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The Condensation–Polymerization of Pentamethyldisilanyl Cyanide[1] and Related Compounds[2]

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Pentamethyldisilanyl cyanide and heptamethyltrisilanyl cyanide have been found to undergo a condensation–polymerization reaction on heating to give trimethylsilyl cyanide and higher methylcyanopolysilanes. Pentamethyldisilanyl chloride and a mixture of methylchlorodisilanes were also found to undergo analogous reactions when heated with silver cyanide.

In a previous paper[4] it was shown that pentamethyldisilanyl cyanide, $(CH_3)_3SiSi(CH_3)_2CN$, decomposed upon heating to give trimethylsilyl cyanide and less volatile products. The present investigation was carried out in order to study this reaction in greater detail.

Experimental

Materials.—Pentamethyldisilanyl chloride and cyanide were prepared as previously described[4] and were of a similar state of purity. The cyanide was obtained in improved yields (77%) and it was found to melt sharply at 25.0–25.5°. The mixture of methylchlorodisilanes[5] employed boiled at 153–156° and consisted mainly of $Cl_2CH_3SiSiCH_3Cl_2$ and $Cl_2CH_3SiSi(CH_3)_2Cl$.[6,7] Unless otherwise stated all reactions were carried out in an atmosphere of dry nitrogen.

Condensation–Polymerization of Pentamethyldisilanyl Cyanide. I.—A Nester gold-plated monel metal semimicro spinning band distillation column (23 theoretical plates) was employed. When $(CH_3)_3SiSi(CH_3)_2CN$ (12.2 g.) was refluxed (oil-bath temperature 175°) in a 25-ml. flask attached to the column it began to turn dark brown. After heating at this temperature for 7 hr. all volatile material was removed by distillation. The maximum oil-bath temperature employed was 230°.

The most volatile fraction consisted of $(CH_3)_3SiCN$ (5.7 g., b.p. 116–117.5°, $n^{26}\text{D}$ 1.3899, d^{30}_4 0.7830). The infrared spectrum was essentially identical with that reported in the literature.[8] The reported values are: b.p. 117.8°,[8] $n^{25}\text{D}$ 1.3910,[9] $n^{26}\text{D}$ 1.3883,[9] and d^{30}_4 0.7834.[8] The next most volatile fraction was unreacted $(CH_3)_3SiSi(CH_3)_2CN$, (0.8 g., b.p. 85° at 34 mm., reported[4] 87° at 34 mm.; confirmed by infrared spectrum[4]).

Redistillation of a 4.0-ml. fraction of an orange colored oil (b.p. 87–95° at 34–0.6 mm.) produced: (a) $(CH_3)_3Si[Si(CH_3)_2]_4CN$, (1.5 ml., b.p. 67.5–71.0° at 0.2 mm. *Anal.*[10] Calcd. for $C_{12}H_{33}Si_5N$: C, 43.43; H, 10.02; Si, 42.32; N, 4.22; mol. wt., 331.8. Found: C, 43.37; H, 10.83; Si, 42.09; N, 4.27; mol. wt.,[10] 330). (b) $(CH)_3)_3Si[Si(CH_3)_2]_{4.5}CN$ (2.0 ml., b.p. 92.5–100.0° at 0.25 mm. *Anal.* Calcd. for $C_{13}H_{36}Si_{5.5}N$: C, 43.26; H, 10.05; Si, 42.80; N, 3.88; mol. wt., 360.9. Found: C, 43.21; H, 11.11; Si, 42.01; N, 4.11; mol. wt., 360).

The brown tarry residue which remained was dissolved in diethyl ether and the solution was passed through an alumina chromatography column. After removing the ether, the oil which remained was molecularly distilled in a micro sublimator. This produced $(CH_3)_3Si[Si(CH_3)_2]_7CN$ (0.5 ml. *Anal.* Calcd. for $C_{18}H_{51}Si_8N$: C, 42.70; H, 10.15; Si, 44.38; N, 2.77; mol. wt., 506.3. Found: C, 41.35; H, 10.01; Si, 44.38; N, 2.72; mol. wt., 494).

II.—$(CH_3)_3SiSi(CH_3)_2CN$ (12.79 g.) was heated in the apparatus described above at oil-bath temperatures from 100 to 160° but no major reaction occurred until the temperature was maintained at 175–180°. The material was heated at this temperature until distillation produced 3.94 g. of $(CH_3)_3SiCN$, b.p. 116–118°, $n^{25}\text{D}$ 1.3915. Fractionation of the dark colored less volatile material produced: (a) Impure $(CH_3)_3SiSi(CH_3)_2CN$, 2.11 g., b.p. 71–73° at 21 mm., $n^{30}\text{D}$ 1.4301, m.p. 17–20°; pure $(CH_3)_3SiSi(CH_3)_2CN$, b.p. 73.1° at 18 mm., $n^{30}\text{D}$ 1.4373,[4] m.p. 25.0–25.5°). (b) $(CH_3)_3Si[Si(CH_3)_2]_2CN$, 2.52 g., b.p. 36–40° at 0.4 mm., mol. wt. found 223, mol. wt. calcd. 215.4. A liquid of similar b.p. (0.55 g.) which was partly hydrolyzed during preparation for analysis was also obtained. *Anal.* Calcd. for $C_8H_{21}Si_3N$: C, 44.60; H, 9.78; Si, 39.12; N, 6.50. Found: C, 44.58; H, 9.78; Si, 39.17; N, 6.34. It is believed that in this compound the cyanide group is attached to a terminal silicon atom since the proton magnetic resonance spectrum of this material gave three peaks in the ratio 2:2:3. The chemical shifts with respect to $CHCl_3$ (upfield) were 7.16, 7.30, 7.34 p.p.m.[11] By analogy, it is assumed that the cyanide group is present on a terminal silicon atom in other members of the series $(CH_3)_3Si[Si(CH_3)_2]_xCN$. (c) $(CH_3)_3Si[Si(CH_3)_2]_3CN$, 1.16 g., b.p. 65–75° at 0.4 mm. *Anal.* Calcd. for $C_{10}H_{27}Si_4N$: C, 43.88; H, 9.95; Si, 41.05; N, 5.12; mol. wt., 273.7. Found: C, 44.14; H, 10.00; Si, 41.20; N, 4.97; mol. wt., 286. (d) $(CH_3)_3Si[Si(CH_3)_2]_4CN$, 0.91 g., b.p. 81–85° at 0.4 mm. *Anal.* Calcd. for $C_{12}H_{33}Si_5N$: C, 43.43; H, 10.02; Si, 42.32; N, 4.22; mol. wt., 331.8. Found: C, 43.40; H, 9.82; Si, 42.48; N, 4.30; mol. wt., 333. (e) A fraction, 0.10 g., b.p. 27–35° at 0.4 mm., which was not analyzed but was believed to be a mixture of methylcyanopolysilanes. (f) A dark brown tarry residue (0.86 g.) which upon molecular distillation produced: (1) A viscous yellow oil which had the composition $NC(CH_3)_2Si[Si(CH_3)_2]_7CN$, 0.24 g. *Anal.* Calcd. for $C_{18}H_{48}Si_8N_2$: C, 41.79; H, 9.35; Si, 43.44; N, 5.42; mol. wt., 517.3. Found: C, 40.84; H, 10.15; Si, 43.73; N, 5.26; mol. wt., 507. This substance, which represented 2.1% by weight of the volatile material produced in the reaction, could have been formed from a small amount of $NC(CH_3)_2SiSi(CH_3)_2CN$ (approximately 0.6%) impurity present in the starting material. This could have resulted from the presence of a very small amount of $Cl(CH_3)_2SiSi(CH_3)_2Cl$ impurity in the $(CH_3)_3SiSi(CH_3)_2Cl$ used to prepare $(CH_3)_3SiSi(CH_3)_2CN$. (2) A dark gummy nondistillable residue (0.62 g.) which represented 4.86% of the weight of the starting material. It had the appearance and consistency of plycine wax. It was soluble in ether and when warmed it melted to a gummy resin.

The total weight of material recovered from the reaction was 94.2% of the weight of the $(CH_3)_3SiSi(CH_3)_2CN$ employed.

Condensation–Polymerization of Heptamethyltrisilanyl Cyanide.—$(CH_3)_3Si[Si(CH_3)_2]_2CN$ (0.9850 g.) was sealed under vacuum in a magnetic break-seal tube and was heated in an oil bath at 175–195° for approximately 60 hr., by which time it had turned dark brown. On opening the tube on a high vacuum

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[1] No assumption is made as to whether this compound or any other organosilicon cyanide described in this communication has the normal cyanide or the isocyanide structure. For convenience they are all written as normal cyanides.

[2] This report is based on portions of a thesis to be submitted by Joseph V. Urenovitch to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The work is, in part, a contribution from the Laboratory for Research on the Structure of Matter, University of Pennsylvania, supported by the Advanced Research Projects Agency, Office of the Secretary of Defense.

[3] Alfred P. Sloan Research Fellow.

[4] A. D. Craig, J. V. Urenovitch, and A. G. MacDiarmid, *J. Chem. Soc.*, 548 (1962).

[5] The sample of mixed methylchlorodisilanes was kindly presented by the General Electric Co., Waterford, N. Y.

[6] M. Kumada and M. Kuriyagawa, Japanese Patents 7222 and 7223 (1954); *Chem. Abstr.*, **50**, 10125 (1956).

[7] G. D. Cooper and A. R. Gilbert, *J. Am. Chem. Soc.*, **82**, 5042 (1960).

[8] J. J. McBride and H. C. Beachell, *ibid.*, **74**, 5247 (1952).

[9] T. A. Bither, W. H. Knoth, R. V. Lindsey, and W. H. Sharkey, *ibid.*, **80**, 4151 (1958).

[10] All analyses and molecular weight measurements were performed by Galbraith Laboratories, Knoxville, Tenn. Molecular weights were determined by vapor pressure osmometry in benzene solution. The precision of the measurements was approximately 3% in the molecular weight range investigated.

[11] The proton magnetic resonance spectra of a number of pentamethyldisilanyl compounds will be reported in greater detail elsewhere.

system no noncondensable gases were observed. Less volatile material was separated from $(CH_3)_3SiH$ (3.1 mg.; confirmed by infrared spectrum[12]), by passage through a trap at −96°. The $(CH_3)_3SiH$ represented 0.31% by weight of the $(CH_3)_3Si[Si(CH_3)_2]_2CN$ used. The condensate in the −96° trap consisted primarily of $(CH_3)_3SiCN$. After several fractional evaporations from a trap at −23°, $(CH_3)_3SiCN$ (0.2379 g., mol. wt. found 102.4, mol. wt. calcd. 99.2, m.p. 9.9–10.4°, m.p. reported[13] 11.5°; confirmed by infrared spectrum[8]) was obtained. Some difficulty was experienced in quantitatively removing last traces of $(CH_3)_3SiCN$ dissolved in the oily residue.

Molecular distillation of the material which remained in the reaction flask produced: (a) $(CH_3)_3Si[Si(CH_3)_2]_5CN$. *Anal.* Calcd. for $C_{14}H_{39}Si_6N$: C, 43.11; H, 10.08; Si, 43.22; N, 3.59; mol. wt., 390.0. Found: C, 43.22; H, 10.08; Si, 43.19; N, 3.37; mol. wt., 370. (b) A residual tan colored, sticky grease which was soluble in ether.

Condensation–Polymerization of Pentamethyldisilanyl Chloride.—$(CH_3)_3SiSi(CH_3)_2Cl$ (16.0 ml., 13.7 g.) and AgCN (11.2 g.) were sealed in a thick walled flask and were heated at 190–210° for 20 hr. with magnetic stirring. A small Vigreux column was attached to the flask and upon distillation there was obtained: (a) $(CH_3)_3SiCl$ (6.0 g., b.p. 59–61°, lit.[14] 57.3°; hydrolyzable chlorine found 32.7%, calcd. 32.6%; confirmed by infrared spectrum[15]). (b) An unidentified liquid, (3.0 ml., b.p. 67–102°, found 30.4% hydrolyzable chlorine; infrared spectrum showed no cyanide grouping and it was not similar to $(CH_3)_3SiCl$). (c) An unidentified sticky residue.

Condensation–Polymerization of Methylchlorodisilanes Using Cyanide Catalysts. I. With Methyl Cyanide.—A mixture of $CH_3Cl_2SiSiCl_2CH_3$ and $(CH_3)_2ClSiSiCl_2CH_3$ (83.2 g.) was refluxed with CH_3CN (2.5 g.) for 24 hr. The reflux temperature (150°) remained constant during this period. Silver cyanide (2.5 g.) was then added and within 4 hr. the temperature had decreased to 128°.

II. With Silver Cyanide.—A similar mixture of methylchlorodisilanes (105.3 g.) was refluxed with AgCN (8.4 g.) for 27 hr. during which time the reflux temperature fell to 88° and remained constant at this value for 4 hr. Distillation through a Vigreux column yielded 34.7 g. of material, b.p. 65–75°. Distillation was stopped when the flask temperature reached 147°. Another 1.1 g. of AgCN was added and the initial reflux temperature of 116° dropped to 88° in 32 hr. and remained constant at this value for an additional 7 hr. Distillation produced 13.4 g. of material, b.p. 65–75°. Distillation was stopped when the flask temperature reached 132°. Addition of two further 1.1-g. samples of AgCN produced similar decreases in reflux temperatures. The total weight of volatile material collected was 57.2 g. Distillation of the less volatile material gave 12.3 g. of a liquid, b.p. 75–139°, which was then added to the distillate previously collected. A dark brown sticky residue remained.

Refractionation of the combined distillates through a Podbielniak still (mini-Cal series 3400) produced: (a) A mixture of methylchlorosilanes (58.0 g., b.p. 66–70°; lit.[14] b.p. for CH_3SiCl_3 65.7°, for $(CH_3)_2SiCl_2$ 70.0°, for $(CH_3)_3SiCl$ 57.3°; found 65.4, 65.3% hydrolyzable chlorine; calcd. for CH_3SiCl_3 71.2%, for $(CH_3)_2SiCl_2$ 54.9%, for $(CH_3)_3SiCl$ 32.6%). If it is assumed that no $(CH_3)_3SiCl$ was present, the chlorine content of the mixture indicates that it consisted of 57% CH_3SiCl_3 and 43% $(CH_3)_2SiCl_2$. (b) A mixture of methylchlorodisilanes (6.3 g., b.p. 137–140°; lit.[16] b.p. for $(CH_3)_3SiSi(CH_3)_2Cl$ 134–135°, for $Cl(CH_3)_2SiSi(CH_3)_2Cl$ 148°; found 29.5, 29.1% hydrolyzable chlorine; calcd. for $(CH_3)_3SiSi(CH_3)_2Cl$ 21.3%, for $Cl(CH_3)_2SiSi(CH_3)_2Cl$ 37.9%). (c) Approximately 2 ml. of an unidentified viscous oil.

III. With Silver Cyanide and Methylmagnesium Bromide.—A mixture of methylchlorodisilanes (166.5 g.) was refluxed with AgCN (18.3 g.) for 17 hr., during which time the reflux temperature had decreased to 84.5°. It then remained constant at this temperature for 5 hr. Distillation yielded 73.5 g. of volatile material, b.p. 66.5–125.5°. An excess of an ethereal solution of CH_3MgBr was added to the material remaining in the reaction flask and after refluxing for approximately 8 hr. excess Grignard reagent was destroyed by the addition of 10% hydrochloric acid until most of the solid material had dissolved. After filtration the ethereal layer was dried with anhydrous Na_2SO_4. After removing the ether by distillation the residue was fractionated through a Vigreux column. This produced: (a) $(CH_3)_3SiSi(CH_3)_3$ (7.5 ml., b.p. 111–113°; $n^{20}\mathrm{D}$ 1.4221; reported: b.p. 112°,[16] $n^{20}\mathrm{D}$ 1.4229,[16] and $n^{24.4}\mathrm{D}$ 1.4207[17]). (b) $(CH_3)_3Si[Si(CH_3)_2]_2CH_3$ (4.5 ml., b.p. 174–178°, $n^{20}\mathrm{D}$ 1.4551; mol. wt. found 198.2, calcd. 204.5; reported: b.p. 175–176° at 750 mm.,[18] 180° at atm.,[19] $n^{20}\mathrm{D}$ 1.4612,[18] 1.4599[19]). The infrared spectrum was consistent with that expected for octamethyltrisilane. (c) A viscous oily residue. After removal of traces of siloxane impurity by H_2SO_4,[18] fractionation on the Nester spinning band column produced: (1) $(CH_3)_3Si[Si(CH_3)_2]_3CH_3$ (10.5 ml., b.p. 110–111° at 15.0 mm., $n^{20}\mathrm{D}$ 1.4871, d^{20}_4 0.8073; mol. wt. found 259.6, calcd. 262.7; reported[18]: b.p. 112–113° at 16 mm.; $n^{20}\mathrm{D}$ 1.4877, and d^{20}_4 0.8066). (2) $(CH_3)_3Si[Si(CH_3)_2]_4CH_3$ (5.5 ml., b.p. 118–120° at 3.6 mm., $n^{20}\mathrm{D}$ 1.5096, d^{20}_4 0.8377. *Anal.* Calcd. for $C_{12}H_{36}Si_5$: C, 44.92; H, 11.31; Si, 43.77; mol. wt., 320.9. Found: C, 44.98; H, 11.36; Si, 43.69; mol. wt., 320). (3) Three higher boiling fractions together with an oily residue were also obtained in this fractionation. It appeared that these may have been mixtures of methylpolysilanes and species containing Si–CH_2–Si linkages. The latter species could possibly be formed by cleavage of Si–Si bonds during the Grignard reaction.[20a,b]

Results and Discussion

On heating pentamethyldisilanyl cyanide at 175° for 7 hr. a novel condensation reaction was found to occur and 74% of the cyanide present in the $(CH_3)_3SiSi(CH_3)_2CN$ was liberated as $(CH_3)_3SiCN$. The material remaining consisted of a mixture of methylcyanopolysilanes of general composition $(CH_3)_3Si[Si(CH_3)_2]_xCN$[21] from which there was isolated the new compounds $(CH_3)_3Si[Si(CH_3)_2]_4CN$ and $(CH_3)_3Si[Si(CH_3)_2]_7CN$. A material which appeared to be a mixture of the methylcyanopenta- and hexasilanes was also obtained and only a small amount of unreacted $(CH_3)_3SiSi(CH_3)_2CN$ was recovered. Thus the reaction which occurred can be represented by the equation

$$x(CH_3)_3SiSi(CH_3)_2CN \longrightarrow (x-1)(CH_3)_3SiCN + (CH_3)_3Si[Si(CH_3)_2]_xCN \quad (1)$$

Seventy-nine per cent of the cyanide present in the $(CH_3)_3SiSi(CH_3)_2CN$ consumed was recovered as $(CH_3)_3SiCN$ and from this the calculated average value of x was 4.8.

In another experiment it was found that the new compound heptamethyltrisilanyl cyanide, $(CH_3)_3Si[Si(CH_3)_2]_2CN$, could be produced in 42% yield by heating pentamethyldisilanyl cyanide until distillation gave an amount of $(CH_3)_3SiCN$ which represented 49% of the cyanide present in the $(CH_3)_3SiSi(CH_3)_2CN$. The proton magnetic resonance spectrum of this compound showed that the cyanide group was attached to a terminal silicon atom. In addition, smaller quantities of $(CH_3)_3Si[Si(CH_3)_2]_3CN$, $(CH_3)_3Si[Si(CH_3)_2]_4CN$, and $NC(CH_3)_2Si[Si(CH_3)_2]_7CN$ were formed and approximately 16% of the $(CH_3)_3SiSi(CH_3)_2CN$ was recovered unchanged. The quantity of $(CH_3)_3SiCN$ isolated (based on the amount of $(CH_3)_3SiSi(CH_3)_2CN$ consumed) corresponded to an average value of 2.4 for x in eq. 1.

It was found that heptamethyltrisilanyl cyanide also underwent a condensation–polymerization reaction upon heating to give $(CH_3)_3SiCN$ and higher methylcyanopolysilanes from which $(CH_3)_3Si[Si(CH_3)_2]_5CN$ was isolated. The reaction which occurred can be represented by the equation

$$x(CH_3)_3Si[Si(CH_3)_2]_2CN \longrightarrow (x-1)(CH_3)_3SiCN + (CH_3)_3Si[Si(CH_3)_2]_{2x}CN \quad (2)$$

The value of x calculated from the quantity of $(CH_3)_3SiCN$ recovered was 2.1.

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(13) C. Eaborn, *J. Chem. Soc.*, 3077 (1950).

(14) C. Eaborn, "Organosilicon Compounds," Butterworths Scientific Publications, London, 1960, p. 177.

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(21) A detailed discussion of the infrared spectra of the cyanides of the higher silanes and related compounds will be presented elsewhere.

In all the above condensation reactions there was obtained a small quantity of grease-like or tarry material (presumably higher methylcyanopolysilanes) which could not be readily distilled but which was completely soluble in ether. It therefore appears that the condensation reactions proceeded smoothly to give almost exclusively higher molecular weight species of general formula $(CH_3)_3Si[Si(CH_3)_2]_xCN$.

Although the Si–Si bonds in all other pentamethyldisilanyl compounds[4,16,22] and in methylpolysilanes[18,19] have good thermal stability,[23] it seems that the Si–Si bond in $(CH_3)_3SiSi(CH_3)_2CN$ may be weakened by the formation of an intermediate species in which a lone pair of electrons from the cyanide group of one molecule interacts with vacant silicon 3d-orbitals of an adjacent molecule as previously suggested.[4] Rearrangement and cleavage (at the dashed line, Fig. 1) of an Si–Si bond in this activated species with the elimination of $(CH_3)_3SiCN$ could then take place, *viz.*

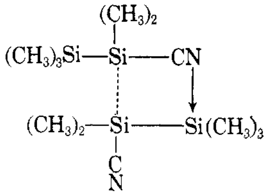

Figure 1.

$$2(CH_3)_3SiSi(CH_3)_2CN \longrightarrow (CH_3)_3SiCN + (CH_3)_3Si[Si(CH_3)_2]_2CN \quad (3)$$

However, the intermediate species may rearrange with the formation of free $(CH_3)_3Si\cdot$ radicals. This is suggested by the fact that under appropriate experimental conditions a very small amount of $(CH_3)_3SiH$ could be detected in the condensation of a methylcyanopolysilane. Reaction could therefore proceed as

$$(CH_3)_3SiSi(CH_3)_2CN \longrightarrow (CH_3)_3Si\cdot + \cdot Si(CH_3)_2CN \quad (4)$$

$$(CH_3)_3Si\cdot + (CH_3)_3SiSi(CH_3)_2CN \longrightarrow (CH_3)_3SiCN + (CH_3)_3Si\dot{S}i(CH_3)_2 \quad (5)$$

$$(CH_3)_3Si\dot{S}i(CH_3)_2 + (CH_3)_2\dot{S}iCN \longrightarrow (CH_3)_3SiSi(CH_3)_2Si(CH_3)_2CN \quad (6)$$

The small amount of $(CH_3)_3SiH$ might arise from attack of a C–H bond by a $(CH_3)_3Si\cdot$ radical, *viz.*

$$(CH_3)_3Si\cdot + H_3C\text{–}Si(CH_3)_2\text{–} \longrightarrow (CH_3)_3SiH + \cdot CH_2Si(CH_3)_2\text{–} \quad (7)$$

The formation of considerable quantities of $(CH_3)_3SiH$ has been observed when $(CH_3)_3SiSi(CH_3)_3$ is heated to 600°.[24] This reaction is believed to proceed by the formation of $(CH_3)_3Si\cdot$ radicals.

Either of the above reaction mechanisms is consistent with the nature of the more highly polymerized species obtained both from the condensation of $(CH_3)_3SiSi(CH_3)_2CN$ and $(CH_3)_3Si[Si(CH_3)_2]_2CN$. For example, the formation of $(CH_3)_3Si[Si(CH_3)_2]_3CN$ from $(CH_3)_3SiSi(CH_3)_2CN$ could occur as indicated by eq. 3 and 8.

$$(CH_3)_3Si[Si(CH_3)_2]_2CN + (CH_3)_3SiSi(CH_3)_2CN \longrightarrow (CH_3)_3SiCN + (CH_3)_3Si[Si(CH_3)_2]_3CN \quad (8)$$

This appears reasonable since some unreacted $(CH_3)_3SiSi(CH_3)_2CN$ was recovered from the reaction. It is possible that the condensation of the higher methylcyanopolysilanes might also occur with the elimination of $(CH_3)_3SiSi(CH_3)_2CN$ as well as $(CH_3)_3SiCN$. Thus the formation of $(CH_3)_3Si[Si(CH_3)_2]_5CN$ from $(CH_3)_3Si[Si(CH_3)_2]_2CN$ could take place as

$$2(CH_3)_3Si[Si(CH_3)_2]_2CN \longrightarrow (CH_3)_3SiSi(CH_3)_2CN + (CH_3)_3Si[Si(CH_3)_2]_3CN \quad (9)$$

$$(CH_3)_3Si[Si(CH_3)_2]_3CN + (CH_3)_3Si[Si(CH_3)_2]_2CN \longrightarrow (CH_3)_3SiCN + (CH_3)_3Si[Si(CH_3)_2]_5CN \quad (10)$$

Other species could be formed by an appropriate combination of reactions of the type given in eq. 3, 8, 9, and 10.

It was found that silver cyanide acted as an effective "catalyst" in the condensation–polymerization of pentamethyldisilanyl chloride, $(CH_3)_3SiSi(CH_3)_2Cl$, at 200° when it was mixed with an equimolar quantity of the chloride. The over-all reaction which occurred was analogous to that involving $(CH_3)_3SiSi(CH_3)_2CN$ and can be represented by the equation

$$x(CH_3)_3SiSi(CH_3)_2Cl \longrightarrow (x - 1)(CH_3)_3SiCl + (CH_3)_3Si[Si(CH_3)_2]_xCl \quad (11)$$

No $(CH_3)_3SiSi(CH_3)_2Cl$ was recovered unchanged and the amount of $(CH_3)_3SiCl$ produced represented 82% of the chloride present in the $(CH_3)_3SiSi(CH_3)_2Cl$ used. This gave an average value of 5.5 for x. The less volatile material formed was not identified but it was believed to be a mixture of methylchloropolysilanes.

Silver cyanide was also found to be a very effective catalyst in causing the condensation–polymerization of a mixture of methylchlorodisilanes consisting chiefly of $Cl_2CH_3SiSiCH_3Cl_2$ and $Cl_2CH_3SiSi(CH_3)_2Cl$. When the mixture was refluxed with 11.3% by weight of silver cyanide, CH_3SiCl_3 and $(CH_3)_2SiCl_2$ were evolved, the combined weight of which represented 55.1% of the weight of the methylchlorodisilanes used. It therefore appeared that a reaction of the type given by eq. 12 took place.

$$xCl_2CH_3SiSiCH_3Cl_2 \longrightarrow (x - 1)CH_3SiCl_3 + CH_3Cl_2Si(SiCH_3Cl)_xCl \quad (12)$$

The sticky resinous material remaining was treated with methylmagnesium bromide and distillation yielded octamethyltrisilane, $(CH_3)_3Si[Si(CH_3)_2]_2CH_3$; decamethyltetrasilane, $(CH_3)_3Si[Si(CH_3)_2]_3CH_3$; and the new compound dodecamethylpentasilane, $(CH_3)_3Si[Si(CH_3)_2]_4CH_3$. In view of the condensation–polymerization observed with $(CH_3)_3SiSi(CH_3)_2CN$, it appears likely that the catalytic effect of the silver cyanide is due to the transient formation of a cyanide such as $(CH_3)_2Si_2Cl_3CN$ which then undergoes a reaction of the type

$$x(CH_3)_2Si_2Cl_3CN \longrightarrow (x - 1)CH_3SiCl_2CN + CH_3Cl_2Si(SiCH_3Cl)_xCN \quad (13)$$

The Si–CN bonds are then presumably reconverted to Si–Cl linkages by silver chloride with regeneration of silver cyanide. This appears likely since it has been shown previously[25] that at elevated temperatures the reaction of $(CH_3)_3SiCl$ with AgCN is reversible. A similar type of mechanism is probably involved in the analogous reaction with $(CH_3)_3SiSi(CH_3)_2Cl$, although

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(22) J. V. Urenovitch and A. G. MacDiarmid, *J. Chem. Soc.*, 1091 (1963).

(23) *It was found in this Laboratory that a sample of* $(CH_3)_3Si[Si(CH_3)_2]_3CH_3$ when held at 260° *in vacuo* for 7 hr. showed no sign of decomposition.

(24) K. Shiina and M. Kumada, *J. Org. Chem.*, **23**, 139 (1958).

(25) E. C. Evers, W. O. Frietag, J. N. Keith, W. A. Kriner, A. G. MacDiarmid, and S. Sujishi, *J. Am. Chem. Soc.*, **81**, 4493 (1959).

good conversions could only be obtained if relatively large quantities of silver cyanide were employed.

An attempt to cause the condensation–polymerization of the mixture of methylchlorodisilanes using methyl cyanide as a catalyst was unsuccessful.

The condensation–polymerization of cyanodisilanes appears to offer a convenient method for synthesizing derivatives of the methylated polysilanes. In particular, the use of $(CH_3)_3SiSi(CH_3)_2CN$ makes it possible to synthesize, for the first time, monosubstituted derivatives of methylated higher silanes. These methylcyanopolysilanes should provide a convenient route for the preparation of many other monosubstituted derivatives.

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF WASHINGTON, SEATTLE, WASH., AND THE UNIVERSITY OF NEW ENGLAND, ARMIDALE, N.S.W., AUSTRALIA]

The Equilibrium between Peroxydisulfuryl Difluoride and Fluorosulfate Free Radicals

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Peroxydisulfuryl difluoride and fluorosulfate free radicals have been shown to exist in equilibrium below 600°K.[2] The temperature dependence of pressure at constant volume was used to calculate a series of K_p values between 450°K. and 600°K. This method indicated an enthalpy change of 22.0 kcal./mole, whereas a spectrophotometric method based on the temperature dependence of the absorption of the fluorosulfate radical at 474 mμ gave an enthalpy change of 23.3 kcal./mole.

The known chemistry of peroxydisulfuryl difluoride provides strong evidence for the equilibrium

$$S_2O_6F_2 \rightleftarrows 2SO_3F\cdot$$

Rupture of the relatively weak O–O peroxy linkage in the otherwise strongly bonded parent material results in two fluorosulfate radicals which add readily to molecules with ethylenic double bonds (*e.g.*, perfluoroethylene and perfluorocyclopentene[3]) and which will replace even chlorine from a large number of halogen-containing organic and inorganic molecules.[3]

The oxidizing capacity and structural stability of this fluorosulfate radical is shown by the ability of peroxydisulfuryl difluoride to oxidize substances such as nitric oxide,[4] nitrogen dioxide,[4] iodine,[5] bromine,[5] sulfur dioxide,[6] and sulfur tetrafluoride[3] to fluorosulfate derivatives. The preparation of peroxydisulfuryl difluoride by anodic oxidation[7] of a solution of an alkali metal fluorosulfate in fluorosulfuric acid, or from metallic fluorosulfates[7] by displacement reactions involving the use of elementary fluorine, are both strongly suggestive of the intermediate formation of fluorosulfate radicals.

Of similar equilibrium systems involving dissociation of a molecular species into two free radicals, that which has been most extensively studied is the nitrogen tetroxide–nitrogen dioxide equilibrium,[8,9] while a recently investigated one is that between tetrafluorohydrazine and the difluoroamino radical.[10]

When gaseous samples of the dimeric parent material were heated to about 100°, a yellow color developed. Convincing evidence that this was due to a reversible dissociation is provided by Fig. 1, which shows the temperature dependence of the visible and ultraviolet absorption spectrum in the 320–600 mμ region, at a constant concentration of the peroxy compound. The absorbance measurements in this wave length range were reproducible with increasing and decreasing temperatures up to 120°. Above this temperature, reaction apparently occurred with the quartz cell; on cooling the cell, the measured absorbance was always less than that recorded at a corresponding temperature during heating. As a result, absorbance was not measured for highly dissociated samples; therefore, equilibrium constants were not obtained from spectrophotometric measurements by a procedure like that used by Johnson and Colburn[10] in their investigation of the dissociation of tetrafluorohydrazine. The fine structure that is evident between 474 and 518 mμ is presumably due to electronic transitions to different vibrational energy levels in the excited electronic state.

The concentration dependence of the absorbance at constant temperature is evident from the experimental data shown in Fig. 2, but is further emphasized by Fig. 3 which shows plots of absorbance *vs.* the square root of the concentration of the peroxydisulfuryl difluoride at constant temperature.

The linear relationship shown in Fig. 3 is to be expected for any equilibrium

$$R_2 \rightleftarrows 2R\cdot$$

if the absorbance is due to R· but not to R_2 and if $C_{R_2} >> C_{R\cdot}$, where these symbols refer to the concentration of the undissociated and dissociated species, respectively. In this study R_2 is $S_2O_6F_2$ and R· is considered to be $SO_3F\cdot$. Since $A = C_{R\cdot}\epsilon l$ (where A is absorbance, $C_{R\cdot}$ is the concentration of the absorbing species, ϵ is the molar absorbancy index in l./mole-cm., and l is the path length in cm.), K_C, the equilibrium constant in terms of concentration, is given by

$$K_C = (C_{R\cdot})^2/C_{R_2} = A^2/(\epsilon^2 l^2 C_{R_2})$$

It follows that

$$\ln K_C = 2 \ln A - \ln \epsilon^2 l^2 C_{R_2}$$

If the absorbancy index is temperature independent and any change in C_{R_2} is negligible by comparison with C_{R_2}, a plot of log A *vs.* T^{-1} should be a straight line, having a slope corresponding to the change in internal energy for the reaction. The least squares "best fit" of the experimental spectrophotometric absorbance data to an equation of the form $\log A = B \times 10^3 T^{-1} + C$ gave the results shown in Table I for seven samples having different concentrations. An

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(1) Work done at the University of Washington while on sabbatical leave from the University of New England, Armidale, N.S.W., Australia.

(2) In a prefluorinated nickel vessel that had been conditioned with $S_2O_6F_2$ to render it inert to $S_2O_6F_2$ and dissociation or decomposition products.

(3) J. M. Shreeve and G. H. Cady, *J. Am. Chem. Soc.*, **83**, 4521 (1961).

(4) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 353 (1960).

(5) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 352 (1960).

(6) J. E. Roberts and G. H. Cady, *ibid.*, **82**, 354 (1960).

(7) F. B. Dudley, *J. Chem. Soc.*, 3407 (1963).

(8) M. Bodenstein, *Z. physik. Chem.*, **100**, 68 (1922).

(9) F. Verhoek and F. Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931).

(10) F. A. Johnson and C. B. Colburn, *ibid.*, **83**, 3043 (1961).