reaction points to a more tight and stabilized transition state in this reaction.³

When considering the bonding of the transition state as a three-centre four-electron type,¹⁰ the overlap of the single *p* orbital of the electrophilic centre with the orbitals of the incoming cyanide ion and the outgoing thiosulfate ion, thus appears to be most favourable for the selenium atom.

Experimental. Acetonitrile and tetraphenylphosphonium cyanide were purified as reported.³

Tetraphenylarsonium telluropentathionate was precipitated from an aqueous solution of sodium telluropentathionate¹¹ by means of tetraphenylarsonium chloride in nearly quantitative yield. The purification was performed in the same way as reported for the analogous pentathionate salts.³ Dec. 230 °C. (Found: C 52.18; H 3.79; S 12.26. Calc for C₄₈H₄₀O₈S₄TeAs₂: C 51.55; H 3.58; S 11.49).

The rate of the reaction was determined by measuring the formation of ionic thiocyanate or tellurocyanate by applying IR.³ The kinetic plots were analysed according to the second-order rate equation,

$$dx/dt = k_2(a-x)(b-6x)$$

where *x* is the concentration of ionic thiocyanate (tellurocyanate), and *a* and *b* are the initial concentrations of ionic telluropentathionate and cyanide, 2.50×10^{-3} M and 1.50×10^{-2} M, respectively. The rate constants were reproduced with an accuracy better than $\pm 4\%$.

Iodometric determination of ionic thiosulfate was performed as reported.³ The yield was 96–97 %, based on the amount of reacted telluropentathionate.

From conductivity measurements of tetraphenylarsonium telluropentathionate in acetonitrile at 25 °C, the equivalent conductivities at infinite dilution were found to be:

$$\lambda^\circ[(\text{Ph}_4\text{As})_2\text{TeS}_4\text{O}_6] = 173 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1},$$

$$\lambda^\circ[\text{TeS}_4\text{O}_6^{2-}] = 61.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

From the plot, λ versus $\sqrt{c}$, the salt appeared to be completely dissociated in the concentration range used in the kinetic runs.

The IR measurements were performed on a SP 200 G Infrared Spectrophotometer using 1 mm liquid cells.

The conductivity measurements were performed on a conductivity meter type CD M3 with a conductivity cell, type CDC 304 (immersion type) with a cell constant $1.00 \text{ cm} \pm 10\%$.

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The Systems $\text{BF}_3\text{—H}_2\text{O}$ and $\text{SbCl}_5\text{—H}_2\text{O}$ in Acetone and Methylene Chloride as Solvents

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Bernander and Olofsson have recently reported a study of the $\text{H}_2\text{O—SbCl}_5$ adduct system in methylene chloride by ^1H NMR.¹ They interpret their results in terms of the formation of a 1:1 adduct $\text{SbCl}_5\cdot\text{H}_2\text{O}$, and a 1:2 adduct $\text{SbCl}_5\cdot 2\text{H}_2\text{O}$ in which the second water molecule is more weakly held. They also measured the ^1H chemical shift of a solution of $\text{BF}_3\cdot\text{H}_2\text{O}$ in CH_2Cl_2 . In discussing their results they make a comparison with our earlier work on the $\text{BF}_3\text{—H}_2\text{O}$ system in solution in acetone² and they claim that two of the main conclusions of our work are incorrect.

Bernander and Olofsson draw attention to the large difference in the chemical shift between that which we observed for $\text{BF}_3\cdot\text{H}_2\text{O}$ in acetone ($\delta=12.46$) and that which they observed in CH_2Cl_2 ($\delta=8.2$) and they claim that it is probable that we were not observing the $\text{BF}_3\cdot\text{H}_2\text{O}$ adduct but rather the $\text{BF}_3\cdot\text{acetone}\cdot\text{H}_2\text{O}$ ternary adduct. While it is clear that there must be hydrogen-bonded interaction between the protons of $\text{BF}_3\cdot\text{H}_2\text{O}$ and the acetone solvent this interaction is certainly much weaker than that between the BF_3 and the H_2O . The NMR spectra indicate for example

that there is rapid exchange between any such hydrogen bonded acetone molecules and the bulk of the solvent whereas the water molecule is firmly held. Such an interaction can be reasonably described as solvation and cannot be regarded as being in principle any different from the weaker interaction that presumably exists between $\text{BF}_3 \cdot \text{H}_2\text{O}$ and $\text{SbCl}_5 \cdot \text{H}_2\text{O}$ and the solvent CH_2Cl_2 . We were indeed fully aware of the possibility of ternary complexes and in fact we postulated the existence of the ternary complex $\text{F}_3\text{B} \cdot \text{OH}_2 \cdot \text{OH}_2$ in order to explain the rapid proton exchange that occurs in the presence of water in excess of the 1:1 composition. Moreover, in a subsequent paper³ we have discussed the $\text{BF}_3 \cdot \text{MeOH}$ and $\text{BF}_3 \cdot 2\text{MeOH}$ complexes and have proposed a structure for the 1:2 adduct involving a weak hydrogen bond between the first directly bonded molecule and the second methanol molecule. Our work on this system has subsequently been repeated and confirmed.⁴

Bernander and Olofsson also claim that our statement that "acetone is much inferior to water as an electron pair donor to BF_3 " is not corroborated by comparison of donor strengths towards SbCl_5 . However, at low temperatures in excess acetone the NMR spectra of both the $\text{acetone} \cdot \text{BF}_3$ and the $\text{H}_2\text{O} \cdot \text{BF}_3$ complex can be observed directly in the same solution and it is quite clear that the equilibrium

lies far to the right. Moreover, we observed proton-fluorine coupling in $\text{BF}_3 \cdot \text{H}_2\text{O}$ even in the presence of a large excess of acetone. Both of these observations clearly indicate that BF_3 is bonded to water much more strongly than to acetone and if a ternary complex does exist the primary bond must be between the BF_3 and a water molecule with the acetone molecule held weakly by hydrogen bonds to the water molecule. Bernander and Olofsson report thermochemical measurements demonstrating that SbCl_5 ester, SbCl_5 ketone, and SbCl_5 water complexes all have very similar stabilities and they make the assumption that this should also be true for the BF_3 adducts. Quite apart from the fact that this is inconsistent with our NMR results such an assumption is also not justified on the basis of previous work on the Lewis acidity of BF_3 with respect to different bases.⁵ Indeed it is a well known problem in comparing the strengths of Lewis acids and bases that there is no absolute scale of relative basicities that is valid for all Lewis acids. Ethers, ketones, and water need not have the same relative donor strengths with respect to BF_3 as they do with respect to SbCl_5 . There are examples of base strength reversal even between Lewis acids as similar as BF_3 and BCl_3 ,⁶ and it has been found that even the replacement of a single fluorine in BF_3 by a chlorine can have striking effects on Lewis acid properties.⁷

If Bernander and Olofsson's conclusion that water and acetone have similar base strengths towards SbCl_5 is correct then their results taken in conjunction with ours, which show that acetone is a much weaker base towards BF_3 than is water, demonstrate once again that one cannot establish a single consistent set of base strengths towards different Lewis acids and in particular towards BF_3 and SbCl_5 .

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A Simple Parameterfree Expression for the Activity Coefficient of Potassium Chloride in Water in the Range $0.1 \leq m \leq 4.8$

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The following expression¹ for the activity coefficient of a simple 1:1 electrolyte can be derived using in principle the same approach as that of Stokes and Robinson² but using the *molarity scale* instead of the molality scale used by them

$$\log \gamma_{\text{A}}\gamma_{\text{B}} = - \frac{2 \times 0.5115\sqrt{C}}{1 + Ba\sqrt{C}} - 2 \log \left[\frac{1}{a_0} \left\{ d + 0.001C(2 \times 18.015 - M_{\text{AB}}) \right\} \right] - \log S \quad (1)$$

$$\text{where } S = \sum K_n a_w^n \quad (2)$$