different chemical partners provides a mechanism for the reshuffling of siloxane linkages which, with the dimethylsiloxanes and in the absence of substantial amounts of chain-terminating groups, leads to high polymeric forms. With sulfuric acid, it is possible that both acid hydrogens may take part in this sort of mechanism. It appears unlikely that chain exchange involving only silyl ester groups as active agents is at all significant under the usual reaction conditions, and the known mechanism of base-catalyzed siloxane bond rearrangement also makes this an unlikely possibility.

The failure of strong organic acids to act as effective catalysts for the rearrangement of dimethylsiloxanes is surprising, since certain of these, such as the perfluoroaliphatic acids, are very strong acids in water solution. However, if cleavage of the siloxane bond were to occur essentially completely, then the mechanism for siloxane bond rearrangement would be relatively ineffective and such rearrangement, if it occurred at all, would be a slow process. Since the presence of small amounts of trifluoroacetic acid acts to restrict the viscosity of the product obtained when polymerization of tetramer is catalyzed by sulfuric acid, and since infrared analysis of mixtures of trifluoroacetic acid and tetramer clearly indicates the presence both of silanol groups and silyl ester groups in the absence of any apparent degree of polymerization, the hypothesis that the cleavage reaction proceeds essentially to completion is attractive. It may be pointed out that such acids well may be effective in causing rearrangement in other organosiloxane systems and under different reaction conditions.

The anhydrous hydrogen halides cleave siloxane bonds fairly readily, with the formation of silicon halide groups and silanol groups. However, this process can be followed by removal of silanol groups by further reaction with hydrogen halide,[13] or by other processes resulting in the condensation of silanol groups and the elimination of water. The net effect is the formation of an equilibrium mixture of siloxane, hydrogen halide, halosilane, silanol and water. As long as an excess of hydrogen halide is present, there is an effective mechanism for keeping the concentration of silanol groups at a low level, namely, by reaction with the hydrogen halide and removal as water. This process is aided by the formation of a concentrated aqueous phase of hydrogen halide solution. Meanwhile, effective chain-terminating groups are incorporated into the siloxane system in the form of silyl halide end groups. Under such conditions, the viscosity and boiling point of the mixture as compared to the original siloxane may decrease rather than increase. If one places a polydimethylsiloxane in contact with an aqueous solution of hydrogen halide having somewhat less than the saturation concentration of hydrogen halide, the effective catalyst concentration in the siloxane phase will be low because of the great difference in solubility of the hydrogen halide in this phase as compared to that in water. However, although the rearrangement may be slow, the decrease in concentration of silyl halide groups acting as chain-terminators will allow the formation of higher siloxane polymers. Both the nature of the products of siloxane bond redistribution and the rate of attainment of equilibrium among these products will depend on the concentrations of acid, water, siloxane, silanol groups and silyl halide groups, and the equilibrium constants relating these quantities. One might expect to find similar concentration effects with other monoprotonic acid catalysts and the results with nitric acid appear to be consistent in this respect. Catalysis with concentrated sulfuric acid is different, however, in that the difunctional normal sulfate groups can take part in chain formation and thus do not necessarily restrict the molecular weight of the polymer by acting as chain-terminating units.

Conclusions

1. Silanol end groups appear to be active intermediates in the acid-catalyzed rearrangement and polymerization of diorganosiloxanes by strong protonic acids. In this respect, acid-catalyzed siloxane rearrangement differs from base-catalyzed rearrangement.
2. The nature of the products resulting from acid-catalyzed rearrangement of siloxane bonds in diorganosiloxanes, and the rate of attainment of equilibrium in such systems, depend on the effective concentrations in the siloxane phase of silanol and silyl ester (or halide) end groups.

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(13) A graphic demonstration of this reaction may be seen by exposing a crystalline silanol, such as tetramethyldisiloxanediol, to an anhydrous hydrogen halide.

Fractionation of Chlorine Isotopes between Gaseous Chlorine and Aqueous Chloride Ion[1]

By A. C. Rutenberg

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Some experiments were performed to determine the equilibrium distribution of chlorine isotopes between gaseous molecular chlorine and chloride ion in aqueous solution. This exchange has been shown[2] to be rapid in acid solution. The single stage fractionation factor was in the range of 1.0024–1.006, with Cl^{37}concentrating in the gaseous chlorine (Cl_2) phase.

Experimental

The apparatus for this study is shown in Fig. 1. The chlorine gas from a tank used as an "infinite reservoir" was passed up a column countercurrent to an acidified aqueous solution containing chloride ion. The column was water jacketed and packed with $^1/_{16}$ inch glass helices. It was 12 ft. long and 15 mm. in inside diameter. Only the lower 9 ft. of the column were used for the exchange reaction. In the upper portion of the column the chlorine gas was reduced to chloride ion by a solution of alkaline nitrite ion containing an indicator. Hydrogen ion was liberated during the reduction, giving an acid medium which minimized chlorine hydrolysis in the column, and furnished a means for

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(1) This article is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

(2) F. A. Long and A. R. Olson, This Journal, **58**, 2214 (1936).

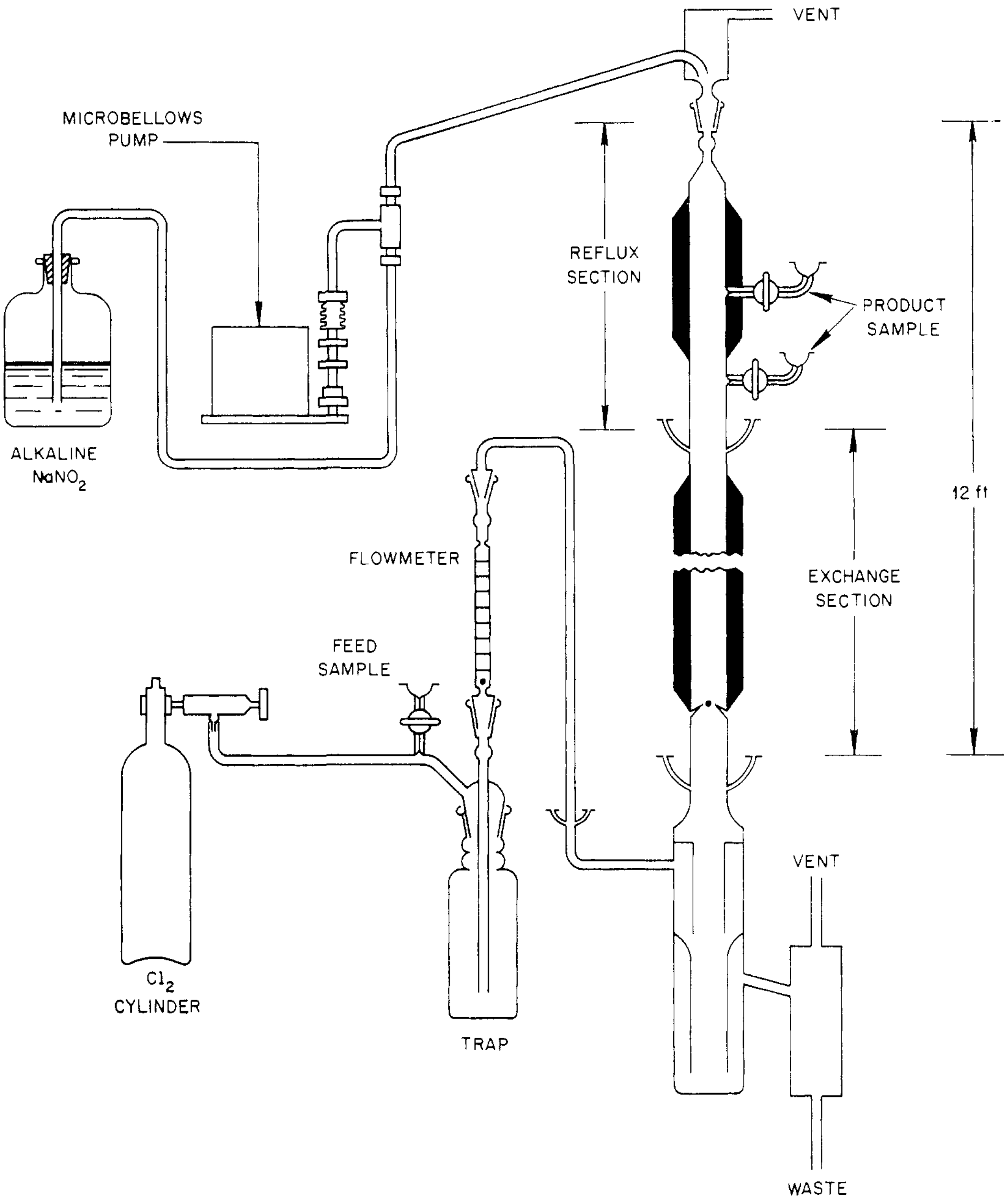

Fig. 1.

visually locating the portion of the column in which the reflux reaction took place. Samples of chlorine gas were taken periodically from the feed line, and from the column just below the reflux section. The sampling system utilized capillary tubing and stopcocks, to reduce holdup and also reduce the amount of air introduced into the samples. The chlorine gas samples were purified to remove air, water and oxides of nitrogen before they were submitted for mass spectrometric analyses. The column was operated for at least six hours per experiment and the isotopic analyses indicated the system attained equilibrium in less than two hours.

Results and Discussion

The total separation achieved in a number of experiments is presented in Table I. The separation was not reduced appreciably by the amount of chlorine dissolved in the aqueous phase, since the dissolved chlorine represented only 3% of the total chlorine stream. It is believed that the small separation achieved in the first experiment was due to inefficiencies in the reflux section allowing Cl_2 to pass through without reacting. In the subsequent experiments a larger portion of the column was used for reflux and the nitrite reducing solution was made more alkaline, so that less disproportionation of the reducing agent occurred. The third experiment showed the least fluctuation in reflux level

TABLE I

FRACTIONATION OF CHLORINE ISOTOPES AT 16–18°

Exp. no.	Molarity of aq. phase Cl^-	H^+	Total separation (90% C.I.) $\frac{(37/35)\text{ product }Cl_2}{(37/35)\text{ feed }Cl_2}$
1	3.65	1.30	1.023 ± 0.015
2	3.85	0.64	1.036 ± .010
3	4.00	0.68	1.048 ± .008

and more confidence should be put in this value for the total separation than in the others. The chlorine losses at the top of the column for a period of stable operation under conditions similar to those of experiments 2 and 3, amounted to only 0.1% of the chlorine refluxed and would not lessen the separation significantly.

Since the total separation was small, the single stage separation factor could only be estimated. It was assumed that the total separation obtained in the third experiment, which exhibited the most satisfactory column operation, was the best value, and that the 9 ft. exchange section had 8–20 stages. A single stage separation factor in the range 1.0024–1.006 is indicated, with the Cl^{37} concentrating in the gaseous chlorine.

Chloride ion is known to be relatively unhydrated and one would expect the Cl_2 to be the more "strongly bonded" state. This expectation is confirmed by the observed concentration of Cl^{37} in the gaseous phase. From spectroscopic data Urey[3] has calculated the separation factor between gaseous Cl_2 and free Cl atoms to be 1.0074, and the separation factor between gaseous Cl_2 and gaseous HCl to be 1.003 at 25°, with Cl^{37} concentrating in the Cl_2 molecules in both instances. In addition, Urey and co-workers[4] found a small enrichment of Cl^{37} in HCl gas for the system HCl(gas) *vs.* HCl (aqueous) indicating HCl gas to be more "strongly bonded" than Cl^-. Since Cl^- must interact to some extent with the solvent water it is reasonable to expect a lower separation factor for the present system than that between Cl_2 and the Cl atom, but one slightly larger than for the system Cl_2–HCl gas. Some work in this Laboratory indicated little if any isotopic fractionation between chlorine and its hydrolysis products (ClO^- and Cl^-). If this is the case, the separation factor between ClO^- and Cl_2 should be of the same magnitude as for the system Cl_2–Cl^- with Cl^{37} enriching in the ClO^- species.

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[3] H. C. Urey, *J. Chem. Soc.*, 574 (1947).

[4] H. C. Urey, A. Mills, I. Roberts, H. G. Thode and J. R. Huffman, *J. Chem. Phys.*, **7**, 138 (1939).

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The Reported Oxychloride of Germanium, $GeOCl_2$

BY WALTER C. SCHUMB AND DONALD M. SMYTH

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Schwarz and Heinrich have reported the preparation of an oxychloride of germanium, $GeOCl_2$, by the exothermic reaction which results from the passage of trichlorogermane vapor over silver oxide in a vacuum system.[1] Analysis of the product, collected as droplets of oily liquid on the walls of the apparatus, indicated a composition close to $GeOCl_2$. The product was described, however, to exhibit several properties which are entirely unexpected in a compound of this type. The material was stated to be insoluble in all organic and inorganic solvents. This is not in accord with the high solubilities of the oxyhalides of silicon and that of the germanium oxychloride, Ge_2OCl_6. The product was said to undergo extremely rapid hydrolysis, but, instead of forming GeO_2, it yielded a precipitate of germanous hydroxide. This behavior is completely inconsistent with the assigned identity. Although germanium does have a well-defined oxidation state of two, it is obtained only by rather drastic conditions, and most certainly water alone is insufficient to effect a reduction of this type. The reported $GeOCl_2$ was non-volatile and underwent a slow, reversible decomposition at room temperature to give a citron-yellow solid and chlorine. The yellow solid was stated to be germanium monoxide, but the reasons for this identification are not obvious. Although a yellow form of GeO has recently been shown to exist,[2] it is unstable with respect to transformation into the more usual dark brown modification. Other properties of this product indicate further the peculiar tendency for it to be converted into divalent germanium and in each case the yellow solid product is reported to be GeO. A more obvious identity of this solid would seem to be that of germanium dichloride, which fits the reported properties much more closely than does GeO. In view of these peculiar properties it was felt that the material should be subjected to further examination.

The trichlorogermane for these experiments has been made most conveniently by the reaction of germanium monosulfide and hydrogen chloride at 50°. This reaction has been reported previously,[3] but the subsequent publication in "Inorganic Syntheses"[4] of a very simple preparation for GeS makes this reaction a much more convenient preparation for $GeHCl_3$ than those previously reported. It has been found, however, that the GeS prepared by the "Inorganic Syntheses" method is appreciably impure. Two separate lots were found to contain 10 and 20% chloride, respectively. Apparently this method does not lend itself to the preparation of GeS of high purity. Since the impurities did not react with HCl at the temperature required for the formation of $GeHCl_3$, the product was still useful for this preparation.

The reaction of $GeHCl_3$ with Ag_2O was carried out in a manner similar to that previously reported. The general observations were confirmed for the most part, and, in addition, it was found that insufficient product was usually formed for any identification. Several modifications of reaction technique were attempted and in every case the yield consisted of tiny droplets, widely scattered on the walls of the apparatus. Since it was impossible to collect enough of this material to weigh a sample for analysis, a more indirect approach was attempted. An apparatus was constructed and composed of two chambers, each of which contained a boat of Ag_2O and the reaction was allowed to proceed in the usual manner. As soon as the reaction ceased, the two sections were broken from the apparatus, the boats removed, and the tubes and the product which they contained were dropped into large erlenmeyer flasks fitted with ground glass stoppers. One of these contained standard iodine solution and the other distilled water. These were both allowed to stand for 48 hours to ensure complete reaction. The iodine solution was back-titrated with standard thiosulfate to determine divalent germanium and the total germanium content of the same sample was then determined

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[2] W. L. Jolly and W. M. Latimer, THIS JOURNAL, **74**, 5751 (1952).

[3] L. M. Dennis and R. E. Hulse, *ibid.*, **52**, 3553 (1930).

[4] W. C. Fernelius, Editor, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 102.