silyl ethers and amines should be stronger Lewis bases than their methyl analogs and that the base strength should decrease as silyl groups are replaced by methyl groups. However, in the amine series, the reverse has been found to be the case, $(SiH_3)_3N$ being the weakest base and $(CH_3)_3N$ being the strongest in the series.[20,26] This has been attributed to $d_\pi-p_\pi$ bonding involving the lone pair of electrons on the nitrogen and the 3d orbitals of the silicon[20,26-28] It also has been observed by using B_2H_6 as a reference acid that $(SiH_3)_2O$ is a much weaker Lewis base than $(CH_3)_2O$,[29] the latter, but not the former compound forming an adduct with B_2H_6 at $\sim -78°$.[19,29]

The results of the present investigation show that SiH_3OCH_3 is also a much weaker Lewis base than $(CH_3)_2O$ since it forms no addition compound with B_2H_6 at $-78°$. However, diborane is not a sufficiently strong acid to differentiate between the relative base strengths of SiH_3OCH_3 and $(SiH_3)_2O$. Boron trifluoride was of no use in measuring the base strength of SiH_3OCH_3 since SiH_3F was liberated at $-127.8°$ and on warming to room temperature the reaction represented by equation 8 occurred. This reaction is completely analogous

$$SiH_3OCH_3 + BF_3 \longrightarrow SiH_3F + CH_3OBF_2 \quad (8)$$
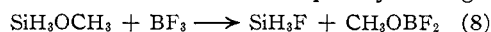
to that occurring between $(SiH_3)_2O$ and BF_3 under similar experimental conditions.[29,30]

(26) A. B. Burg and E. S. Kuljian, *J. Am. Chem. Soc.*, **72**, 3103 (1950).

(27) S. Sujishi and S. Witz, *ibid.*, **76**, 4631 (1954).

(28) A. G. MacDiarmid, *Quart. Rev.*, **10**, 208 (1956).

(29) (a) S. Sujishi, E. L. Gasner and A. D. Payton, Jr., Abstracts of papers presented at 133rd National Meeting of the American Chemical Society, San Francisco, 1958, p. 52-Q. (b) S. Sujishi, Ordnance Re-

The relative basicities of the ethers given above may be explained in two ways: (1) One SiH_3 group in SiH_3OCH_3 abstracts electrons from the oxygen atom by means of $d_\pi-p_\pi$ back-coördination approximately as strongly as do two SiH_3 groups in $(SiH_3)_2O$. Until the Si-O-C bond angle is ascertained, the validity of this somewhat unlikely assumption cannot be determined. (2) The enthalpy for the process

$$B_2H_6 \longrightarrow 2BH_3 \quad (9)$$
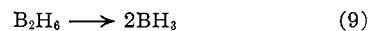
is 28.4 kcal./mole.[31] If the interaction energy of a BH_3 group with both SiH_3OCH_3 and $(SiH_3)_2O$ were less than that required to dissociate B_2H_6, then neither ether would form an isolable addition compound with B_2H_6; hence, even if SiH_3OCH_3 were in reality a considerably stronger base than $(SiH_3)_2O$, it would appear to have the same base strength. That this is indeed quite likely is apparent from the fact that $(CH_3)_2O \cdot BH_3$ is an unstable compound[19,32] and therefore any slight decrease in electron-donor ability of the oxygen could readily decrease the ether-BH_3 interaction energy to a point where insufficient energy for the B_2H_6 dissociation step would be available.

Acknowledgment.—The authors wish to thank Dr. E. R. Nixon for helpful discussions on the interpretation of infrared spectral data.

search Project No. TB 2-0001-(817), Contract No. DA-11-022 ORD-1264, Final Report, Aug., (1957).

(30) H. J. Emeléus and M. Onyszchuk, private communication, 1954.

(31) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 206 (1956).

(32) F. G. A. Stone, *Chem. Revs.*, **58**, 101 (1958).

The Reaction of Active Nitrogen with Liquid Siloxane Heptamer, D₇

BY JOSEPH L. WEININGER

The reaction of active nitrogen with the liquid cyclic siloxane heptamer D₇, $[(CH_3)_2SiO]_7$, was studied quantitatively in a flow system at -24 to $136°$. The chemical stability of the siloxane is shown by the fact that atomic nitrogen can be bubbled through the liquid to some extent, giving the characteristic afterglow downstream from the reaction vessel. The nitrogen atoms can, however, attack any bond of the compound D₇ in a reaction which leads mainly to the products HCN and NH_3. The comparable attack of active nitrogen on liquid n-hexadecane is more than ten times as vigorous, with 85% of the nitrogen atoms being converted to degradative N-containing gaseous compounds.

In an investigation of the reactions of active nitrogen with compounds in condensed states, the reaction with the cyclic siloxane heptamer D₇[1] was studied. Emphasis was placed on pure starting materials, an extended temperature range over which the reaction was observed, accurate determinations of the concentration of nitrogen atoms as well as reaction products and hence the determination of reaction yields. For comparison of the liquid siloxane with a liquid hydrocarbon the reaction of active nitrogen with n-hexadecane also was studied.

Experimental

The condenser-discharge system which was used in the study of the reaction of active nitrogen with polymers[2] was

modified for the reaction with liquid siloxane by converting a trap into a reaction vessel. A special glass lock in an inner ground joint surface locked a showerhead in place. This arrangement allowed the exchange of showerheads with orifices of different size as well as their removal to convert the apparatus to solid-state or vapor-phase work. The glass system was not poisoned except insofar as the siloxane vapor may have formed a film on the walls. In the course of an experiment purified dry nitrogen was passed through the discharge tube at the rate of 5 to 8 m./sec. and also flowed through the liquid in the reaction vessel. The liquid level was maintained 5 to 10 mm. above the gas entry ports so that the residence time of the gas in the liquid was at least 0.01 second. In that interval the nitrogen atoms produced in the discharge reacted with the siloxane, others recombined with each other and an appreciable fraction passed through the liquid and gave the yellow afterglow in the system downstream from the reaction vessel. After the reaction the liquid as well as

(1) $[(CH_3)_2SiO]_7$, tetradecyl methyl cycloheptasiloxane, m.p. $-26°$, b.p. 154° (20 mm.).

(2) J. L. Weininger, *J. Phys. Chem.*, **65**, 941 (1961).

TABLE I

REACTION OF ACTIVE NITROGEN WITH SILOXANE HEPTAMER D_7

Temperature, °C.	−24	0	24	71	100	136
Duration, min.	12.00	7.01	5.10	4.00	3.50	3.00
N_2 flow, ml./min.	520	520	520	520	520	520
N flow, ml./min.	417	414	401	414	396	401
Partial pressure of N atoms, microns	1880	1830	1770	1590	1675	1580
Total pressure, microns	4230	4130	4070	3590	3875	3630
Conversion						
$N_2 \rightarrow 2N$, %	40.0	39.8	38.6	39.8	38.1	38.6
Products:						
HCN, micron-liters	473	316	289	281	210	192
NH_3, micron-liters	106	61	68	66	59	92
Total N equivalent, micron-liters	579	377	357	347	269	284
Conversion						
N → N equivalent, %	6.2	7.1	9.8	13.2	11.6	15.0
Over-all yield, %	2.5	2.8	3.8	5.3	4.4	5.8

the condensable products were examined by gas chromatography and mass spectrometry.

Results

Table I gives the experimental conditions and results of experiments with D_7, and Table II contains data concerning the reaction of active nitrogen with *n*-hexadecane. The results of mass-spectrometric and chromatographic analyses are discussed separately.

Experiments were performed between −24 and 136°. The lower limit of this range is determined by the freezing point of the heptamer and the upper limit depends on its vapor pressure. The duration of the experiments was limited to a period sufficient to collect products for analyses, yet short enough to ensure a constant concentration of nitrogen atoms. From the short duration of the experiments it follows that only very small fractions of the liquid substrates were consumed. Other data in Table I refer to nitrogen atom concentration, measured by gas titration with nitric oxide, and the calculated value of about 40% for the conversion of nitrogen molecules to atoms in the present system. Next, the condensable nitrogen-containing products are tabulated. Quantitatively, these were HCN and NH_3 although traces of C_2N_2 and CH_3CN also were present. There was no evidence of the presence of NH_4CN, either in the liquid substrate or as a deposit from the vapor phase in the low-temperature experiments. Apparently, the concentrations or partial pressures of NH_3 and HCN were so small that these compounds did not combine to an appreciable extent. Except at the highest temperature of 136°, the percentage of ammonia in the product was constant at about 20%, whereas the reaction yield, from original molecular nitrogen to the final product, increased with temperature from 2.5% (at −24°) to 5.8% (at 136°). These values represent a lower limit. Since the atom concentration was measured 43 cm. upstream from the reaction vessel, a small but finite amount of the nitrogen atoms, at most 5%, was lost by recombination before reaching the reaction vessel. The "total nitrogen equivalent" stands for the sum of nitrogen-containing products. The conversion of N atoms to N equivalent, *i.e.*, the ratio of product formed to N atoms present, was plotted logarithmically against

reciprocal absolute temperature. A least-square fit of the slope of that plot gave an activation energy of 1.12 ± 0.03 kcal./mole for the process of formation of gaseous N-containing products.

Mass-spectrometric Analyses.—For each of the above experiments two gas samples were analyzed with a mass spectrometer. One sample was obtained by directly tapping the gas stream during the course of the reaction; the other sample was the reaction product, condensed in liquid nitrogen. Although the former contained mostly nitrogen, whereas the bulk of the latter was made up of HCN and NH_3, the remaining constituents were present in trace amounts to the same extent for both samples as well as for the different temperature at which the reaction was studied. A trace of methane was present; acetonitrile (mass numbers 39–41) was definitely identified and also peaks corresponding to mass numbers 42–44, 54–57 and 66–70. These would correspond to the following siloxane fragments: CH_3SiH, CH_3SiCH_2 or $SiOCH$ and $CSiOCH_2$.

Vapor-Phase Chromatography.—The liquid reaction substrate and the liquid condensate of the reaction product were examined with a temperature-programmed silicone-grease column. The present starting material, D_7, was extremely pure, since 0.002% D_6 was the only detectable impurity. The analyses showed that the reaction substrate retained lower cyclic siloxanes in the low temperature experiments whereas at high temperature these breakdown products of D_7 were carried with the volatile reaction products to the liquid nitrogen trap. For experiments at 100 and 136° the cyclic compounds D_4, D_5 and D_6 as well as the linear siloxane MD_4M were collected. In all cases only traces of these siloxanes were obtained, *i.e.*, at most 0.01%.

Reaction of Active Nitrogen with *n*-Hexadecane. —At comparable temperatures the vapor pressure of *n*-hexadecane (cetane) is slightly lower than that of D_7. Thus, *n*-hexadecane is a suitable choice for comparing the reactions of active nitrogen with a liquid hydrocarbon and a liquid siloxane. The reaction with *n*-hexadecane was studied at 26° in an analogous procedure to that used with D_7, with the results shown in Table II. In addition to the three major products (HCN, C_2N_2 and NH_3)

TABLE II

REACTION OF ACTIVE NITROGEN WITH n-HEXADECANE

Temp., 26°   Products

Duration, 6:00 min.	HCN	3230 μ-l (85.8%)
N$_2$ flow. 757 ml./min.	NH$_3$	327 μ-l (8.7%)
N flow, 398 ml./min.	C$_2$N$_2$	213 μ-l (5.6%)
Partial pressure of N		Total N
atoms, 1920 μ		Equivalent, 3983 μ-l
Total pressure, 4620 μ		Conversion
		N → N-equiv., 85.2%
Conversion		
N$_2$ → 2N, 26.3%		Over-all yield, 22.4%

there were seven unknowns, mostly in trace amounts, in the chromatogram of the gaseous reaction products. These were not identified, but mass spectrometry of the same sample established the presence of CH_3CN, H_2O and all hydrocarbon fractions from C_1 to C_6, the latter being about at the limit of resolution of the mass spectrometer. Some of these hydrocarbon fragments may be due to the same compound in the mass spectrometer, but fractions up to C_{16} are to be expected from the fragmentation of $C_{16}H_{34}$ by active nitrogen.

Discussion

Stability of Siloxane toward Active Nitrogen.—The present experiments show the chemical stability of the cyclic siloxane toward active nitrogen. It is remarkable that at least some of the nitrogen atoms can pass through the liquid in a fast flow system in concentration sufficient to give a distinct yellow afterglow in the vacuum system beyond the reaction vessel. Comparison with n-hexadecane shows the hydrocarbon ten times more reactive than D$_7$ in its reaction with active nitrogen.

Course of the Reaction with D$_7$.—From the study of the radiolysis of hexamethyldisiloxane (M$_2$) by Dewhurst and St. Pierre[3], it can be inferred that active nitrogen will attack the C–H and Si–C bonds, and to a lesser extent the Si–O bond in D$_7$. The formation of HCN as the main product of the reaction shows the breaking of Si–C bonds, and the formation of NH$_3$ and all other hydrogen-containing products show the rupture of the C–H bond. In addition, the mass-spectrometric observation of siloxane fragments such as CH_3SiH and CH_3-$SiCH_2$ point to some attack on the Si–O bond, although the possibility may not be excluded that these radicals may have been produced in the mass spectrometer. The destruction of a Si–O bond is indeed necessary for the opening of the D$_7$ ring which must be postulated to explain the presence of smaller siloxane compounds observed in the v.p.c. analysis of the liquid after the reaction.

Although siloxanes are stable compounds, the nitrogen atom can react with any bond in the compound D$_7$. After abstraction of one or more hydrogen atoms, or even a methyl group, the remaining free radicals will rearrange into new stable compounds. If the radical breaks at an internal

(3) H. A. Dewhurst and L. E. St. Pierre, J. Phys. Chem., 64, 1063 (1960).

site, it is possible that smaller ring structures, such as D$_4$, can be formed. The compounds D$_4$, D$_5$ and MD$_4$M have been identified in the reaction product by v.p.c. with the usual practice of comparing the unknown's retention time of the chromatogram with those of standards. It is possible, however, that the unknown peaks are actually due to some other non-cyclic isomers, which happen to have similar retention times. In any case, their presence gives some indication of the course of reaction of siloxanes with active nitrogen.

Effect of Temperature.—The effect of temperature on the production of N-containing compounds from N atoms is shown in Table I. The activation energy of 1.1 kcal./mole is typical of free radical reactions and is consistent with previously obtained activation energies for the reaction of active nitrogen with polyolefins.[2]

Reaction of Active Nitrogen with n-Hexadecane. —In view of this vigorous reaction a profusion of gaseous products was to be expected. Table II shows a conversion of N atoms to products of 85%, which is more than ten times as large as that of the reaction of active nitrogen with D$_7$. An over-all yield of 22.4% is appreciable, but the product consists of degradative nitrogen compounds. Only the appearance of acetonitrile in the present reactions is a step toward chemical synthesis by active nitrogen reactions. Recently it was reported[4] that active nitrogen reacts with butadiene
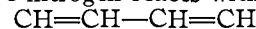
$$CH{=}CH{-}CH{=}CH$$

to form pyrrole, $\lfloor$————NH————$\rfloor$, and trans-crotononitrile, $CH_3{\cdot}CH{=}CH{\cdot}CN$, in addition to degradative compounds, such as HCN.

Formation of Ammonia.—The formation of ammonia in the reaction of active nitrogen with polydimethylsiloxanes is of particular interest because of the previous observation of Dewhurst and Cooper[5] of a connection between ammonia formation and methyl substitution in gaseous methylsilanes. This correlation also appeared in the reaction of active nitrogen with polyolefins.[2] Together with the present results this supports the conclusion of Dewhurst and Cooper that ammonia is formed directly by a molecular process in which the nitrogen atom removes two or three hydrogen atoms from the methyl group in one step, either through formation of the amine radical, NH$_2$, or by a displacement reaction. The latter possibility seems most likely because it connects directly the formation of ammonia with the presence of methyl groups. A similar mechanism of a one-step displacement also has been proposed by Henchman, et al.,[6] for the displacement of hydrogen from methane with hot hydrogen atoms.

(4) A. Tsukamoto and N. N. Lichtin, J. Am. Chem. Soc., 82, 3798 (1960).

(5) H. A. Dewhurst and G. D. Cooper, ibid., 82, 4220 (1960).

(6) M. Henchman, D. Urch and R. Wolfgang, Can. J. Chem., 38, 1722 (1960).