

Acknowledgment. This work was supported, in part, by Public Health Service Grant CA-07182 from the National Cancer Institute. J.P.A. was on leave of absence from the Departement de Recherche Fondamentale, Centre d'Etudes Nucleaires, Grenoble, France.

Registry No. PH₃, 7803-51-2; CH₃PH₂, 593-54-4; CF₃PH₂, 420-52-0; (CF₃)₂PH, 460-96-8; acetylene, 74-86-2; P₂H₄, 13445-50-6; (CH₃PH)₂, 53684-00-7; CH₃PHPH₂, 53684-01-8; CF₃PHPHCF₃, 462-57-7; HC≡CPH₂, 34627-31-1.

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Carbon-Chalcogen Bonds in Organosilicon Pseudohalides¹

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Received July 17, 1974

AIC40488R

Kinetic studies show that the reaction between trialkylcyanosilanes and sulfur in 1-chloronaphthalene is second order. Ease of C-X bond cleavage increases sharply for the heavier chalcogens. Organoisotellurocyanosilanes are not stable at room temperature.

Introduction

Cyanotrimethylsilane reacts with molten sulfur to give (CH₃)₃SiNCS as the sole product.²⁻⁵ A similar reaction occurs with selenium.⁴ In order to learn more about these systems, we have investigated the properties of the carbon-chalcogen bond in the series R₃SiNCX (X = O, S, Se) and have attempted to prepare the tellurium analog.

Results

I. Kinetic Studies. 1-Chloronaphthalene proved to be an excellent reaction medium; it had a high boiling point (263°) and would dissolve sulfur without solvolyzing the cyanosilanes. The reaction was monitored by following the growth of the NCS asymmetric stretching band (Table I; Figure 1).

When sulfur was allowed to react with a large excess of cyanotrimethylsilane, the reaction followed pseudo-first-order kinetics (Table II). At a stoichiometric ratio, as given by

$$8R_3SiCN + S_8 \rightarrow 8R_3SiNCS \quad (1)$$

the reaction followed second-order kinetics. Similar results are found for triethylcyanosilane, triisopropylcyanosilanes, and *tert*-butyl isocyanide. The measured rate constants are given in Table III.

II. Tellurocyanate Studies. Downs⁶ isolated Et₄N⁺TeCN⁻ and Austad, *et al.*,⁷ isolated tetramethylammonium and tetraphenylarsonium tellurocyanates. The asymmetric stretching mode of TeCN⁻ appears at 2082.0 ± 0.5 cm⁻¹ in both acetone and acetonitrile (lit. 2079,⁶ 2087 cm⁻¹). The saturation concentration in acetonitrile was 5.60 ± 0.06 × 10⁻³ M, giving a calculated molar extinction coefficient of 51 ± 2 l./mm mol).

Triphenylphosphine readily extracts selenium from solutions of selenocyanate ion⁸ to form triphenylphosphine selenide, which also can be made by direct combination. Triphenyl-

Table I. Infrared Peaks (cm⁻¹)

	-CN	-NCS
(CH ₃) ₃ Si-	2189.5 (7.17) ^a	2076 (217.5)
(C ₂ H ₅) ₃ Si-	2187.0 (6.8)	2072 (213)
(<i>i</i> -C ₃ H ₇) ₃ Si-	2185.5 (5.43)	2069 (226)

^a Molal extinction coefficient in kg/(mol mm).

Table II. (CH₃)₃SiCN-S₈ Kinetic Data

80.10°, [Me ₃ SiCN] = 0.593 m			100.20°, [Me ₃ SiCN] = 0.06170 m		
<i>t</i> , hr	10 ⁴ [S ₈], m	-ln [S ₈]	<i>t</i> , hr	10 ³ [S ₈], m	1/[S ₈], m ⁻¹
0.00	8.15	7.11	0.0	7.636	131.0
0.50	7.32	7.22	29.8	6.311	158.4
2.08	5.15	7.57	145.6	4.011	249.3
3.42	3.71	7.90	175.4	3.669	272.5
5.75	2.16	8.44	317.1	2.581	387.4
25.20	(0.0235) ^a	(12.96) ^a	404.4	2.177	459.4

^a Calculated.

Table III. Second-Order Rate Constants (80.10°)

	10 ³ k ₂ , kg/(mol hr)
(CH ₃) ₃ SiCN	8.38 ± 0.38
(C ₂ H ₅) ₃ SiCN	3.04 ± 0.14
(<i>i</i> -C ₃ H ₇) ₃ SiCN	1.93 ± 0.14

phosphine does not react with tellurium.⁹ Addition of triphenylphosphine to K⁺TeCN⁻ in acetonitrile gave a yellow solution, which, upon evaporation, left a mixture of unreacted triphenylphosphine and [(C₆H₅)₃P]₂Te recently reported by Austad, *et al.*¹⁰ Attempts to remove the second triphenylphosphine molecule by recrystallization give rapid and complete decomposition. This compound also decomposes when dissolved in acetone, CCl₄, pentane, or THF, unless a large excess

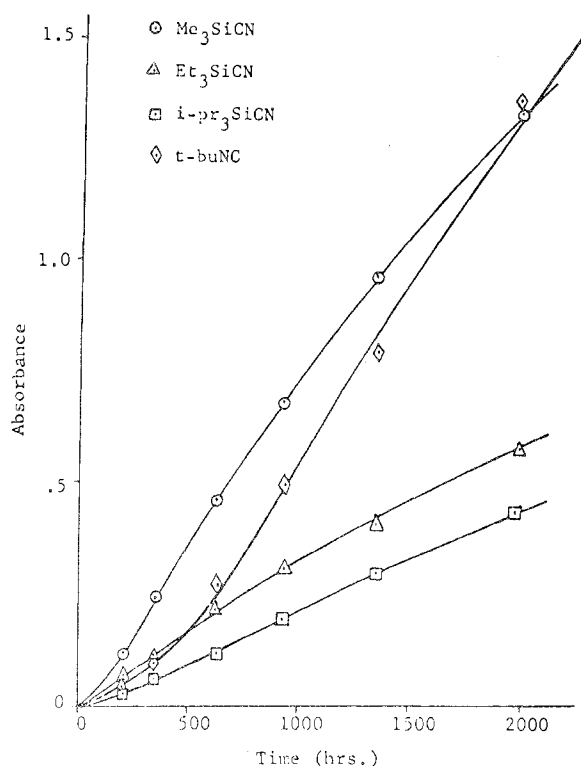
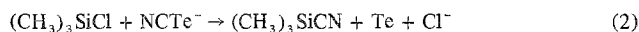


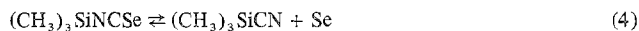
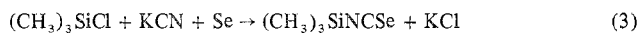
Figure 1. Rate plots of various cyanides reacting with sulfur.

of triphenylphosphine is present. Solutions of KNCTe^- were allowed to react with various chlorosilanes and triphenylbromogermane. In all cases the 2082-cm^{-1} band disappeared and another band grew in around 2190-cm^{-1} . The sole organometallic product isolated was the cyanide.



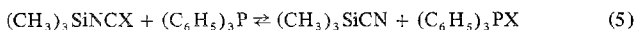
In the presence of excess KCN , eq 2 goes to completion, after which the NCTe^- band reappears. At no time did we observe any band around $2020\text{--}2050\text{-cm}^{-1}$ that might be attributable to $(\text{CH}_3)_3\text{SiNCTe}$, nor could any isothiocyanate be isolated, even transiently. No reaction occurs between a chlorosilane and KCN in the absence of tellurium.

The same system was studied using selenium in place of tellurium. Three reactions occur



Comparative rate studies indicate that reaction 3 seems to be the dominant one.

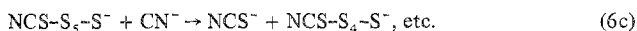
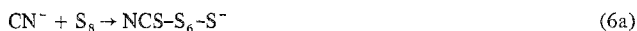
III. Chalcogen Exchange. Triphenylphosphine will extract selenium from $(\text{CH}_3)_3\text{SiNCSe}$.⁴ We investigated various combinations of pseudohalide and triphenylphosphines.



This reaction does not proceed in either direction where X is oxygen or sulfur. By contrast, $(\text{C}_6\text{H}_5)_3\text{PSe}$ reacts with $(\text{CH}_3)_3\text{SiCN}$ in 1-chloronaphthalene solution to form small quantities of $(\text{CH}_3)_3\text{SiNCSe}$. An equilibrium exists at 80° , with a constant of 6.4×10^{-5} , indicating 0.8% conversion to the isoselenocyanate. At room temperature, triphenylphosphine quantitatively removes all selenium from $(\text{CH}_3)_3\text{SiNCSe}$ in a 24-hr period. Triphenylarsine oxide quantitatively converts $(\text{CH}_3)_3\text{SiCN}$ to $(\text{CH}_3)_3\text{SiNCO}$ at room temperature. Attempts to get double exchange between $(\text{CH}_3)_3\text{SiNCX}$ and $(\text{C}_6\text{H}_5)_3\text{PY}$ were uniformly unsuccessful, even at temperatures up to 150° .

Discussion

Bartlett and Davis¹¹ have discussed the mechanism of the reaction between cyanide ion and sulfur in methanol. They found it to be a second-order reaction, with a rate constant of 33.6 l./mol sec ($=26.6\text{ kg./mol sec}$) at 25° . On the basis of their work and earlier work by Foss,¹² they proposed the mechanistic sequence



The first step determines the rate. Such ring opening seems to be the basic step in most reactions of elemental sulfur.¹³ In the molten state, this does not become important below 159° ; however, in solvents it occurs sufficiently at lower temperatures to enable rapid reaction with various thiophilic species.¹³

Recent spectroscopic studies have firmly established the existence of small amounts (*ca.* 5%) of trimethylisocyanosilane in equilibrium with the cyano isomer.^{14,15} Similar equilibria are found for triethyl and triisopropyl compounds. The rate at which the iso form converts to the normal form has been measured¹⁶ and appreciably decreases as the size of the alkyl group increases. A similar variation occurs in the rate of reaction with sulfur. In all cases this reaction is slow; even at 100° a 0.0617 m solution of $(\text{CH}_3)_3\text{SiCN}$ is only 17% converted to the isothiocyanate after 3 months. In view of the marked similarity of kinetics between the thionation of the cyanosilanes and that of cyanide ion, the most probable mechanism will involve attack of the silyl isocyanide on the S_8 ring in the rate-determining step. The slowness of the rate relative to that of cyanide ion reflects the lower nucleophilic character of covalent isocyanides, the lower polarity of 1-chloronaphthalene relative to methanol, and the low concentration of silyl isocyanide present. *tert*-Butyl isocyanide reacted at about the same rate as $(\text{CH}_3)_3\text{SiCN}$ under comparable conditions. The alternative mechanism, involving attack on the Si-CN bond,⁴ now seems less likely, since the proximity of the large S_8 ring to the trialkylsilyl group should give rise to a substantially larger steric effect than is actually observed.

The same mechanism is consistent with the observed reaction between cyanosilanes and selenium. Gray selenium reacts rapidly with cyanosilanes at room temperature, while red and vitreous seleniums react more slowly.⁴ Gray selenium consists of chains, while the other two forms contain cyclic species. The Se-Se bond energy is appreciably lower than the S-S bond energy ($172\text{ vs. }226\text{ kJ/mol}$).¹⁷ Hence the chains should cleave appreciably at room temperature, making gray Se more reactive toward cyanosilanes than S_8 . The reactivity of the other allotropes of selenium remains low and in fact is less than their rate of conversion to gray selenium.

Organosilyl azides, fulminates, and isoselenocyanates show unexpectedly high thermal stability.^{4,5} This stabilizing power apparently is not enough to enable the isolation of R_3SiNCTe at room temperature. There exists the intriguing possibility that the "normal" isomer $(\text{CH}_3)_3\text{SiTeCN}$ would be stable enough for isolation. Compounds such as $(\text{C}_2\text{H}_5)_3\text{SiTeH}$,¹⁸ $[(\text{C}_2\text{H}_5)_3\text{Si}]_2\text{Te}$,¹⁸ and $[(\text{CH}_3)_3\text{Si}]_2\text{Te}$ ¹⁹ are known. No "normal" organosilicon pseudohalide has ever been isolated, though evidence exists for the transient $(\text{CH}_3)_2\text{C}_4\text{H}_9\text{SiOCN}$,²⁰ which easily rearranges to the more stable "iso" form.

Exchange reactions with triphenylphosphine further emphasize the difference between the O and S on the one hand and the Se and Te species on the other. Bartlett¹¹ reported no sulfur exchange between CN^- and SCN^- , CN^- and $(\text{C}_6\text{H}_5)_3\text{PS}$, or SCN^- and $(\text{C}_6\text{H}_5)_3\text{P}$. Triphenylphosphine will remove Se and Te from the chalcocyanate ions in solution and likewise will remove Se from $(\text{CH}_3)_3\text{SiNCSe}$. The C-Te bond

is too weak to exist in ordinary covalent compounds, and the compound $(C_6H_5)_3PTe$ itself can only exist as its triphenylphosphine adduct.⁹ The ease of oxygen transfer from triphenylarsenic oxide suggests that the corresponding sulfide and selenide may serve as chalcogenating agents. These compounds, like $[(C_6H_5)_3P]_2Te$, cannot be prepared by direct combination.²¹

Experimental Section

General Data. Because of the extreme sensitivity of organosilyl pseudohalides to moisture and in order to get reproducibility of kinetics data, rigorous precautions were used to exclude water. Glassware was generally flame-dried and stored in ovens (110°) before use. Reactants and solvents were dried as thoroughly as possible before use. Tellurocyanate and exchange reactions were carried out in a drybox under a nitrogen atmosphere.

Reagents. Acetone, acetonitrile (Fisher ACS Certified), and 1-chloronaphthalene (Matheson Practical grade) were dried over P_4O_{10} , distilled, and used immediately. Potassium cyanide (Fisher) was precipitated from methanol solution by addition of ethanol, dried, and used immediately. Potassium selenocyanate was prepared from aqueous KCN and selenium, dried, and stored for use. Tellurium (Alfa/Ventron 200-mesh powder) was washed several times with concentrated aqueous KCN to remove selenium impurity and then once with concentrated HCl, dried, and stored. Selenium (Fisher powder reagent grade) was used without further purification. Triphenylphosphine (Alfa/Ventron) was recrystallized from methanol and used immediately. Trimethylchlorosilane (Fisher) was distilled; the fraction boiling at 57.2–57.4° was collected and used immediately. Triphenylchlorosilane and triphenylbromogermane (Alfa/Ventron) were recrystallized from petroleum ether (bp 85–110°) three times before using. Rhombic sulfur was purified by hot-filtering from benzene solution, followed by recrystallization three times from benzene.

Instrumentation. Infrared spectra were run on a Beckman IR-12 recording spectrophotometer, using matched KBr solution cells of 0.5-mm path length. Peak positions were determined to ± 1 cm^{-1} . Chromatographic purification was done on a Hewlett-Packard 700 laboratory chromatograph containing a 6-in. stainless steel column (1/2-in. o.d.) packed with 10% SE-30 on Chromosorb W (60–80 mesh). Helium was used as carrier gas.

Cyanosilanes. Trimethylcyanosilane and triethylcyanosilane were prepared by allowing Me_3SiCl and Et_3SiBr to react with silver cyanide and purified using vapor-phase chromatography. Triisopropylcyanosilane was prepared by mixing the chloride with excess Me_3SiCN in a sealed vial for 3 days at room temperature. Exchange was complete under these conditions. (*i*- C_3H_7) $_3SiCN$, bp 226.8° (743 mm), was separated and purified by vapor-phase chromatography. *Anal.* Calcd for $C_{10}H_{21}NSi$: C, 65.5; H, 11.6. Found: C, 65.1; H, 11.3.

Kinetic Studies. All reactions were done in a constant-temperature bath using Fisher stabilized oil at temperatures of 80.10 or 100.20 \pm 0.05°. Reactions were carried out using glass reaction vessels with Teflon stopcocks attached to a glass manifold through which dry N_2 passed. Up to ten reactions could be done simultaneously. Samples were withdrawn using carefully dried long capillary droppers and immediately studied by infrared spectroscopy. Rigorous cleaning of reaction vessels and purification of reactants were required to ensure reproducibility.

Organometal Halide Addition to KCN + Te. To a 250-ml flask under a nitrogen atmosphere containing a stirring bar, 2.45 g (37.6 mmol) of KCN, and 5.94 g (46.6 mg-atoms) of Te powder was added 100 ml of acetonitrile. The mixture was refluxed for 19 hr to give a reddish brown solution, which showed a sharp band at 2081.5 cm^{-1} in the infrared spectrum. This solution was mixed for 1 day at room temperature and then placed in a Dry Ice–3-pentanone bath (–42°). To the cooled solution was added dropwise 5.0 ml (38 mmol) of $(CH_3)_3SiCl$. The solution was stirred for 4 hr, after which the excess Te and KCN were allowed to settle. The solution then warmed slowly at room temperature. No further black precipitate formed. Infrared spectroscopy showed the absence of any band at 2082 cm^{-1} , but an intense band at 2191 cm^{-1} and weaker bands at 2090 and 2104 cm^{-1} had appeared.

Trimethylchlorosilane Addition to KCN + Se. Gray selenium (0.197 g, 249 mg-atoms) and KCN (0.164 g, 2.52 mmol) were placed in a 50-ml erlenmeyer flask and dried for 5 hr in an evacuated desiccator. Upon the addition of 25.0 ml of a 0.101 M solution of $(CH_3)_3SiCl$ in CH_3CN , reaction could be observed. Infrared samples were removed periodically. Peaks at 2067 and 2191 cm^{-1} appeared almost immediately and grew steadily with time; the former peak was always the stronger. In addition, a peak at 2090 cm^{-1} could be observed; this was attributed to HCN. Relative intensities of the three peaks varied somewhat during different runs, depending on the care with which water was excluded. When $(CH_3)_3SiCN$ was added to gray selenium, nearly identical results were observed, except that the peak at 2067 cm^{-1} grew more slowly.

Pseudohalide–Phosphine Exchange. These reactions were done both as neat and in solution. The two reagents (the phosphine compound usually in excess) were put in a Bantaware flask, which was sealed and heated. The reactions would be monitored by infrared spectroscopy, studying the 2000–2300- cm^{-1} region.

Reaction of KCN + Te with Triphenylphosphine. A mixture of 0.33 g (2.6 mg-atoms) of Te and 0.17 g (2.6 mmol) of KCN was placed in a 50-ml erlenmeyer flask equipped with magnetic stirring bar. To this 25 ml of acetonitrile was added. The mixture was stirred for 24 hr, after which 0.74 g (2.8 mmol) of triphenylphosphine was added. No black solid precipitated. The mixture was stirred for 48 hr at room temperature, after which the unreacted KCN and Te were filtered off. Evaporation of solvent left a mixture of yellow and white crystals. A portion dissolved in CCl_4 to give a yellow solution whose coloration rapidly disappeared, and black tellurium settled out. The white solid could be removed through its preferential solubility in acetonitrile, though upon occasion the yellow solid would suddenly turn black. No distinct melting point was observed, but decomposition occurred about 81° (lit. dec pt 83–85°). *Anal.* Calcd for $C_{36}H_{30}P_2Te$: Te, 19.57. Found: Te, 19.34.

Acknowledgment. We are grateful to Mr. Kenneth V. Smith for his aid in handling bis(triphenylphosphine)tellurium and for helpful discussions. Some of the equipment and chemicals used in this work were purchased under a Frederick Gardner Cottrell grant from the Research Corp. J.S.T. thanks the University of Cincinnati for a Summer Faculty Fellowship in support of this work in its early stages.

Registry No. $(CH_3)_3SiCN$, 7677-24-9; $(C_2H_5)_3SiCN$, 18301-88-7; (*i*- C_3H_7) $_3SiCN$, 35856-38-3; S₈, 10544-50-0; $[(C_6H_5)_3P]_2Te$, 53432-65-8; $(C_6H_5)_3P$, 603-35-0; $(CH_3)_3SiCl$, 75-77-4; $(C_6H_5)_3PSe$, 3878-44-2; Se, 7782-49-2; Te, 13494-80-9; KCN, 151-50-8.

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