Figure 2. Proton nmr spectrum of a 1.4 M solution of dimethyl-cadmium in tetrahydrofuran saturated with cadmium bromide at $-110°$. The highest peak marked 4 is at about 52 ± 2 cps upfield from tetramethylsilane.

Figure 1. Experimental and calculated proton nmr spectra for a neat sample of dimethylcadmium. The experimental spectra were taken on a Varian A56/60 spectrometer with the temperatures calibrated by the temperature dependence of the chemical shift of the ethylene glycol hydroxyl proton. The spectra on the right were drawn by a Calcomp plotter connected to an IBM 360/75 computer using the program GMW.[8] The spectrum may be calibrated by knowing that the distance between the outer satellites corresponds to 103.6 Hz.

case may be. Actually, detection of intermolecular exchange of methyl groups in dimethylcadmium is relatively easy because of the spectral changes which occur as the result of such exchange on the ^{111}Cd-C-H and ^{113}Cd-C-H spin-spin couplings. The isotopes ^{111}Cd (12.9%) and ^{113}Cd (12.3%) each have spin $^1/_2$ while the other abundant cadmium isotopes, mainly ^{112}Cd, have zero spin. The proton spectra in the absence of exchange therefore display five lines, the center line of which represents the molecules with cadmium having zero spin. Exchange of methyls proceeds between cadmium atoms in five nuclear states, $+^1/_2$ and $-^1/_2$ for ^{111}Cd and ^{113}Cd, and zero for the other isotopes, thereby providing a five-site random intermolecular exchange problem, the line shapes for which can be simulated by the procedure of Sack.[6]

A substantial sensitivity of the exchange to catalytic amounts of methylcadmium methoxide has been reported earlier[3,4] and was confirmed in this work. With considerable care in handling the sample by vacuum-line techniques, we achieved exchange rates comparable to those of Ham and coworkers[3] but not zero as has been suggested recently.[5] Experimental proton

spectra of neat dimethylcadmium as a function of temperature and theoretical spectra as a function of the lifetime τ are shown in Figure 1. The coalescence temperature corresponding to these spectra is about 100°, the activation energy E_a 15.7 $\pm$ 0.1 kcal/mol, and $\Delta S^{\ddagger}$ -9.8 ± 0.2 eu.[7] Both the activation energy and entropy are similar to the values reported for methyl exchange between dimethylcadmium and dimethylzinc[5] and suggest a similar mechanism for exchange.

The rate of exchange is very much increased in tetrahydrofuran, the coalescence temperature in 10% solution being $-10°$ with an E_a of 6.8 $\pm$ 0.1 kcal/mol and $\Delta S^{\ddagger}$ of -28.3 ± 0.4 eu. Cadmium bromide further increases the rate of exchange and it is probably significant in this connection that cadmium bromide is not very soluble in tetrahydrofuran unless dimethylcadmium is present. At $-110°$, solutions of dimethylcadmium in tetrahydrofuran saturated with cadmium bromide show proton resonances which correspond to methylcadmium bromide (Figure 2). The peaks 2, 4, and 5 in Figure 2 are assigned to dimethylcadmium and its Cd-C-H satellites with J of 52 Hz while 1, 3, and 6 are assigned to methylcadmium bromide and its Cd-C-H satellites with J of about 80 Hz. The large change in J in going from $(CH_3)_2Cd$ to CH_3CdBr has a parallel in similar mercury derivatives.[8] This spectrum provides the first clear evidence for a Schlenk-type equilibrium involving alkylcadmium compounds.

(7) For comparison with results reported by Ham and coworkers,[3] we assume toluene to be an inert solvent and the exchange rate $v = 1/\tau = k_1 [Cd(CH_3)_2]$. From this equation and Ham's data we estimate a mean lifetime of 0.007 $\pm$ 0.002 sec for neat dimethylcadmium at 120°. Extrapolation of our rate to 120° gives 0.004 sec which is in reasonable agreement considering the difference in the experimental conditions.

(8) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Long Island City, N. Y., 1966, pp 689–690.

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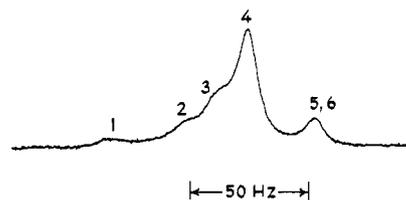
The Te_n^{n+} Cation

Sir:

In a recent communication[1] we showed that tellurium can be oxidized in strongly acidic media, *e.g.*, HSO_3F or oleum to the red cation Te_4^{2+} and that this cation could be further oxidized to a yellow species which was not at that time identified. We have now found that in solution in fluorosulfuric acid at room temperature,

(1) R. J. Gillespie, J. Barr, R. Kapoor, and G. P. Pez, *J. Amer. Chem. Soc.*, **90**, 6855 (1968).
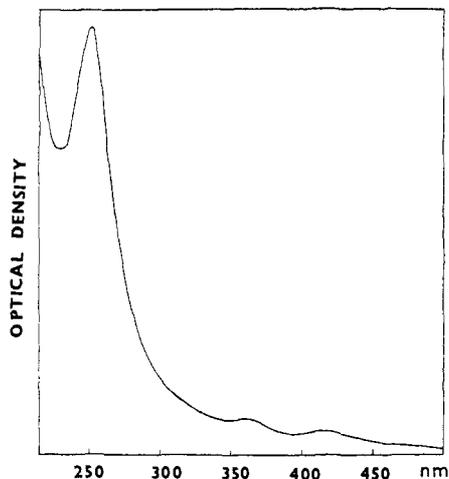
Figure 1. Absorption spectrum of the $Te_n{}^{n+}$ cation.

Figure 2. Freezing-point depressions for solutions of $TeSO_3F$ in fluorosulfuric acid: A, $Te_2{}^{2+}$; B, $Te_4{}^{4+}$; C, $Te_6{}^{6+}$; D, $Te_8{}^{8+}$; E, $Te_\infty{}^{+}$.

after making allowance for a small amount of oxidation of tellurium by the solvent to red $Te_4{}^{2+}$, 2.1 mol of $S_2O_6F_2$ was required to oxidize tellurium to the yellow species, which has a strong characteristic absorption at 250 nm and two very weak absorptions at 360 and 420 nm (Figure 1). On the basis of this result we conclude that tellurium is in the 1+ oxidation state in this species and is presumably either Te^+ or a polyatomic cation such as $Te_2{}^{2+}$, $Te_3{}^{3+}$, $Te_4{}^{4+}$, etc.

Antimony pentafluoride has been found to react with tellurium at $-23°$ in liquid sulfur dioxide to give a red sulfur dioxide-soluble product and a small amount of a yellow sulfur dioxide-insoluble product. The red compound was shown to be $Te_4{}^{2+}(Sb_2F_{11}{}^-)_2$. On heating the yellow compound at approximately $100°$ a white sublimate of SbF_3 was obtained. After all the SbF_3 had sublimed off the remaining material had an analysis corresponding to the formula $TeSbF_6$. The infrared spectrum of the compound showed the characteristic $SbF_6{}^-$ peak at 699 cm^{-1} and a solution in HSO_3F-SbF_5 had the characteristic absorption spectrum of the tellurium(1+) species shown in Figure 1.

Reaction of tellurium with excess sulfur trioxide at room temperature for several days gave a yellow compound, which after removal of excess SO_3 had an analysis corresponding to the composition $Te_2S_3O_{10}$. A solution of this compound in 30% oleum gave an identical spectrum to that shown in Figure 1. Both solid materials and their solutions in acid had a characteristic strong Raman frequency at 199 cm^{-1}. The compositions of these compounds confirm that tellurium is in the 1+ oxidation state. Magnetic measurements showed that the cation is diamagnetic. Presumably, therefore, odd electron species such as Te^+ and $Te_3{}^{3+}$ can be ruled out and the most likely possibilities would appear to be $Te_2{}^{2+}$, $Te_4{}^{4+}$, $Te_6{}^{6+}$, or $Te_8{}^{8+}$. Determination of the exact molecular weight of this new tellurium cation has proved difficult. It was found that if tellurium was oxidized by $S_2O_6F_2$ in solution in HSO_3F at $-23°$ no oxidation of tellurium to the red $Te_4{}^{2+}$ by the solvent occurred, and a quantitative reaction between 2 mol of tellurium and 1 mol of $S_2O_6F_2$ gave a dark yellow-brown solution, which on addition of sulfur dioxide precipitated a bright yellow compound. Unfortunately this compound was not stable above $-75°$ but we presume that it is Te-
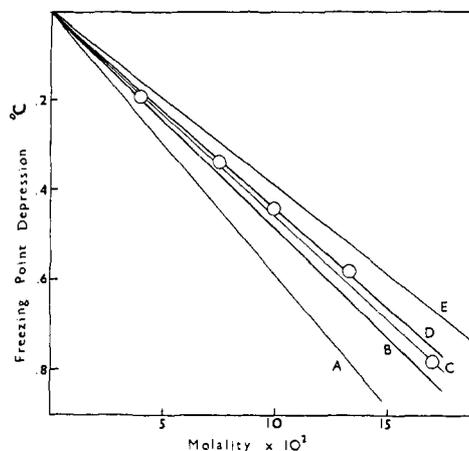
SO_3F. It was however found possible to make some freezing-point depression measurements on solutions of this compound in HSO_3F. The results are compared with calculated curves for $Te_2{}^{2+}$, $Te_4{}^{4+}$, etc., in Figure 2. It is clear that the ion cannot be $Te_2{}^{2+}$, but the scatter of the experimental results resulting from the considerable experimental difficulties associated with these measurements and the small differences between the freezing-point depressions produced by the higher polymeric species make it difficult to distinguish between the various possibilities such as $Te_4{}^{4+}$, $Te_6{}^{6+}$, and $Te_8{}^{8+}$. The results in Figure 2 agree best with the octameric formulation $Te_8{}^{8+}$ for which it would appear reasonable to propose the interesting cubic structure I. However, the other possibilities $Te_4{}^{4+}$ and $Te_6{}^{6+}$ cannot be ruled out. On the assumption that these clusters contain normal two-electron bonds they would be expected to have tetrahedral and trigonal prism structures, respectively (II and III). $Te_4{}^{4+}$ is isoelectronic with tetrahedral P_4.

Studies of the vibrational spectra and attempts to obtain X-ray crystallographic data on the compounds continue in order to obtain definite structural information on this novel cation.
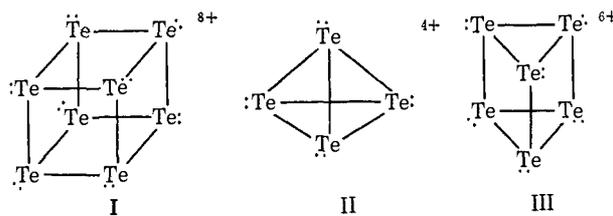
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Solvolysis Reaction of Triarylhaloallenes

Sir:

The current interest in vinyl cations derived from solvolysis reactions is indicated by the flurry of publications in this area in recent months. The substrates