

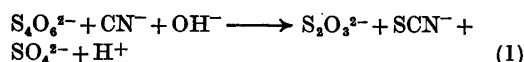
Short Communications

Polythionates. I. The Reaction between the Tetrathionate Ion and the Cyanide Ion in Acetonitrile

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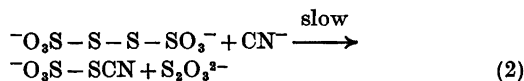
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It is known that the tetrathionate ion in aqueous solution reacts rapidly and quantitatively with the cyanide ion, giving ionic thiocyanate, thiosulfate, and sulfate, eqn. (1),¹

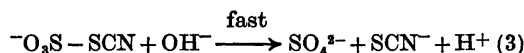


a reaction which forms the basis of the well-known cyanide method for the analysis of polythionates.^{2,3}

Kinetic studies by Davis⁴ suggest the mechanism to be in consistence with the one postulated by Foss,⁵ involving a nucleophilic displacement of ionic thiosulfate by the cyanide ion, eqn. (2),



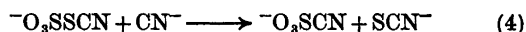
followed by a fast hydrolysis, eqn. (3).



The dielectric constant of the solvent and the solvation of the leaving group are probably very important in the reaction between ionic tetrathionate and the cyanide ion. The rate of the reaction between ionic trithionate and the cyanide ion being about 50 times faster in water⁶ than in a 50% water-methanol solution,⁷ seems to confirm this view.

To get a better insight into the solvation effects and the intermediates of the tetrathionate-cyanide reaction, this reaction has been studied in the dipolar aprotic solvent, acetonitrile. Tetraphenylarsonium tetrathionate was used as the substrate and tetraphenylphosphonium cyanide was used as the nucleophilic reagent. Results from conductivity measurements suggested these salts to be completely dissociated in acetonitrile in the concentration range used in the kinetic runs.

Product analysis showed that when reacting 1 mol of ionic tetrathionate and 2 mol of cyanide ion, 1 mol of ionic thiocyanate and 1 mol of ionic thiosulfate were obtained. The reaction, followed by measuring the formation of ionic thiocyanate, showed good second-order kinetics up to three half-lives. These observations would be in accordance with a rate determining step similarly to what is the case in aqueous solution (eqn. 2). The thiocyanatosulfonate ion, $\text{^-O}_3\text{SSCN}$, might then react with a second cyanide ion to give ionic thiocyanate and the cyanosulfonate ion (eqn. 4).



This reaction (eqn. 4) is, according to the kinetics, a much faster step. The rate constant of this step has been observed to be about 10 times higher than the rate constant of the first step.⁸ The unstable thiocyanatosulfonate ion is converted, probably by a direct nucleophilic substitution by the cyanide ion, to a more stable cyanosulfonate ion. Stable salts, however, of the cyanosulfonate ion have not been isolated. Jander⁹ and co-workers have found the cyanosulfonic acid to exist from potentiometric titration of a mixture of sulfur trioxide in excess hydrogen cyanide. From the present kinetic investigation the cyanosulfonate ion may be stable in acetonitrile, but several attempts to prepare the tetraphenylarsonium salt of this anion, using different synthetic routes, were unsuccessful.

The existence of the thiocyanatosulfonate ion as a reaction intermediates has further been postulated in the sulfur dicyanide-thiosulfate reaction in acid aqueous solution.¹⁰ Schmidt¹¹ has been able to prepare the thiocyanatosulfonic acid *in situ* in ether at -78°C , but at room temperature neither the acid nor the sodium salt is stable.

The second-order rate constants and the activation parameters for the reaction between ionic tetrathionate and the cyanide ion in acetonitrile and in water are listed in Table 1.

The rate constant in water is about 400 times greater than in acetonitrile even though the nucleophilicity of the cyanide ion towards methyl iodide is 4.1×10^4 times greater in a dipolar aprotic than in a protic solvent.¹² The solvation of the leaving group may, however, be responsible for the large fall in the rate constant observed in acetonitrile relative to water. The sulfate ion is one of the anions which interacts

Table 1. Second-order rate constants k_2 , and activation parameters for the reaction between ionic tetrathionate and the cyanide ion in acetonitrile and in water.

	k_2 M ⁻¹ s ⁻¹ 25 °C	35 °C	45 °C	ΔH^* kcal/mol	ΔS^* cal/mol deg	ΔG^* kcal/mol
MeCN ^a	2.9×10^{-3}	5.0×10^{-3}	9.0×10^{-3}	9.8	-37	20.8
H ₂ O ^b	1.2			11.0	-22	17.5

^a Ionic strength $\mu = 2.55 \times 10^{-2}$, this work. ^b Ionic strength $\mu = 1.77 \times 10^{-2}$, Ref. 4.

most strongly with protic solvents,¹³ and Kolthoff¹⁴ has stated that the sulfate ion is virtually unsolvated in acetonitrile and dimethyl sulfide. The thiosulfate ion, which is the leaving group in eqn. (2), probably exhibits much the same solvation properties as does the sulfate ion.

When considering the significance of the activation parameters, which are also presented in Table 1, it is seen that the decrease in the second-order rate constant in going from water to acetonitrile, is governed by a more unfavourable entropy of activation in the dipolar aprotic solvent,

$$\Delta S^*(\text{MeCN}) - \Delta S^*(\text{H}_2\text{O}) = -15 \text{ cal/mol deg.}$$

The large negative entropy of activation observed in acetonitrile may be caused by a more tight transition state in this solvent,¹⁵ which provides no hydrogen bonding stabilization of the leaving group. Because of the large difference between the dielectric constants of water and acetonitrile, it is difficult to compare the results any further. However, it seems probable that the transition state is much better solvated in water than in acetonitrile.

The second-order rate constant, k_2 , is a function of the ionic strength, μ . The addition of an inert salt, tetraphenylarsonium perchlorate, increases the rate (see Table 2). The data are in accordance with the predictions of the Brønsted-Christiansen-Scatchard equation

$$\log k = \log k_0 + 2AZ_1Z_2\sqrt{\mu}$$

When using $\epsilon_{\text{MeCN}} = 35.8$, the Debye-Hückel constant A in acetonitrile at 25 °C was calculated

Table 2. Salt effects on the rate constant of the tetrathionate-cyanide reaction in acetonitrile at 25 °C. (Ph₄AsClO₄ as inert salt).

$\mu \times 10^2$	2.55	3.05	3.55	4.55
$k_2 \times 10^3$ M ⁻¹ s ⁻¹	2.90	3.43	3.79	4.63

to be 3.756. The experimental value of A was found to be 3.9 ± 0.2 . This appears to be a rare case of verification of the Debye-Hückel limiting law in a non-aqueous solvent.¹⁶

Acetonitrile was purified as reported previously.¹⁷ Tetraphenylphosphonium cyanide was prepared in the same way as reported for tetraphenylarsonium cyanide.¹⁷ Acetone, "Baker Analyzed" reagent, was used without further purification. Potassium tetrathionate was prepared by the method of Kurtenacker and Laszlo.¹⁸

Tetraphenylarsonium tetrathionate was precipitated from an aqueous solution of potassium tetrathionate, K₂S₄O₆, with tetraphenylarsonium chloride, Ph₄AsCl, in nearly quantitative yield. After filtration and washing several times with cold water, the product was washed with cold acetone to remove water and finally washed with ether. The product was recrystallized from acetonitrile by the addition of an equal amount of acetone. Dec. 253 °C. (Found: C 58.53; H 4.24; S 12.94. Calc. for C₄₈H₄₀O₆S₄As₂: C 58.20; H 4.04; S 12.95).

Product analysis. Two solutions of tetraphenylarsonium tetrathionate and tetraphenylarsonium cyanide, 1.00×10^{-3} M and 3.00×10^{-2} M respectively, were prepared, and 10 ml of each solution were pipetted out and mixed. After 4½ h at about 30 °C, two portions of 5 ml of the solution were pipetted out. The first was immediately analysed for ionic thiocyanate using IR¹⁷ and found to contain 3.32×10^{-5} mol. The other solution was analysed for ionic thiosulfate, yield 3.48×10^{-5} mol, by iodometric titration.⁸ The amounts of ionic thiocyanate and ionic thiosulfate in the reaction mixture were thus found to be the same within the experimental error.

Kinetic experiments. The rate was followed by measuring the formation of ionic thiocyanate, applying IR liquid cells with a path length of 1 mm.¹⁷ The kinetic plots were analysed according to the rate-equation:

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

where x is the concentration of ionic thiocyanate and a and b are the initial concentration of ionic tetrathionate and cyanide, 5.0×10^{-3} M and

1.0×10^{-2} M, respectively. The rates were determined with a Unicam SP 200 G Infrared Spectrophotometer and the rate constants were reproduced with an accuracy better than $\pm 3\%$.

Conductivity measurements. When using $\lambda_{\text{PhAs}^+}^{\circ} = 55.8 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$ ¹⁹ the following equivalent conductivities at infinite dilution in acetonitrile at 25 °C were found:

$$\lambda_{(\text{PhAs})_2\text{SiO}_6}^{\circ} = 172 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$$

$$\lambda_{\text{SiO}_6}^{\circ} = 60.4 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$$

$$\lambda_{\text{PhAsCN}}^{\circ} = 150 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$$

$$\lambda_{\text{CN}^-}^{\circ} = 94.2 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ mol}^{-1}$$

From the plots, λ versus \sqrt{c} , the salts appeared to be completely dissociated in acetonitrile. 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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Hydrogen Bonding of Diphenylamine. Part I. A Near Infrared Study of Its Complexes with Some Proton Acceptors

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In the literature two quite different series of equilibrium constants K_c have been reported for the hydrogen bonded complexes formed by diphenylamine (DPA) with some proton acceptors. The values of Bhowmik and Basu¹ are appreciably greater than the values obtained by Sannigrahi and Chandra² by the same method (UV) and in similar conditions (Table 1). The proton acceptors used in the two studies mentioned above were not the same, but their proton-accepting power should be of the same order of magnitude.

To obtain a more reliable estimate of the proton donor strength of diphenylamine, we have measured the equilibrium constants for some diphenylamine-proton acceptor complexes by the IR method.

Experimental. Chemicals. Diphenylamine (*purum* grade, Schering-Kahlbaum AG) and benzophenone (zur Synthese, E. Merck AG) were used as received. 1,4-Dioxan (Uvasol grade, E. Merck AG) and dimethyl sulfoxide (DMSO, *purum* grade, Fluka AG) were purified by fractional crystallization. Hexamethylphosphoric triamide (HMPA, zur Synthese, E. Merck AG) was boiled with calcium oxide at diminished pressure for about 15 h and then distilled through a Vigreux column (b.p. 80 °C/2 mmHg). *N,N*-Dimethylacetamide (*purissimum* grade, Fluka AG) and carbon tetrachloride (Uvasol grade, E. Merck AG) were dried with molecular sieves 4A.

Table 1. Literature values of the equilibrium constants for the hydrogen bonding of diphenylamine with proton acceptors. Method UV, solvent cyclohexane, temperature 27 °C.

Proton acceptors	$\frac{K_c}{M^{-1}}$	Ref.
Benzophenone	14.4	1
Quinoxaline	17.4	1
Diethylnitrosoamine	28.2	1
Diethyl ether	0.28	2
Dioxan	0.58	2
Tetrahydrofuran	0.40	2