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Thermal Decomposition of *n*-Hexyl Silicate[1]

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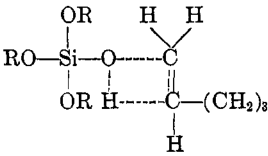
The pyrolysis of gaseous *n*-hexyl silicate, in the temperature range 370 to 450°, yielded hydrocarbons, small amounts of silicates with shorter alkyl chains, and unidentified polymers. The kinetics are based on the rate of disappearance of hexoxyl groups for the temperature range 417 to 450°. The decomposition was approximately first order, homogeneous, and proceeded at a rate given by $k = 8.3 \times 10^{10} \exp 49{,}100/RT$ sec.$^{-1}$ An intramolecular cyclic transition complex analogous to that present in carboxylic ester pyrolysis, where large quantities of α-olefin are produced, does not appear to be important in *n*-hexyl silicate pyrolysis. The cyclic complex mechanism predicts a hexene-1 concentration during pyrolysis which is much higher than that observed. A more probable first step mechanism is homolytic scission occurring on the alkyl chain.

No previous work on the mechanism of pyrolysis of alkyl or aryl silicates appears in the literature. The high alkyl content of alkyl silicates suggests that their mode of decomposition may be like that of hydrocarbons, *i.e.*, homolytic scission of carbon-carbon or carbon-oxygen bonds to form free radicals which propagate further reaction, or terminate by elimination or combination. In agreement, Blake *et al.*[2] suggest, on the basis of preliminary data, that the alkyl silicates decompose *via* a free radical mechanism involving scission of the C—O bonds and the C—H bonds of the α-carbon.

An intramolecular cyclic rearrangement, analogous to that in carboxylic ester[3-6] and possibly in alkyl phosphate pyrolysis,[7] is also a possible first step path. The corresponding activated complex would be represented as:



for which the activation energy is presumably lower than that required for homolytic scission of the C—C or C—O bond, and from which the initial product is the α-olefin. *n*-Hexyl silicate for example, would yield a mixture of volatile hydrocarbons. The identified products of pyrolysis of *n*-hexyl silicate are given in Table I. The distribution of products is typical for all samples pyrolyzed in the range 370° to 420° for eight hours. However, pyrolysis of several pure samples of hexene-1 in the same temperature range yielded the same hydrocarbon products. Consequently, it was not possible to distinguish whether the hydrocarbons resulted from chain scission or from the subsequent decomposition of hexene-1 on the basis of product analysis alone.

TABLE I

PRODUCTS OF 30.5 MG. OF *n*-HEXYL SILICATE PYROLYZED AT 420.7° FOR EIGHT HOURS

Product	Mass (Mg.)	Product	Mass (Mg.)
Methane	0.33	*cis*-Butene-2	0.01
Ethane	1.29	Pentene-1	0.78
Ethylene	1.04	Hexene-1	0.76
Propane	0.30	Methanol[a]	0.76
Propene	1.23	Ethanol[a]	0.72
n-Butane	0.30	1-Propanol[a]	0.72
Butene-1	0.44	1-Hexanol[a]	11.0
Isobutylene	0.04	Calculated silicon	1.97
trans-Butene-2	0.01		

[a] Formed by hydrolysis of the silicate esters remaining after pyrolysis.

However, if the over-all reaction involving the cyclic mechanism is written as: *n*-hexyl silicate $\xrightarrow{k_1}$ hexene-1 $\xrightarrow{k_2}$ mixed hydrocarbons, and if k_1 and k_2 are for homogeneous, nonreversible first order reactions, then the appropriate expression predicting the hexene-1 concentration at any time is[8]:

$$[\text{Hexene-1}] = \frac{(A_0)\, k_1}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad (1)$$

in which A_0 is the initial concentration of hexoxyl groups. This predicted quantity may then be compared with experiment in order to test whether or not alkyl silicate decomposition actually does follow this kinetic scheme. It is only necessary to obtain independent values for k_1, k_2, A_0, and the hexene-1 concentration.

The experimental approach was to pyrolyze gaseous samples of *n*-hexyl silicate and analyze both the reaction products and the residual silicate esters. The details of the procedure are given

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[1] The authors express appreciation to the Ordnance Corps, Department of the Army, for support of this work.

[2] E. S. Blake, W. C. Hammann, J. W. Edwards, T. E. Reichard, and M. R. Ort, *J. Chem. Eng. Data*, **6**, 86 (1961).

[3] C. D. Hurd and F. H. Blunk, *J. Am. Chem. Soc.*, **60**, 2419 (1938).

[4] R. T. Arnold, G. G. Smith, and R. M. Dodson, *J. Organic Chem.*, **15**, 1256 (1950).

[5] B. A. Benkeser, J. J. Hazdra, and M. L. Burrous, *J. Am. Chem. Soc.*, **81**, 5374 (1959).

[6] A. Maccoll, *J. Chem. Soc.*, 3398 (1958).

[7] H. E. Baumgarten and R. A. Setterquist, *J. Am. Chem. Soc.*, **79**, 2605 (1957).

[8] See for example, A. Frost and R. G. Pearson, *Kinetics and Mechanisms*, New York, Wiley, p. 193 (1953).

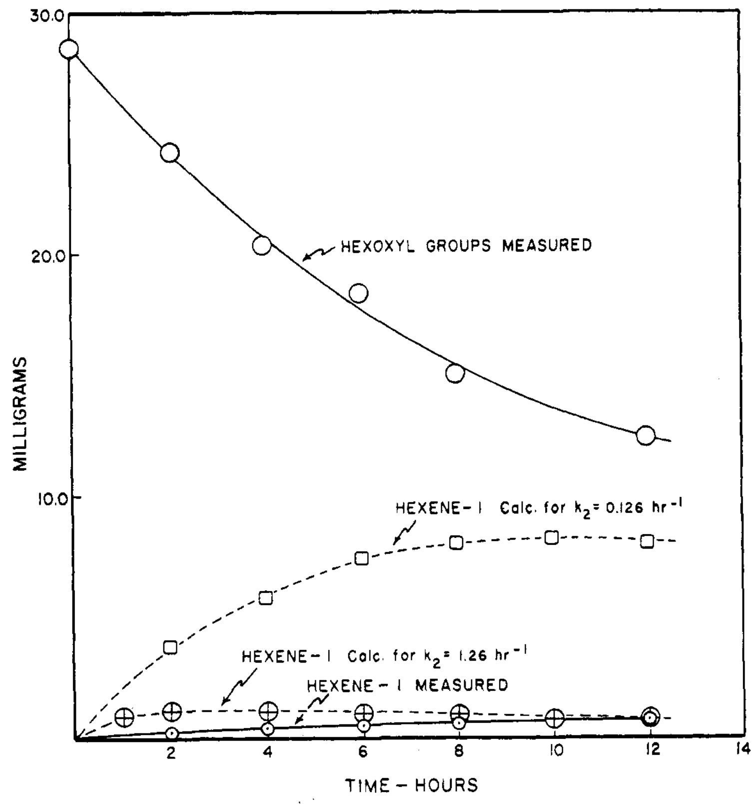

Fig. 1. Pyrolysis of n-hexyl silicate at 417.3°; hexoxyl and hexene-1 analyses

in the Experimental section. Values for k_1 were obtained by measuring the amounts of 1-hexanol recovered on hydrolysis of the silicate ester remaining after pyrolysis. The data are given in Table II.

TABLE II

KINETICS OF PYROLYSIS OF n-HEXYL SILICATE

Temperature	Reaction Order	First Order Rate Constant, k_1 (Hr.$^{-1}$)
417.3	1.2	0.08 ± .02[a]
420.7	1.2	0.12 ± .02
434.9	0.9	0.19 ± .02
450.5	0.9	0.51 ± .03

[a] 95% confidence limits.

Plots of mass of n-hexoxyl group *vs.* time were all similar to that shown in Fig. 1. In a few cases, the initial points up to three hours were slightly higher at the higher temperatures than the smooth curve indicating the possibility of a small induction period. Most of the reactions were run to greater than 50% completion, and at 450° the runs were to about 90% completion, which demonstrated the nonreversible character of the reaction.

The order of the reaction was determined directly from the plot of the amount of hexoxyl groups remaining *vs.* time. The activation energy based upon first order kinetics is 49.1 (kcal./mole) and the frequency factor is 8.3×10^{10}/sec. The over-all reaction order is about unity with respect to hexoxyl group disappearance indicating that the decomposition occurs mostly within the hexoxyl group and not by interaction between hexoxyl groups.

The homogeneity of the reaction was tested using pyrolysis bulbs packed with capillary tubes to increase the surface area twentyfold and decrease the volume by one half. Analysis for hexoxyl groups was made on samples pyrolyzed at 419.8° for eight hours. The specific reaction rate constant, k_1, corresponding to the amount of hexoxyl groups remaining in the packed reactor was 0.11 hr.$^{-1}$ whereas that calculated for 419.8 was 0.10 hr.$^{-1}$ This result indicates that the decomposition of the hexoxyl group is homogeneous. With the thermal decomposition of the hexoxyl groups established as homogeneous, first order, and nonreversible, it was possible to use the experimentally determined rate constant (k_1) and a previously reported value for k_2, to calculate the hexene-1 concentrations expected for decomposition *via* the cyclic mechanism.

The pyrolysis of hexene-1 was investigated by Molera and Stubbs[9] and found to be first order and homogeneous, the decomposition rate being given by: $\log k_2$ (sec.$^{-1}$) $= 12.414 - 53.3 \times 10^3/2.3\,RT$. Thus k_1 at 417.3 = 0.126 hr.$^{-1}$ The concentrations of hexene-1 were calculated for the above consecutive reactions using this value for k_2 and the meas-

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[9] M. J. Molera and F. J. Stubbs, *J. Chem. Soc.*, Part I, 381 (1952).

ured value of 0.08 hr.$^{-1}$ for k_1. These and the measured amounts of hexene-1 and hexoxyl are shown in Fig. 1. It was recognized that Molera and Stubbs used a preconditioned reaction vessel in which the apparent rate constant for the decomposition of hexene-1 may be lower than in clean glassware in which the rate may be increased by reaction at the walls. To allow for this the lower dotted line in Fig. 1 represents the amount of hexene-1 calculated using Equation 1 when k_2 = 1.26 hr.$^{-1}$, *i.e.*, ten times Molera and Stubbs' value, and k_1 = .06, the lower limit of the rate constant at 417.3° in this work. The conclusion drawn from these results is that hexene-1 is not a major intermediate in the pyrolysis, and therefore the cyclic mechanism cannot be the first step in the thermal decomposition of *n*-hexyl silicate. The obvious alternative is that these compounds decompose by homolysis in the alkyl chains.

EXPERIMENTAL

Materials. n-Hexyl silicate was prepared by the reaction 1-hexanol and silicon tetrachloride. The product obtained was fractionated three times at reduced pressure under nitrogen using a 30-cm. length Vigreux column. The middle $^2/_3$ fraction had a b.p. at 1.5 mm. of 185.5–186.3°, n_D^{25} 1.4266.

Anal. Calcd.: Si, 6.49. Found: Si, 6.38.

Further analysis of the *n*-hexyl silicate was performed by hydrolysis of the ester after which the alcohols produced were determined by gas chromatography by the method described below. A single impurity peak, which was probably 1-pentanol, emerged. On the basis of area comparison, this indicated that the original silicate was about 98.5% pure. The preparation was stored in the dark in a dry nitrogen atmosphere.

Pyrolysis. Weighed samples of 30 mg. (7 × 10^{-5} mole) of the silicate[10] were pipetted into cylindrical Pyrex pyrolysis tubes of about 40 cc. capacity equipped with a break-off seal. Each tube was evacuated to about 5 microns under nitrogen, and the upper part of the glass walls were outgassed repeatedly by heating with a Bunsen flame. When the vessel was again cooled, the liquid was gently heated to expel dissolved gases. The reaction vessel was then flame sealed under nitrogen at 5 microns. The out-gassing technique entailed no loss of sample as determined by zero time runs. Each sample was pyrolyzed in one of six close fitting cylindrical cavities of an aluminum heating block whose temperature was controlled to ±0.15°. Temperature was measured at frequent intervals during each run by means of a N.B.S. calibrated platinum resistance thermometer and portable Wheatstone bridge.

Analyses. Gas chromatography was used for the analysis of the reaction products. Before breaking the seal, the nonvolatile portion of the products (which included the undecomposed silicate) was collected at the very bottom of the pyrolysis tube by heating the upper part of the tube while keeping the bottom in liquid nitrogen. The pyrolysis tube was attached to a vapor collection apparatus consisting essentially of a "U" tube trap equipped with taps to permit the product vapors to be collected then swept onto the chromatographic column. The seal was then broken, and the volatile hydrocarbon products were evacuated through the "U" tube which was immersed in liquid nitrogen. The "U" tube was then warmed, and the gases swept onto the chromatographic column with a helium stream.

Analysis of the undecomposed silicate in the nonvolatile residue was accomplished by alkaline hydrolysis to yield alcohols which were separated chromatographically. The procedure was as follows: 15 to 20 mg. of a 25% potassium hydroxide solution was placed in the tube containing the nonvolatile products. This tube was cooled in a liquid nitrogen bath, evacuated, and resealed under nitrogen at atmospheric pressure. The tube was placed in an oven at 85° for 10 hr. to effect complete hydrolysis of the silicate after which the alcohols formed were pumped out onto the "U" tube trap and swept onto the column for analysis as previously described. This procedure gave quantitative recovery on samples of pure hexyl silicate.

Three different "U" tubes were used to collect products. These consisted of: (a) a 45-cm. length of 4 mm. I.D. copper tubing containing 20% by weight dimethylsulfolane on Johns Manville Chromosorb for light hydrocarbons (C_2–C_5); (b) a 24-cm. length of 30–60 mesh Molecular Sieve 5A, for methane; (c) a 38-cm. length of loosely packed glass wool for C_6–C_{10} hydrocarbons or (C_1–C_6) alcohols. This last "U" tube and the tubing leading to the column was externally heated to about 80° when eluting heavier hydrocarbons and to about 145° when eluting alcohols. Four different chromatographic columns were used. These consisted of: (a) a 13.7-m. (coiled) length of 20% dimethylsulfolane on chromosorb maintained at 0° in an ice water bath for the separation of light hydrocarbons[11]; (b) a 1-m. length of 20% by weight squalene on chromosorb maintained at 73° for the separation of heavier hydrocarbons[12]; (c) a 1-m. length of molecular sieve 5A (30–60 mesh) maintained at 50° for hydrogen and methane[13]; (d) a 2.2-m. length of carbowax 400 maintained at 140° for alcohols.[14] Thus, the volatile portion of a given sample could be analyzed for either light hydrocarbons (C_2–C_5), heavy hydrocarbons (C_6–C_{10}), or hydrogen and methane.

For each compound appearing as a peak on the recorder chart, the area under the curve was measured and converted into actual mass of material by calibration factors obtained by analysis of known materials. Identification of the unknown peaks was established by comparison of retention times with the knowns. The relative retention times on each column were sufficiently reproducible that peaks could be identified without ambiguity. Also, each column used in this work gave nearly symmetrical peaks which were completely resolved except in the case of ethane and ethylene on the dimethylsulfolane column and water (from the potassium hydroxide solution) and 1-butanol on the "carbowax 400" column. The instrument used was a Perkin-Elmer Model 154B Vapor Fractometer.

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[10] The vapor pressures of hexyl silicate, determined by an isoteniscope method, are given by: $\log p_{mm} = -4000/T + 9.18$, so that a 30 mg. sample is completely gaseous at 400° and above in the tubes used.

[11] E. M. Fredricks and F. R. Brooks, *Anal. Chem.*, 28, 297 (1956).

[12] F. T. Eggertsen, H. S. Knight, and S. Groennings, *Anal. Chem.*, **28**, 303 (1956).

[13] G. Kyriacos, *Anal. Chem.*, **29**, 878 (1957).

[14] S. J. Bodnar and S. J. Meyeux, *Anal. Chem.*, **30**, 1384 (Aug. 1958).