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Short Communications

Polythionates. III. The Reaction between the Telluropentathionate Ion and the Cyanide Ion in Acetonitrile

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In aqueous solution, according to Foss,[1] the telluropentathionate ion does not react with ionic cyanide. Instead, due to the alkalinity of the cyanide solution, a rapid and complete hydrolysis takes place, according to the reaction, eqn. 1:

$$2\,\mathrm{TeS_4O_6^{2-}} + 6\,\mathrm{OH^-} \xrightarrow{\mathrm{H_2O}} 4\,\mathrm{S_2O_3^{2-}} + \mathrm{Te} + \mathrm{TeO_3^{2-}} + 3\,\mathrm{H_2O} \tag{1}$$

If the telluropentathionate ion would react with the cyanide ion in the same way as the corresponding pentathionate and selenopentathionate reactions, reaction (2) should take place.

$$\mathrm{TeS_4O_6^{2-}} + 2\,\mathrm{CN^-} + 2\,\mathrm{OH^-} \xrightarrow{\mathrm{H_2O}} \mathrm{S_2O_3^{2-}} + \mathrm{SCN^-} + \mathrm{TeCN^-} + \mathrm{SO_4^{2-}} + \mathrm{H_2O} \tag{2}$$

Due to the instability of the tellurocyanate ion in protic solvents,[2] the telluropentathionate-cyanide reaction has been studied in the dipolar aprotic solvent acetonitrile, where we have found that ionic cyanide readily reacts with the telluropentathionate ion without any liberation of elemental tellurium.

This paper reports a kinetic investigation of this reaction in acetonitrile. This kinetic study appears to be the first one concerning nucleophilic substitution at divalent tellurium. Tetraphenylarsonium telluropentathionate was used as the substrate, and tetraphenylphosphonium cyanide was used as the nucleophilic reagent. Conductivity measurements in acetonitrile proved that these salts were completely dissociated in the concentration range used in the kinetic runs.

The reaction was found to be second order, first order in each of the reactants, and 1 mol of ionic telluropentathionate was found to consume 6 mol of cyanide ions. IR and iodometric measurements showed that 1 mol of ionic thiocyanate, 1 mol of ionic tellurocyanate and 1 mol of ionic thiolsulfate were formed, simultaneously. According to these observations, the following reaction is postulated, eqn. (3).

$$\mathrm{TeS_4O_6^{2-}} + 6\,\mathrm{CN^-} \xrightarrow{\mathrm{MeCN}} \mathrm{TeCN^-} + \mathrm{SCN^-} + \mathrm{S_2O_3^{2-}} + \mathrm{SO_3^{2-}} + \mathrm{(CN)_4^{2-}} \tag{3}$$

In this respect, even in acetonitrile the tellurium derivative differs markedly from the analogous sulfur and selenium compounds.[3]

The rates of the reaction were followed by measuring the formation of ionic thiocyanate or ionic tellurocyanate by applying IR.[2] The kinetic plots were linear up to three half-lives. The rate data and the activation parameters for the telluropentathionate-cyanide reaction and the corresponding pentathionate and selenopentathionate reactions are presented in Table 1.

With regard to the postulated sulfite ion formed, eqn. 3, this is rapidly oxidized to ionic sulfate due to traces of oxygen in the acetonitrile solution.[4]

Obviously the mechanism of the telluropentathionate-cyanide reaction is different from the penta- and selenopentathionate-cyanide reactions in acetonitrile.[3] However, the first step is presumably the same in all three cases, eqn. (4).

$$\mathrm{^-O_3S-S-Te-S-SO_3^-} + \mathrm{CN^-} \xrightarrow{\mathrm{slow}} \mathrm{^-O_3S-S-TeCN} + \mathrm{S_2O_3^{2-}} \tag{4}$$

The sulfonated sulfur tellurocyanate ion, $\mathrm{^-O_3S-S-S-TeCN}$, then may react rapidly with a second cyanide ion. The electrophilic centre probably is the divalent sulfur atom, and ionic sulfite is displaced, eqn. (5).

$$\mathrm{^-O_3S-S-TeCN} + \mathrm{CN^-} \xrightarrow{\mathrm{fast}} \mathrm{SO_3^{2-}} + \mathrm{NCS-TeCN} \tag{5}$$

The asymmetric pseudohalogen, $\mathrm{NCS-TeCN}$, is then attacked by a third cyanide ion, probably at the sulfur atom, displacing ionic tellurocyanate, eqn. (6).

$$\mathrm{NCS-TeCN} + \mathrm{CN^-} \xrightarrow{\mathrm{fast}} \mathrm{S(CN)_2} + \mathrm{TeCN^-} \tag{6}$$

It is further known that sulfur dicyanide reacts very rapidly with three cyanide ions, presum-

Table 1. Rate data and activation parameters for the reactions of ionic pentathionate, selenopentathionate and telluropentathionate with the cyanide ion in acetonitrile.

Reaction	k_2 M^{-1} s^{-1}			ΔH^*	ΔS^*	ΔG^*
	20 °C	25 °C	35 °C	kcal/mol	cal/ mol deg	kcal/mol
$S_5O_6^{2-}+CN^-$ [a]	–	0.250	0.335	6.3	−40	18.2
$SeS_4O_6^{2-}+CN^-$ [b]	–	20.6	22.8	1.7	−48	16.0
$TeS_4O_6^{2-}+CN^-$ [c]	0.082	0.107	0.169	8.1	−36	18.9
	0.085	0.104	0.173			

[a] Ref. 4, $\mu=1.25\times10^{-2}$. [b] Ref. 4, $\mu=9.88\times10^{-3}$. [c] $\mu=2.25\times10^{-2}$.

ably according to the following reaction,[5] eqn. (7).

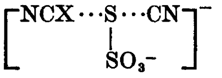
$$S(CN)_2+3\ CN^- \xrightarrow{\text{fast}} SCN^- + (CN)_4^{2-} \qquad (7)$$

The mechanism outlined above is in accordance with the stoichiometry of the reactants observed by the kinetic experiments.

With regard to eqn. (5), this step is different from the corresponding step in the pentathionate-cyanide and selenopentathionate-cyanide reactions, in which the pseudohalide ion is the leaving group.[3] Supposing the tellurocyanate ion to be displaced as depicted by eqn. (8),

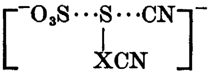
$$^-O_3S-S-TeCN+CN^- \xrightarrow{\text{fast}} {}^-O_3S-SCN+TeCN^- \qquad (8)$$

ionic tellurocyanate and thiocyanate would not be formed at the same rate, due to the much slower reaction between the thiocyanatosulfonate ion and the cyanide ion.[3] This is not in accordance with the experimental data.



$$\left[\begin{array}{c} NCX\cdots\underset{\displaystyle SO_3^-}{\underset{|}{S}}\cdots CN \end{array}\right]^-$$

I



$$\left[\begin{array}{c} {}^-O_3S\cdots\underset{\displaystyle XCN}{\underset{|}{S}}\cdots CN \end{array}\right]^-$$

II

(X = S, Se and Te.)

Considering the transition states I and II, the transition state I is favoured for X = S and Se. For X = Te the transition state II appears to be the most favourable. Thus, with regard to nucleophilic substitution at sulfenyl sulfur in acetonitrile, the thiocyanate ion and the selenocyanate ion are better leaving groups than the sulfite ion, while the latter is a better leaving group than is the tellurocyanate ion.

Eqn. (6) of the mechanism outlined above requires some further comments. Both of the chalcogen atoms of the asymmetric pseudohalogen, NCS – TeCN, may be regarded as potential electrophilic centres. Supposing that the nucleophilic attack occurs at the divalent tellurium atom, the products may be ionic thiocyanate and tellurium dicyanide as depicted by eqn. (9).

$$NCS-TeCN+CN^- \xrightarrow{\text{fast}} SCN^- + Te(CN)_2 \qquad (9)$$

Ionic cyanide, however, reacts with tellurium dicyanide in acetonitrile to precipitate elemental tellurium.[5] Elemental tellurium was not observed at any stage even in concentrated solutions during the telluropentathionate-cyanide reactions. This might be because, if the reaction goes through the step depicted by eqn. (9), the concentration of tellurium dicyanide at any time has to be very small, and excess cyanide ions may then react with the atomic tellurium to form ionic tellurocyanate.[2] However, since no elemental tellurium was precipitated even when excess ionic telluropentathionate was employed, the step involving nucleophilic attack at the divalent sulfur atom, depicted by eqn. (6), appears to be the most probable one.

The data presented in Table 1, show that the nucleophilicity of the cyanide ion toward the divalent chalcogens, is in the order $Te < S \ll Se$. The order of the chalcogen basicity of the cyanide ion, which may be determined by the stability of the pseudohalide ions, is believed to be $TeCN^- \ll SeCN^- \ll SCN^-$.[2,6]

The poor solvation of anions in dipolar aprotic solvents,[7] and the structural similarities between the pentathionate ions,[8] may allow one to assume that the initial states of these anions in acetonitrile are essentially identical. On these conditions the calculated activation parameters suggest that the transition states of the telluropentathionate-cyanide reaction and the pentathionate-cyanide reaction are rather similar. The higher enthalpy of activation of the former reaction is nearly compensated by a more negative entropy of activation in the case of the latter reaction. The timing of the covalency changes for the cyanide substitution at divalent tellurium thus appears to resemble that for the cyanide substitution at sulfenyl sulfur.[9] The much lower enthalpy and entropy of activation observed in the selenopentathionate-cyanide 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 telluropentathionate[11] 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 $C_{48}H_{40}O_6S_4TeAs_2$: 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.[2] 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 ± 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:

$$\lambda°[(Ph_4As)_2TeS_4O_6] = 173 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1},$$

$$\lambda°[TeS_4O_6{}^{2-}] = 61.4 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$$

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 cm ± 10 %.

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The Systems BF_3—H_2O and $SbCl_5$—H_2O in Acetone and Methylene Chloride as Solvents

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Bernander and Olofsson have recently reported a study of the $H_2O-SbCl_5$ adduct system in methylene chloride by ^1H NMR.[1] They interpret their results in terms of the formation of a 1:1 adduct $SbCl_5.H_2O$, and a 1:2 adduct $SbCl_5.2H_2O$ in which the second water molecule is more weakly held. They also measured the ^1H chemical shift of a solution of $BF_3.H_2O$ in CH_2Cl_2. In discussing their results they make a comparison with our earlier work on the BF_3-H_2O system in solution in acetone[2] 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 $BF_3.H_2O$ 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 $BF_3.H_2O$ adduct but rather the BF_3.-acetone.H_2O ternary adduct. While it is clear that there must be hydrogen-bonded interaction between the protons of $BF_3.H_2O$ 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