $SeCl_6^{2-}$ and $SeBr_6^{2-}$, structures involving seven electron pairs should not be excluded from consideration. Thus, for III, a nonionic arrangement, $\{SeCl_2(CH_3)_2[N(CH_3)_3]_2\}$, can be written, and for II a combination of the ions $[Se(CH_3)_3]^+$ and $\{SeCl_4(CH_3)[N(CH_3)_3]\}^-$ would meet the stoichiometric requirements.[6]

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(5) H. C. Brown, P. F. Stehle, and P. A. Tierney, *J. Am. Chem. Soc.*, **79**, 2020 (1957).

(6) We are grateful to a referee for this suggestion.

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Some Spectral Evidence for the Dioxodifluoroiodate Group and Structure of IO₂F·AsF₅

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The compound $IO_2F \cdot AsF_5$ was first obtained by Schmeisser and Lang[1] and formulated by them as $IO_2^+ AsF_6^-$. Aynsley and Sampath[2] suggested the compound was more likely $AsF_4^+ IO_2F_2^-$ in view of the isolation of $K^+ IO_2F_2^-$ by Helmholz and Rogers.[3] The identification of one of the ionic species involved would resolve the question.

The preparation of KIO_2F_2 and $AgIO_2F_2$ and subsequent characterization by infrared spectroscopy provided us with the necessary tool. We obtained the infrared absorption band for the $IO_2F_2^-$ group and were able to differentiate between the presence of this group or the AsF_6^- group in the compound $IO_2F \cdot AsF_5$.

(1) M. Schmeisser and K. Lang, *Angew. Chem.*, **67**, 156 (1955).

(2) E. Aynsley and S. Sampath, *J. Chem. Soc.*, 3099 (1959).

(3) L. Helmholz and M. T. Rogers, *J. Am. Chem. Soc.*, **62**, 1537 (1940).

The known dioxodifluoroiodate salts include those of Na, K, Rb, Cs, and NH₄ prepared by the method of Weinland, Lauenstein, and Köppen[4,5] from aqueous hydrofluoric acid. We have synthesized AgIO₂F₂ by the reaction of silver iodate with anhydrous liquid hydrogen fluoride. In an alternate procedure, AgIO₂F₂ was obtained in a double replacement reaction with KIO₂F₂ and AgHF₂ in anhydrous liquid hydrogen fluoride.

The reaction of KIO_2F_2 and AsF_5 in anhydrous liquid hydrogen fluoride first precipitates $KAsF_6$, leaving in effect "IO₂F dissolved in the hydrogen fluoride solvent." Further reaction between this solution and AsF₅ yielded the desired product $IO_2F \cdot AsF_5$.

Experimental

Potassium Dioxodifluoroiodate(V).—KIO_2F_2 was prepared by the method of Weinland, Lauenstein, and Köppen[4,5] by allowing a solution of 35 g. of potassium iodate dissolved in approximately 75 ml. of 48% aqueous hydrofluoric acid to evaporate over a 2-day period. The remaining few milliliters of solvent was decanted off and the white crystalline product washed with anhydrous ethyl ether to remove the last traces of solvent. Finally the product was dried in a stream of dry nitrogen.

A yield of 38 g., or 98.5% based on starting potassium iodate, was obtained. On heating, the product decomposed above 295° evolving iodine vapor.

The infrared spectrum of a Nujol mull of the product (see Figure 1) showed distinctive absorption bands at 855 (s), 847 (s),
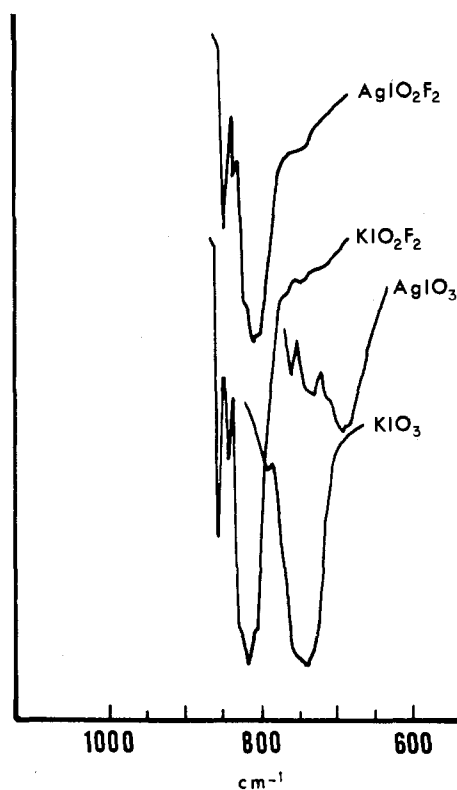

Figure 1.—Infrared absorption spectra of potassium and silver dioxodifluoroiodate compared to potassium and silver iodate.

820 (vs), and 722 (w) cm.⁻¹. Characteristic peaks for potassium iodate at 800 (w) and 746 (vs) cm.⁻¹ were completely absent.

(4) R. F. Weinland and O. Lauenstein, *Z. anorg. allgem. Chem.*, **20**, 30 (1899).

(5) R. F. Weinland and O. Köppen, *ibid.*, **22**, 256 (1900).