

A Study on the Selenocyanate and Thiocyanate Ions in Acetonitrile: Effects of Cations

JON SONGSTAD and LEIV JONN STANGELAND

Chemical Institute, University of Bergen, Bergen, Norway

The selenocyanate and thiocyanate ions are found to associate through the nitrogen atoms with Lewis acids in a dipolar aprotic solvent as acetonitrile. For the selenocyanate ion, this association is sufficient to make selenium electrophilic.

Ultraviolet spectra, solubilities, *etc.*, of salts of these ions are found to be highly dependent upon cations employed.

The selenocyanate and thiocyanate ions are known to be very powerful nucleophiles toward various substrates. Toward hard substrates the nitrogen end is the nucleophilic part of the ions, toward soft substrates the selenium or sulfur atom will be the active part.¹

The corresponding acids, HNCS and HNCSe, are strong acids, the latter suggested to be the stronger one.² The nitrogen end in the NCS^- ion is therefore a better base toward the proton than is the nitrogen end in the NCSe^- ion. The thiocyanate ion is consequently better solvated in protic solvents, reflecting the fact that the nucleophilicity of the nitrogen end of this ion toward aliphatic carbon is increased 2.5 times as much as that of the NCSe^- ion when going from a protic solvent to an aprotic one.³ Similarly, Wagner⁴ has found from MO calculations that the charge on the nitrogen ends in the NCS^- and NCSe^- ions are 0.48 and 0.39, respectively, a difference which is assumed to be due to the higher degree of back-bonding from sulfur in the thiocyanate ion. The electronegativities of sulfur and selenium are of the same order of magnitude, approximately 2.2 on the Pauling scale. Towards very soft substrates both the element basicity and nucleophilicity of selenium nucleophiles is higher than of sulfur nucleophiles.⁵⁻⁷

Recently, Meek *et al.*⁸ found KSeCN and arylphosphines in acetonitrile to give a nearly quantitative yield of the corresponding phosphine selenides and KCN . This reaction was interesting from a special point of view as one might have a rare case where both the electrophile and the nucleophile were negatively charged or had a free pair of electrons, that is, they were both very powerful nucleophiles.

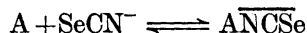
One possible explanation might be that the so-called biphilic⁹ nature of the phosphine was operative to create a transition state that would facilitate the breaking of the weak C—Se bond and consequently give the products.

Because of the hygroscopic and rather unpleasant nature of potassium selenocyanate, tetramethylammonium selenocyanate was used as a reactant together with triphenyl phosphine in our experiments. When "Baker Analyzed" reagent acetonitrile was used as a solvent for the reaction, with or without purification with phosphorus pentoxide, the reaction was rapid, but the rate constant varied considerably from one solvent batch to another. The reaction was followed on a UV spectrophotometer as the extinction coefficients of the products were far less than those of the reactants in the 240–270 $m\mu$ region.

As suggested by Coetzee,¹⁰ minor amounts of acidic impurities in acetonitrile may be removed by distillation from calcium hydride. When acetonitrile, dried first with phosphorus pentoxide and finally purified according to the latter procedure was used as a solvent, no change in UV absorption was found, even after several weeks. Neither was any reaction found to occur when Merck "Uvasol" acetonitrile was used as a solvent.

If, however, minute amounts of lithium perchlorate or acetic acid was added, the usual quantitative yield of phosphine selenide was rapidly encountered. Similarly, when dry methanol was used as a solvent, the reaction was very rapid with excellent second order kinetics over a 10-fold concentration range in the 10^{-4} – 10^{-5} M region, with a second order rate constant of $1.23 \text{ mol}^{-1} \text{ sec}^{-1}$. Traces of water in the methanol did not alter the rate constant nor the quality of the kinetics significantly.

The catalysis by acids, hydroxylic solvents, and electrophilic metal ions indicate that the selenium donor in the reaction between the selenocyanate ion and triphenylphosphine is an associate between the Lewis acid and the selenocyanate ion through the nitrogen end of the ion; this creating a positive charge on the selenium atom will act as the electrophilic center in the reaction.



(A is MeOH, electrophilic cations, CH_3COOH , or acidic impurities).

It is well known that isoselenocyanates as trialkylsilyl isoselenocyanates¹¹ or benzhydryl and trityl isoselenocyanates¹² are powerful selenium donors, the former to yield cyanides by isomerization, the latter the organic isocyanides.

It was further found that the UV spectra of the SeCN^- and SCN^- ions in acetonitrile showed a blue shift upon addition of Lewis acids combined with a decrease of the extinction coefficients, whereas the spectra of triphenylphosphine and its selenide were hardly changed. The results are found in Table 1.

The results indicate that when the cations are large and not very efficient Lewis acids toward nitrogen, the spectra of the SeCN^- and SCN^- ions have peaks at 252.3 $m\mu$ and 235.2 $m\mu$, respectively, whereas a blue shift is observed when electrophilic cations are employed. Treinin¹³ has earlier pointed out the environmental effects on spectra of pseudohalide ions in solution.

In the SCN^- ion case where, as anticipated, the effect of the cation on the spectrum is most pronounced, the rubidium ion is found to make no

Table 1. UV spectra of the SCN^- and SeCN^- ions.

Compound	Solvent	Lewis acid	λ_{max} (m μ)	$\epsilon_{\text{max}} \times 10^{-3}$
Me_4NSCN	MeCN		235.2	3.62
RbSCN	»		235.2	3.62
KSCN	»		234.9	3.50
NaSCN	»		234.5	3.43
Me_4NSCN	»	1:1 LiClO_4	231.0	2.95
Me_4NSCN	»	excess LiClO_4	228.0	2.66
Me_4NSeCN	»		252.3	4.52
CsSeCN	»		252.3	4.52
RbSeCN	»		252.3	4.52
KSeCN	»		252.0	4.52
NaSeCN	»		252.0	4.52
Me_4NSeCN	»	1:1 LiClO_4	250	4.04
»	»	excess LiClO_4	241.0	4.00
»	»	1 molar in MeOH	247.0	
»	MeOH		235.0	
»	H_2O		235.0	

significant blue shift of the spectrum of the SCN^- ion. Interestingly, rubidium, cesium, and several onium selenocyanates and thiocyanates are found to be very stable and non-hygroscopic salts compared with NaNCS and KNCSe which are rather unpleasant to handle. Furthermore, the solubilities of RbNCSe and CsNCSe in alcohols and dipolar aprotic media are far less than those of KNCSe and NaNCS .¹⁴

On the other hand, piperidinium thiocyanate and selenocyanate which are supposed to be highly associated may be purified by crystallization from benzene.¹⁴ Selenocyanate and thiocyanate salts of highly electrophilic cations will be so highly associated that they will be soluble in unpolar solvents, similar to LiClO_4 and LiCN . The latter salt has recently been shown to be an efficient source of cyanide ions in unpolar solvents, in some cases a more efficient one than AgCN .¹⁵

The extent of association between Li^+ ions and selenocyanate and thiocyanate ions was further studied. To solutions of Me_4NSeCN and Me_4NSCN (1.93×10^{-3} mol/l and 1.97×10^{-3} mol/l, respectively) in purified acetonitrile were added known amounts of LiClO_4 , and the UV spectrum was recorded in each case. In the selenocyanate case two isosbestic points at 232 and 246 m μ were found for all concentrations of lithium perchlorate indicating only two species present, the free NCSe^- ion and the assumed associate LiNCSe . Finally the spectrum was recorded with great excess of LiClO_4 present, with the same concentration of LiClO_4 in the reference cell. From the extinction coefficients of the SeCN^- ion and of the assumed associate, the equilibrium constant for the equilibrium $\text{SeCN}^- + \text{Li}^+ \rightleftharpoons \text{LiNCSe}$ was calculated assuming a 1:1 complex. For all concentrations of LiClO_4 employed (1×10^{-3} – 1.5×10^{-2} mol/l) the equilibrium constant was found to be within $(2.5 \pm 0.5) \times 10^2$ at 20°C, calculated at two different wave-lengths.

The same procedure was followed for the thiocyanate ion. Since the absorption of the NCS^- ion occurs at a lower wave length, the lower isosbestic point at $\sim 215 \text{ m}\mu$ was diffuse due to the solvent peak, while all curves passed through an isosbestic point at $228 \text{ m}\mu$. Similar calculations gave an equilibrium constant between Li^+ ion and the SCN^- ion in acetonitrile at all concentrations of LiClO_4 equal to $(8 \pm 2) \times 10^2$ at 20°C . The higher equilibrium constant in the thiocyanate case is as expected.

It has long been realized that salts of these pseudohalide ions are very associated in dipolar aprotic solvents, and that the extent of association is dependent upon the cations employed.^{3,16,17} In this work it is shown that in the selenocyanate case, the degree of association is sufficient to make an electrophile out of a strong nucleophilic anion. The chemistry of these pseudohalide ions may be highly dependent upon the cation employed when non-hydroxylic solvents are used.

EXPERIMENTAL

Preparation of Me_4NSeCN and Me_4NSCN : To 58 g, 0.3 mol, KSeCN in 200 ml MeCN was added 44 g Me_4NCl . The reaction mixture was stirred at reflux for an hour, whereupon KCl was filtered off. The product was precipitated with ether and recrystallized twice from MeCN . Yield 47 g.

Me_4NSCN was prepared similarly.

As both KSeCN and KSCN are far more soluble in acetonitrile than the tetramethylammonium salts, traces of the potassium salts were left in the mother liquor. The tetramethylammonium salts formed big white flakes from acetonitrile and may be stored for long periods in daylight. The salts are non-hygroscopic.

Triphenylphosphine (Fluka puriss *p.a.*) was crystallized five times from ether. M.p. 81°C .

Triphenylphosphine selenide was made according to Meek⁸ and purified by crystallization from benzene and chloroform. M.p. 189°C .

Acetonitrile was purified according to Coetzee.¹⁰

Methanol was distilled from $\text{Mg}(\text{OCH}_3)_2$.

LiClO_4 (Fluka *purum*, wasserfrei) was used without further purification.

UV measurements were made on a Beckmann DB spectrophotometer with 1 mm and 10 mm matched cells, depending upon concentrations of reactants.

In the kinetic runs performed in methanol, two isosbestic points were found at 232 and 297 $\text{m}\mu$. The actual rate constant was calculated from the decrease in absorption at 260 $\text{m}\mu$ taking into account both the absorption of the reactants and the absorption of the phosphine selenide. The absorption due to the cyanide ion could be neglected. For reasons of convenience the concentrations of tetramethylammonium selenocyanate and the phosphine were kept equal throughout the concentration range in which the reaction was examined. The reaction flasks were kept in a water thermostat at $25.0 \pm 0.1^\circ\text{C}$.

Acknowledgement. The authors are indebted to Dr. O. Foss for fruitful discussions and to Mr. S. Hauge who suggested the use of onium salts in this work.

REFERENCES

1. Pearson, R. G. and Songstad, J. *J. Am. Chem. Soc.* **89** (1967) 1827.
2. Boughton, J. H. and Keller, R. N. *J. Inorg. Nucl. Chem.* **28** (1966) 2851.
3. Parker, A. J. *J. Chem. Soc.* **1961** 4398.
4. Wagner, E. L. *J. Chem. Phys.* **43** (1964) 2728.
5. Petti, L. D., Royston, A., Sherrington, C. and Whewell, R. *J. Chem. Commun.* **1967** 1179.

6. Pearson, R. G. and Songstad, J. J. *Am. Chem. Soc.* **90** (1968) 319.
7. Livingstone, S. E. *Quart. Rev. (London)* **20** (1966) 386.
8. Nicpon, P. and Meek, D. W. *Inorg. Chem.* **5** (1966) 1297.
9. Pearson, R. G., Gray, H. B. and Basolo, F. J. *Am. Chem. Soc.* **82** (1960) 787.
10. Coetzee, J. F. *Pure Appl. Chem.* **1967** 429.
11. Thayer, J. S. *J. Organomet. Chem.* **9** (1967) 30.
12. Songstad, J. and Stangeland, L. J. *To be published.*
13. Sperling, R. and Treinin, A. *J. Phys. Chem.* **68** (1964) 897.
14. Songstad, J. and Stangeland, L. J. *Unpublished observations.*
15. Johns, I. B. and diPietro, H. R. *J. Org. Chem.* **29** (1964) 1970.
16. Miller, J. and Parker, A. J. *J. Am. Chem. Soc.* **83** (1961) 117.
17. Eliassaf, J., Fuoss, R. M. and Lind, Jr., J. E. *J. Phys. Chem.* **67** (1963) 1724.

Received August 1, 1969.