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Studies of Thioiminocarbonates. II. The Cyanide Ion-catalyzed Addition of Alcohols to Thiocyanates

Kazuhiko Tanaka
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto

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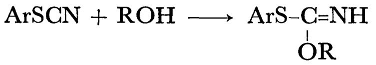
It was found that thiocyanates reacted with methanol in the presence of a catalytic amount of cyanide ion to give thioiminocarbonates. The effects of other catalysts upon the addition of methanol to thiocyanates were examined: the azide ion and the methoxide ion were effective, while triethylamine, sodium thiocyanate, potassium iodide, triphenylphosphine, sodium acetate, and mercuric cyanide were ineffective. A plausible reaction mechanism involving the addition of the cyanide ion to thiocyanates was proposed.

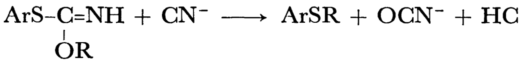
Although the scission of unsymmetrical diaryl disulfides by various S-nucleophiles has been discussed by Parker and Kharasch,[1] the cleavage products have not been isolated and characterized. Hiskey and Carroll investigated the cyanide-ion cleavage of unsymmetrical disulfides in detail.[2]

They reported that, when methyl phenyldithioacetate was treated with the cyanide ion, 12.5% yields of phenyl thiocyanate were obtained. However, no report has appeared concerning the scission of symmetrical diaryl disulfides by the cyanide ion. In a previous paper, we reported that symmetrical diaryl disulfides were readily cleaved by the cyanide ion in alcohol to afford aryl mercaptides and aryl thiocyanates, which then reacted with the alcohol used as the solvent to afford alkyl aryl sulfides:[3]

$$\mathrm{ArS{-}SAr + CN^- \rightleftarrows ArS^- + ArSCN} \quad (1)$$



$$\mathrm{ArSCN + ROH \longrightarrow ArS{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}NH} \quad (2)$$



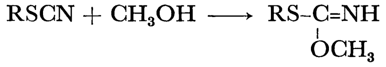
$$\mathrm{ArS{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}NH + CN^- \longrightarrow ArSR + OCN^- + HCN} \quad (3)$$

When *p*-tolyl thiocyanate was treated with an equimolecular amount of the cyanide ion in methanol at a low temperature, a mixture of methyl *p*-tolyl sulfide and *O*-methyl *S*-*p*-tolyl thioiminocarbonate was obtained.[4] In continuing these investigations, we have found that the treatment of thiocyanates with methanol in the presence of a catalytic amount of the cyanide ion gave thioiminocarbonates in good yields.

Results and Discussion

When phenyl thiocyanate (0.1 mol) was treated with methanol in the presence of a catalytic amount of sodium cyanide (0.014 mol) at 0°C for 6 hr, *O*-methyl *S*-phenyl thioiminocarbonate was obtained in a 72% yield. The product showed NMR peaks at τ 5.94 (OCH_3), 2.86 (NH), and 2.27 (C_6H_5), with relative intensities of 3: 1: 5. Its infrared spectrum contained a strong band at 1628 cm^{-1} (C=N) and a weak band at 3300 cm^{-1} (NH). In a similar way, various thioiminocarbonates were prepared from thiocyanates and methanol by using the cyanide ion as the catalyst. The results are summarized in Table 1. Of the various catalysts examined, it was found that sodium azide and sodium methoxide were effective, while triethylamine, sodium thiocyanate, potassium iodide, triphenylphos-

Table 1. Preparations of thioiminocarbonates



$$\mathrm{RSCN + CH_3OH \longrightarrow RS{-}\underset{\displaystyle OCH_3}{\underset{|}{C}}{=}NH}$$

R-SCN R	Catalyst	R-SCN: Catalyst (mol ratio)	Reaction temp. (°C)	Reaction time (hr)	Yield of thioiminocarbonate (%)
C_6H_5-	NaCN	7:1	0	6	72
C_6H_5-	$NaOCH_3$	9:1	0	6	77
C_6H_5-	NaN_3	7:1	0	7	73
p-$CH_3OC_6H_4$-	NaCN	8:1	0	17	84
p-$CH_3C_6H_4$-	NaN_3	5:1	0	1	70
p-$CH_3C_6H_4$-	$NaOCH_3$	5:1	0	1	64
p-$CH_3C_6H_4$-	NaCN	5:1	0	1	70
p-$CH_3C_6H_4$-	NaCN	8:1	0	8.5	74
m-$CH_3C_6H_4$-	NaCN	11:1	0	17	84
p-ClC_6H_4-	NaCN	7:1	0	6	74
C_2H_5-	NaCN	8:1	0	24	60

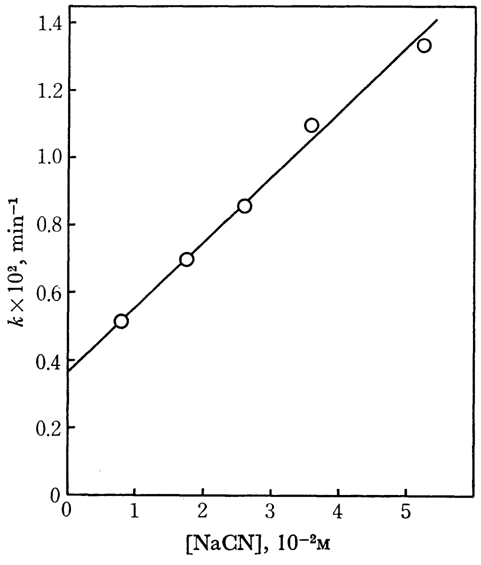


Fig. 1. First-order rate constants for cyanide ion-catalyzed addition of methanol to *p*-tolyl thiocyanate at 0°C.

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[1] A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.*, **82**, 3071 (1960).

[2] R. G. Hiskey and F. I. Carroll, *ibid.*, **83**, 4647 (1961), and references cited therein.

[3] K. Tanaka, J. Hayami, and A. Kaji, This Bulletin, **45**, 536 (1972).

[4] K. Tanaka, J. Hayami, and A. Kaji, *ibid.*, **44**, 2815 (1971).

phine, sodium acetate, and mercuric cyanide were ineffective, in the formation of thioiminocarbonates.

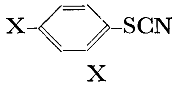
Information about the mechanism of the base catalysis can be obtained by measuring the pseudo-first-order rates at varying cyanide-ion concentrations. The plot of [NaCN] against 10^2k gives a straight line, showing that the catalytic effect is directly proportional to the concentration of the cyanide ion. The calculated values of 10^2k in Table 2 are derived from the expression: $k=3.70\times10^{-3}+1.90\times10^{-1}$[NaCN], where the 3.70×10^{-3} value is that for the slow uncatalyzed reaction and 1.90×10^{-1}, that for the catalytic coefficient (k_c) of the cyanide ion.[5]

The pseudo-first-order rates of the reaction of substituted aryl thiocyanates are listed in Table 3. The rates are slightly accelerated when the substituent is electron-withdrawing. On the basis of the observations presented earlier, the reaction scheme of the addition of methanol to thiocyanates in the presence of a cyanide-ion catalyst may be postulated to be as follows:

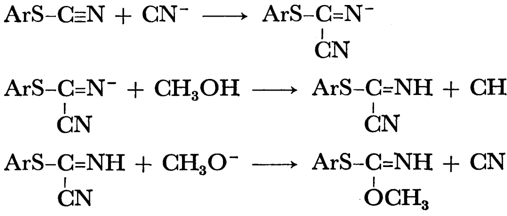
Table 2. Rates of cyanide ion-catalyzed addition of *p*-tolyl thiocyanate with methanol at 0°C

$CH_3C_6H_4SCN$ [M]	NaCN [M]	$k\times10^2$ (min^{-1})	k_c ($l\cdot$mol$^{-1}\cdot$min^{-1})
0.147	0.0084	0.51	0.17
0.147	0.0177	0.70	0.19
0.147	0.0260	0.86	0.19
0.147	0.0357	1.10	0.20
0.147	0.0525	1.33	0.18
		mean	0.19

Table 3. First-order rate constants of the addition of methanol to aryl thiocyanates at 0°C

 X	$k\times10^2$ (min^{-1})	Relative rates
p-CH_3O	0.44	0.85
p-CH_3	0.51	0.98
H	0.52	1.00
p-Cl	0.95	1.83
m-Cl	1.04	2.00

[ArSCN]=0.147M, [NaCN]=0.0058M.



$$\mathrm{ArS{-}C{\equiv}N + CN^- \longrightarrow ArS{-}\underset{CN}{C}{=}N^-} \qquad (4)$$

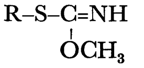
$$\mathrm{ArS{-}\underset{CN}{C}{=}N^- + CH_3OH \longrightarrow ArS{-}\underset{CN}{C}{=}NH + CH_3O^-} \qquad (5)$$

$$\mathrm{ArS{-}\underset{CN}{C}{=}NH + CH_3O^- \longrightarrow ArS{-}\underset{OCH_3}{C}{=}NH + CN^-} \qquad (6)$$

Experimental

Materials. Phenyl thiocyanate,[6] *p*-methoxyphenyl thiocyanate,[7] *p*-chlorophenyl thiocyanate,[8] *m*-chlorophenyl

Table 4. Physical properties and elemental analyses of thioiminocarbonates



$$\mathrm{R{-}S{-}\underset{OCH_3}{C}{=}NH}$$

R	Mp (°C) bp (°C/mmHg)	NMR absorption, τ (Solvent: CCl_4)	Analytical data (%) Found (Calcd) C	H	N	S
C_6H_5–	35—36	2.27 (5H, s, aromatic) 2.86 (1H, s, NH) 5.94 (3H, s, OCH_3)	57.39 (57.46)	5.44 (5.42)	8.35 (8.38)	19.20 (19.17)
p-$CH_3OC_6H_4$–	127.5—129/3.5	2.83 (4H, m, aromatic) 3.30 (1H, s, NH) 6.20 (3H, s, OCH_3) 6.24 (3H, s, CH_3O)	54.83 (54.80)	5.89 (5.62)	7.05 (7.10)	16.46 (16.26)
p-$CH_3C_6H_4$–	106—109/4	3.10 (4H, m, aromatic) 3.45 (1H, s, NH) 6.40 (3H, s, OCH_3) 7.75 (3H, s, CH_3)	59.65 (59.64)	6.21 (6.12)	7.70 (7.73)	17.56 (17.69)
m-$CH_3C_6H_4$–	100—101.5/2	2.68 (4H, m, aromatic) 3.02 (1H, s, NH) 6.20 (3H, s, OCH_3) 7.63 (3H, s, CH_3)	59.74 (59.64)	6.06 (6.12)	7.63 (7.73)	17.94 (17.69)
p-ClC_6H_4–	60—61	2.46 (4H, m, aromatic) 3.00 (1H, s, NH) 6.15 (3H, s, OCH_3)	47.77 (47.64)	4.10 (4.00)	6.84 (6.95)	15.79 (15.90)
C_2H_5–	69—70.5/26	2.66 (1H, s, NH) 6.09 (3H, s, OCH_3) 7.20 (2H, q, –CH_2–) 8.65 (3H, t, CH_3)	40.34 (40.31)	7.81 (7.61)	11.78 (11.75)	26.61 (26.90)

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[5] Triethylamine catalyzed reaction of isocyanates and methanol has been reported. See J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, **1947**, 713.

[6] L. Gattermann and W. Haussknecht, *Ber.*, **23**, 738 (1890).

[7] J. W. Dienske, *Rec. Trav. Chim. Pays-Bas*, **50**, 165 (1931).

[8] A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896).

thiocyanate,[9] and ethyl thiocyanate[10] were prepared as has been described in the literature. *p*-Tolyl thiocyanate and *m*-tolyl thiocyanate were prepared by the same method from the corresponding toluidines. *p*-Tolyl thiocynate, bp 127—129°C/19 mmHg; *m*-tolyl thiocyanate, bp 111—115°C/11 mmHg.

Preparation of Thioiminocarbonates. After a mixture of phenyl thiocyanate (0.1 mol, 13.5 g) and powdered sodium cyanide (0.0143 mol, 0.7 g) in absolute methanol (200 m*l*) has been stirred at 0°C for 6 hr, the methanol was evaporated *in vacuo*. Petroleum ether (200 m*l*) was added, and the mixture was washed with water two times. An organic layer was separated and dried with anhydrous sodium sulfate. The filtrate was evaporated, and the residual oil was distilled *in vacuo*; bp 82—89°C/3 mmHg. The recrystallization of the distillate, which solidified at room temperature, from petroleum ether gave 12 g (72%) of *O*-methyl *S*-phenyl thioiminocarbonate as a transparent rhombic crystal; mp 35—36°C. IR: 3300 (NH), 1628 cm^{-1} (C=N). NMR (in CCl_4) τ 5.94 (3H, s, OCH_3), 2.86 (1H, s, NH), 2.27 (5H, s, C_6H_5). In a similar way, other thioiminocarbonates were prepared. Their physical properties and elemental analyses are listed in Table 4.

Effects of Catalysts. To a solution of *p*-tolyl thiocyanate (0.05 mol) in absolute methanol (50 ml), we added 0.01 mol of a catalyst, after which the mixture was stirred at 0°C for 1 hr. Then the methanol was evaporated under reduced pressure, and ether was added to the residue. A usual work-up and distillation gave a colorless oil. Sodium cyanide, sodium azide, and sodium methoxide were effective, and *O*-methyl *S*-*p*-tolyl thioiminocarbonate was obtained, as is shown in Table 1. Triethylamine, sodium thiocyanate, potassium iodide, triphenylphosphine, sodium acetate, and mercuric cyanide were ineffective, and the *p*-tolyl thiocyanate was recovered unchanged (77—99%).

Determination of the Reaction Rates. Sodium cyanide ($1.17—10.5\times10^{-3}$ mol) was dissolved in a solution of 2.94×10^{-2} mol of aryl thiocyanates in 200 m*l* of absolute methanol placed in a constant-temperature bath at 0±0.05°C. At various intervals, 15-m*l* aliquots were removed and poured into a mixture of *n*-hexane (10 m*l*) and saturated aqueous sodium chloride (50 m*l*). The sample was extracted and again with 10 m*l* of *n*-hexane. From each run thus obtained, the amount of thiocyanate were measured by glc.

The author wishes to thank Professor A. Kaji and Dr. J. Hayami for their discussions.

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9) F. Challenger, C. Higgingbottom, and A. Huntington, *J. Chem. Soc.*, **1930**, 26.

10) P. Walden, *Ber.*, **40**, 3214 (1907).