

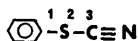
# The Action of Ionic $^{13}\text{C}$ -Cyanide on Aromatic Thiocyanates in Acetonitrile

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The reaction between various X-phenyl thiocyanates (X=H, *o*-NO<sub>2</sub>, *p*-NO<sub>2</sub>, and *p*-Me<sub>2</sub>N) and ionic cyanide has been studied in acetonitrile. On the basis of IR measurements, applying ionic  $^{13}\text{C}$ -cyanide, the reaction mechanism is suggested to involve a fast exchange of the cyano group prior to an adduct formation between the substrate and 2 mol of cyanide ions. In the case of *p*-nitrophenyl thiocyanate the tetraphenylarsonium salt of the adduct is isolated, and the space group is determined by means of X-ray crystallography. The rate of adduct formation is drastically decreased in the order: *p*-NO<sub>2</sub> > *o*-NO<sub>2</sub> > H > *p*-Me<sub>2</sub>N.

Aromatic thiocyanates may, according to Giles and Parker,<sup>1</sup> be regarded as trifunctional electrophiles.

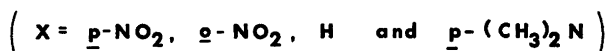
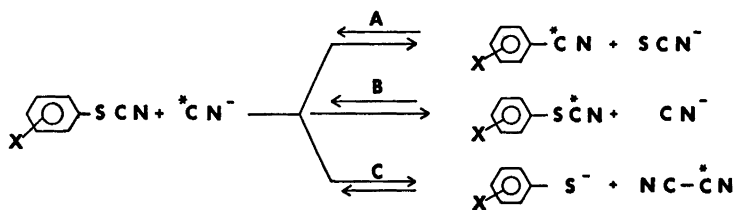
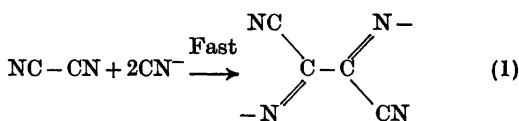


The potential electrophilic centers are; (1) the aromatic carbon atom bonded to the thiocyanate group, (2) the sulfur atom, and (3) the cyanide carbon atom.

If nitro groups are substituents in the benzene ring, Giles and Parker<sup>1</sup> found that only one

of the nucleophiles studied, *i.e.*, the thioethoxide ion, did attack at the sulfur atom of the substrate. All the other nucleophiles did attack at the aryl carbon atom and the cyanide carbon atom in different ratios.

In this paper we report the results of the reaction between ionic  $^{13}\text{C}$ -cyanide and various aryl thiocyanates in acetonitrile at room temperature. The following reactions resulting from nucleophilic attack of  $^*\text{CN}^-$  on aryl thiocyanates may then be possible; Reaction A involves an S<sub>N</sub>Ar process, reaction B involves an exchange of cyanide by means of a substitution on S<sup>II</sup>, and reaction C is assumed to involve an attack at the cyanide carbon. Cyanogen formed in the latter case is believed to add two cyanide ions in a fast reaction forming the postulated diiminosuccinonitrile dianion, eqn. 1.<sup>2</sup>



Scheme 1.

Table 1. IR data for aromatic thiocyanates and the corresponding  $^{13}\text{C}$ -thiocyanates in acetonitrile.

X	$\nu(\text{XArSCN})$ $\text{cm}^{-1}$	$\nu(\text{XArS}^{13}\text{CN})$ $\text{cm}^{-1}$
<i>p</i> -NO <sub>2</sub>	2169	2120
<i>o</i> -NO <sub>2</sub>	2165	2115
H	2164	2115
<i>p</i> -(CH <sub>3</sub> ) <sub>2</sub> N	2162	2116

The frequency of the nitrile stretching vibration in the 2000  $\text{cm}^{-1}$  region has been found to be very sensitive to the mass of the cyano carbon atom. The  $^{13}\text{C}$ -pseudohalides,  $\text{SCN}^-$ ,  $\text{SeCN}^-$ , and  $\text{TeCN}^-$ , have been observed to absorb about 50  $\text{cm}^{-1}$  lower than did the corresponding  $^{13}\text{C}$ -pseudohalides.<sup>2</sup> The sharp cyano-peaks were thus sufficiently apart for both qualitative and quantitative analysis. IR-measurements in the 2000  $\text{cm}^{-1}$  region on the present reactions, Scheme 1, were found to be a satisfactory method for characterizing the various components, Table 1.

*The p-nitrophenyl thiocyanate-cyanide reaction.* Upon mixing *p*-nitrophenyl thiocyanate and tetraphenylarsonium cyanide in acetonitrile at room temperature, the reaction mixture turned deep red, and the IR-spectrum of the solution showed a strong peak at 2142  $\text{cm}^{-1}$ . A stable deep red tetraphenylarsonium salt was isolated, which according to the molecular weight determination by means of X-ray technique and elemental analysis appeared to be an adduct between *p*-nitrophenyl thiocyanate and two mol of tetraphenylarsonium cyanide. The stoichiometry of the reaction (1:2 in substrate and nucleophile, respectively) was found to be compatible with the results obtained by measuring the absorbance of the reaction mixture in acetonitrile at 2142  $\text{cm}^{-1}$  at different cyanide concentrations.

No peak related to ionic thiocyanate,  $\nu_{\text{SCN}^-} = 2059 \text{ cm}^{-1}$ ,<sup>3</sup> could be detected in the IR-spectrum which eliminates an  $\text{S}_{\text{N}}\text{Ar}$  process (Scheme 1, reaction A).

If equal amounts of the substrate and ionic  $^{13}\text{C}$ -cyanide were used, the peak at 2142  $\text{cm}^{-1}$ , related to the adduct, split into two peaks ( $\nu = 2142 \text{ cm}^{-1}$  and  $\nu = 2088 \text{ cm}^{-1}$ ) of equal absorbance but each of half the

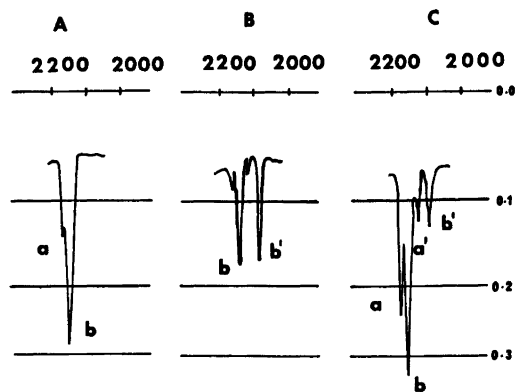


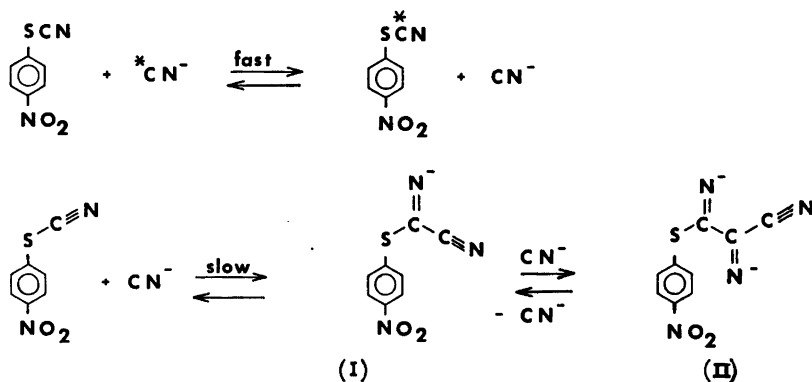
Fig. 1. A and B; IR-spectra of a mixture  $3.0 \times 10^{-3} \text{ M}$  in *p*-NO<sub>2</sub>ArSCN and  $3.0 \times 10^{-3} \text{ M}$  in Ph<sub>4</sub>AsCN or Ph<sub>4</sub>As<sup>13</sup>CN, respectively, in acetonitrile. C; IR-spectrum of a solution containing  $2.0 \times 10^{-2} \text{ M}$  of *p*-NO<sub>2</sub>ArSCN and  $1.0 \times 10^{-2} \text{ M}$  Ph<sub>4</sub>As<sup>13</sup>CN.

a and a' are related to *p*-NO<sub>2</sub>ArSCN and *p*-NO<sub>2</sub>ArS<sup>13</sup>CN, respectively. b and b' are related to the adduct. All the spectra were recorded immediately after the reactants were mixed.

absorbance obtained under the same conditions using  $^{13}\text{C}$ -cyanide, Fig. 1 A and B. Fig. 1 C shows the IR-spectrum of a more concentrated reaction mixture in which the mol ratio is 2:1 in substrate and ionic  $^{13}\text{C}$ -cyanide, respectively. The two new peaks a and a' are related to the aryl thiocyanate and aryl  $^{13}\text{C}$ -thiocyanate, respectively.

Thus, according to these results, a fast exchange of the cyano group appears to take place prior to the adduct formation. The geometrical configuration of the adduct is not known. We suggest, however, that the form represented by (II) is the most reasonable one. This adduct may be formed by an addition of a cyanide ion to the cyano carbon atom of the substrate, forming the intermediate (I), followed by a second cyanide addition to (I). The overall reaction between *p*-nitrophenyl thiocyanate and ionic cyanide may then be represented by Scheme 2.

Evidence for an intermediate of the type (I) has been reported by Hogg<sup>3</sup> and Giles and Parker.<sup>1</sup> The adduct (II) is then of the same type as the postulated diiminosuccinonitrile dianion, eqn. 1.



Scheme 2.

*Other aryl thiocyanate-cyanide reactions.* The other aryl thiocyanates studied, *i.e.*, *o*-nitrophenyl, phenyl, and *p*-dimethylaminophenyl thiocyanate, showed a reaction pattern similar to that outlined above for the *p*-nitrophenyl thiocyanate-cyanide reaction. In all cases a fast exchange of the cyano group was observed, but the rate of adduct formation was drastically decreased in the order;  $p\text{-NO}_2 > o\text{-NO}_2 > \text{H} > p\text{-(CH}_3)_2\text{N}$ . Thus, electron withdrawing groups increase the electrophilic nature of the cyano carbon atom.

The IR-spectra in the  $2000\text{ cm}^{-1}$  region of a solution of phenyl thiocyanate and ionic

$^{13}\text{C}$ -cyanide in acetonitrile at various times after mixing is shown in Fig. 2 (B, C).

The frequencies of the peaks associated with the adduct were found to be the same for all the compounds studied. ( $\nu = 2142\text{ cm}^{-1}$  and  $2088\text{ cm}^{-1}$ ).

As far as the authors know, there has not been reported any exchange between organic thiocyanates and ionic cyanide previously. In protic solvents total exchange occurs between organic selenocyanates and potassium  $^{14}\text{C}$ -cyanide.<sup>4</sup> Likewise, isotopic exchange between the selenocyanate ion and ionic cyanide in protic as well as in dipolar aprotic solvents is reported,<sup>2,5,6</sup> while no measurable exchange occurs between ionic thiocyanate and ionic cyanide.<sup>2,7</sup> Exchange reaction takes place in acetonitrile between selenium dicyanide and ionic cyanide, but no exchange was found between sulfur dicyanide and ionic cyanide.<sup>2</sup>

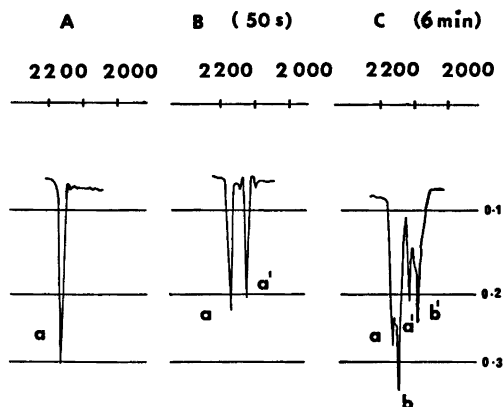


Fig. 2. A; IR-spectra of a  $2.0 \times 10^{-2}$  M solution of  $\text{ArSCN}$  in acetonitrile. B and C; IR-spectra of a solution containing  $2.0 \times 10^{-2}$  M of  $\text{ArSCN}$  and  $2.0 \times 10^{-2}$  M of  $\text{Ph}_4\text{As}^{13}\text{CN}$  in acetonitrile at various times after mixing.

a and a' are related to  $\text{ArSCN}$  and  $\text{ArS}^{13}\text{CN}$ , respectively. b and b' are related to the adduct.

## EXPERIMENTAL

Acetonitrile was purified by distillation from  $\text{P}_2\text{O}_5$  and  $\text{CaH}_2$ .<sup>8</sup>  $\text{Ph}_4\text{AsCN}$  and  $\text{Ph}_4\text{As}^{13}\text{CN}$  were prepared from  $\text{Ph}_4\text{AsCl}$  and  $\text{KCN}$  and  $\text{K}^{13}\text{CN}$  in methanol.<sup>9</sup>  $\text{K}^{13}\text{CN}$  was obtained from British Company Oxygen Limited, and contained more than 90%  $^{13}\text{C}$ .

*p*-Nitrophenyl thiocyanate<sup>10</sup> and phenyl thiocyanate<sup>11</sup> were prepared from diazotized anilines and copper(I) thiocyanate. *p*-*N,N*-Dimethylaminophenyl thiocyanate was prepared from *N,N*-dimethylaniline and thiocyanogen in glacial acetic acid.<sup>12</sup>

*o*-Nitrophenyl thiocyanate was prepared by dissolving 2.0 g of *o*-nitrobenzenesulfonyl chloride and 1.0 g of dry potassium cyanide in 20 ml of acetonitrile. The solution was stirred

for 12 h. The salts were filtered from the solution, and the solvent was removed in vacuum. Pure material was obtained by recrystallization from benzene by addition of some ether. M.p. 116–117 °C.

*The p-nitrophenyl thiocyanate–cyanide reaction.* 0.40 g of *p*-nitrophenyl thiocyanate dissolved in 15 ml of acetonitrile was added to a solution of tetraphenylarsonium cyanide made by dissolving 0.75 g of the nucleophilic reagent in 10 ml of acetonitrile. The reaction was carried out at room temperature, and the mixture turned deep red immediately after mixing the reactants. The solvent was removed in vacuum, and excess of the substrate was washed away by means of 10 ml of benzene and finally 10 ml of ether. The dark red product was dissolved in 10 ml of acetonitrile at room temperature and placed in a freezer (–15 °C), whereupon the salt crystallized. The amount of pure material was 0.50 g. The crystals were deep red and appeared quite stable in the crystalline form. (Found: C 68.57; H 4.48; N 3.02; S 3.64. Calc. for  $C_{15}H_{14}N_4O_2SAs_2$ : C 68.50; H 4.41; N 5.61; S 3.21.)

The crystals of the product from the *p*-nitrophenyl thiocyanate–cyanide reaction form dark red prisms. The space group was determined by oscillation and Weissenberg photographs, and accurate cell constants were obtained by means of least squares on the basis of the reflecting angles of 15 high angle reflections, using a Syntex P2, four-circle diffractometer. Density of the crystals was determined by flotation. The following results were obtained:

Space group:  $P1$  (or  $P\bar{1}$ )

Cell constants:  $a = 10.086(1) \text{ \AA}$   $\alpha = 76.19(1)^\circ$   
 $b = 13.243(2) \text{ \AA}$   $\beta = 96.03(1)^\circ$   
 $c = 9.515(1) \text{ \AA}$   $\gamma = 106.51(1)^\circ$   
 $V = 1182.4 (0.2) \text{ \AA}^3$

Density: Found, 1.402 g/cm<sup>3</sup>, calc. for  $Z = 1$ , 1.403 g/cm<sup>3</sup>. Molecular weight calc.: 998.5.

The molecular weight is in good agreement with the weight based on the formula  $C_{15}H_{14}N_4O_2SAs_2$  (998.9). The space group is probably  $P1$ , as there is only one molecule in the cell and no centrosymmetry in the molecule.

*IR measurements.* The IR-measurements were performed using a  $2.0 \times 10^{-3}$  M solution of the aryl thiocyanate and a  $2.0 \times 10^{-2}$  M solution of tetraphenylarsonium <sup>13</sup>C-cyanide unless otherwise stated. In all cases the cyanide solution was added to the aryl thiocyanate solution at room temperature.

The stoichiometry of the *p*-nitrophenyl thiocyanate–cyanide reaction was tested by reacting the substrate with various amounts of tetraphenylarsonium cyanide and measuring the absorbance at  $\nu = 2142 \text{ cm}^{-1}$   $\frac{1}{2}$  h after the solutions had been mixed.  $4.0 \times 10^{-3}$  M of the

substrate and successively  $2.0 \times 10^{-3}$ ,  $4.0 \times 10^{-3}$ ,  $6.0 \times 10^{-3}$ , and  $8.0 \times 10^{-3}$  M of the nucleophile gave the absorbances 0.085, 0.160, 0.230, and 0.330 respectively, which indicates that 1 mol of the aryl thiocyanate reacts with 2 mol of ionic cyanide.

The IR measurements were performed on a Unicam SP 200 G Infrared Spectrophotometer applying 0.1 cm liquid cells.

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