where the brackets indicate molar concentration and $X$ corresponds to the ethanolamine used.

The reciprocal slope values given in Table I have a wide range of values and this causes some uncertainty in the determination of the values of $K_f$. Therefore, the $K_f$ values in Table II are given to only one significant figure.

For each of the ethanolamines studied, the value of $p$ obtained was four which indicates that the complexes contain four ligand molecules. Since copper(II) ordinarily has a coördination number of four, this shows that the coördinating molecules are monodentate. It is assumed that the coördinate bond occurs through the amine nitrogen.

The diethanolamine complex found was quite similar in behavior to the monoethanolamine and ethylethanolamine complexes, and this points to the likelihood of amino coördination. Diethanolamine has one more hydroxyl than either monoethanolamine or ethylethanolamine. Hence, for hydroxyl coördination, diethanolamine should behave differently from the latter two compounds. All three compounds should act in a similar manner in the formation of complexes through the amine nitrogen. The fact that it was found that four molecules of the ethanolamines were coördinated in all three cases substantiates the assumption that the linkage is through the amine nitrogen.

Some further studies with diethylethanolamine and triethanolamine in this Laboratory indicate that the corresponding complexes are not formed in the same concentration range as the others given here, but show a tendency toward coördination of only two or three molecules per copper(II). The square-planar configuration of copper(II) complexes might produce steric hindrance if the coordination occurs through the tertiary amine nitrogen. This would not be the situation if it were the hydroxyl group which coördinates. This is in agreement with the beliefs of other authors. Breckenridge and Hodgins[4] and Mann[5] have described complexes of 1,3-diamino-2 propanol with copper(II) for which they believe the coördination took place through the amino groups only. Breckenridge[6] states that for N-hydroxyethylethylenediamine the hydroxyl group does not coördinate. Harvey, *et al.*,[1b] describe a number of complexes of N-hydroxyethylethylenediamine studied spectrophotometrically. Among the structures mentioned is $[Cu(HOC_2H_4NHC_2H_4NH_2)_4]^{++}$ for which they reason that only the primary amino group is coördinated. They also give evidence for the existence of a complex of diethanolamine with copper(II) in which the amine group, rather than the hydroxyl group, is coördinated.

If the difference in coördinating ability of the amino and hydroxyl groups is substantially different, then one should expect to find only one type of group coördinated when an excess of the complexing agent is present. This assumes that there are no complications such as steric effects. Thus the experimental conditions of this research favored the formation of the $[CuX_4]^{++}$ complex. However in the presence of a limited amount of the ethanolamines, particularly in non-aqueous solutions where water does not compete, it is possible that one may find chelates formed with both the amino and hydroxyl groups being coördinated. One can find support for this hypothesis in the results of earlier workers based on analyses of compounds prepared under these conditions.

It would be of interest to compare the formation constants for the ethanolamine complexes of copper(II) with the corresponding simple amine complexes, but the data on these do not appear to be available. However the silver complexes have been reported and it has been found that two moles of the complexing agent are coördinated per atom of silver(I). The formation constants reported[7] for the monoethanolamine, diethanolamine, ethylamine and diethylamine complexes of silver are, respectively, $4.8 \times 10^6$, $0.30 \times 10^6$, $0.2 \times 10^6$ and $1.6 \times 10^6$. These values indicate that the simple amines and the hydroxy substituted amines are not very different in coördinating ability.

It is suggested that the water solubility of these ethanolamine complexes is enhanced by the presence of the hydroxyl groups extending into solution. This may explain the fact that certain N-hydroxyethylethylenediaminetriacetic acid complexes are more soluble than the corresponding complexes with ethylenediaminetetraacetic acid.

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[4] J. G. Breckenridge and J. W. R. Hodgins, *Can. J. Research*, **B17**, 331 (1939).

[5] F. G. Mann, *J. Chem. Soc.*, 2904 (1927).

[6] J. G. Breckenridge, *Can. J. Research*, **B26**, 11 (1948).

[7] J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

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# On the Mechanism of the Acid-catalyzed Rearrangement of Siloxane Linkages in Organopolysiloxanes

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It has been well established that the active agent in the base-catalyzed rearrangement of siloxane linkages in polydimethylsiloxanes is the oxygen atom, or ionic form derived therefrom, which acts as an electron donor to silicon in the siloxane linkage exchange mechanism.[1,2] Since the rate of siloxane rearrangement depends on the effective strength of the oxygen as an electron donor, determined in turn by the nature of the group or groups attached to it, it seems improbable that the acid-catalyzed rearrangement of siloxane linkages would follow a course entirely analogous to that of base-catalyzed rearrangement.

It is known that, like basic catalysts, protonic acid catalysts do react with siloxane molecules in the course of the rearrangement reaction and the products formed are formally analogous to those formed with basic catalysts.[3-5] The reaction, either with base or acid, involves a cleavage of the siloxane

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[1] D. T. Hurd, R. C. Osthoff and M. L. Corrin, THIS JOURNAL, **76**, 249 (1954).

[2] W. T. Grubb and R. C. Osthoff, presented at 126th Meeting, Am. Chem. Soc., Sept. 1954, to be published in THIS JOURNAL.

[3] F. P. Price, *ibid.*, **70**, 871 (1948).

[4] L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946).

[5] C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 139 (1947).

bond with the formation of a silanol group and the formation of either a metal silanolate group (with base) or a silyl ester group (with acid). In either case, the condensation of the silanol groups thus formed may reform siloxane linkages with the elimination of water molecules.

Since the rate of reaction of a siloxane with a given protonic acid depends on, and increases with, the ability of the siloxane oxygen to function as an electron donor, depending in turn on the nature of the attached groups,[6] it is likely that the initial step in the reaction of a protonic acid with a siloxane involves the siloxane oxygen as an electron donor to the acid proton, whereas in the base-catalyzed reaction, the initial step is a coördination of the electron donor atom in the base to silicon.

The purpose of the present investigation was to determine whether the silyl esters formed by reaction of an acid with a siloxane were active catalysts *per se* for the rearrangement of siloxane linkages or whether siloxane rearrangement proceeded primarily by reversal of the cleavage reaction, that is, through combination of silanol groups and silyl ester groups to reform siloxane linkages and free acid molecules which then could react with other siloxane linkages. In principle, either mechanism could result in a random reshuffling of siloxane linkages and the conversion of low molecular weight forms of dimethylsiloxane into high polymeric forms. If the rearrangement proceeded primarily by reversal of the cleavage reaction, then the rate of the reaction would depend on the concentration of silanol groups present in the reaction mixture as well as on the concentration of silyl ester groups, whereas if silyl ester groups were effective rearrangement catalysts *per se*, the presence of silanol groups would not be necessary for siloxane bond rearrangement. It has been established that in base-catalyzed siloxane bond rearrangement, the reversal of the cleavage reaction plays only a minor role compared to the action of the silanolate intermediate.[1,2]

## Experimental

The particular siloxane used was octamethylcyclotetrasiloxane, designated herein as "tetramer." The term "anhydrous tetramer" refers to material dried over calcium hydride. Comparative measurements of viscosity have been used as a sensitive indication both of the type of reaction with the catalyst and of the occurrence or non-occurrence of rearrangement reactions by observing the times necessary for equal volumes of tetramer and catalyst-treated tetramer to drain from between marks on a pipet with a small delivery hole; both liquids compared in each case were maintained at the same temperature in a water-bath.

**Stability of Tetramer.**—A sample of anhydrous tetramer was placed in a quartz tube, degassed twice under vacuum, and frozen in liquid nitrogen. The tube then was evacuated and sealed. The sample was subjected to a total of 72 hours at 300–320°. Following this treatment, the viscosity and boiling point of the sample were found to be the same as those of the original tetramer within the limits of experimental error (less than 3% on viscosity determination and 1% on boiling temperature).

**Reaction with Water.**—A sample similar to that above was prepared in which one large drop of deionized water was included with the tetramer. After heating for 72 hours at 300–320°, the sample was opened, and its viscosity was found to be approximately 93% of that of the original tetramer. The boiling point showed no appreciable difference from that of the original tetramer nor was the viscosity at room temperature affected by the boiling point measurement. Thus, it appears that some slight reaction of the tetramer with water may have occurred during the heat treatment.

**Reaction with Silanol.**—As in the above experiments, a sample of tetramer was sealed in a quartz tube, this time with the addition of 5% by weight of dihydroxytetramethyldisiloxane (tetramethyldisiloxanediol). During the 72 hour treatment at 300–320°, a small amount of water collected in the sample. The viscosity of the siloxane following the heat treatment was approximately 87% of that of the original tetramer. The presence of the silanol and the products of its decomposition might account for this decrease, however.

In another experiment, 0.5 g. of the silanol compound was added to 60 ml. of anhydrous tetramer in a 100-ml. flask fitted with reflux condenser and a Drierite tube. This mixture was heated for 16 hours at 175°, but no apparent change in boiling point or viscosity occurred. Thus, it is concluded that the presence of silanol groups *per se* is not sufficient to cause any appreciable amount of siloxane bond rearrangement under the usual conditions of the acid-catalyzed or base-catalyzed rearrangement reaction.

**Reaction with Sulfuric Acid.**—The effect of sulfuric acid on siloxanes has been more thoroughly investigated than that of any other acid.[7–10] The following tests indicate generally the sort of polymerization reactions that occur with diorganosiloxanes.

The addition of 0.05 ml. of fuming sulfuric acid (25% excess $SO_3$) to 10 ml. of anhydrous tetramer, at room temperature and with an initial hard shaking to disperse and dissolve the acid in the siloxane, caused polymerization of the siloxane to a viscous high polymer within 1.5 hours. At 150–175° this same mixture became highly viscous within 5–10 minutes. Sooner or later, depending on the temperature, a small amount of aqueous phase separated from the mixture. The behavior of tetramer with similar amounts of 98% sulfuric acid was like that with fuming acid except that 98% acid did not appear to dissolve readily in the siloxane and the polymerization reaction was somewhat slower. The addition of $^1/_3$ ml. of fuming acid to 10 ml. of tetramer caused an immediate thickening at room temperature and within 10 minutes the mixture had become a thick sirup. With a similar quantity of 98% acid, the reaction mixture was somewhat slower to thicken initially, but within 10 minutes the sample had become much more viscous than that with the fuming acid. Further, on standing overnight at room temperature in stoppered tubes, the samples with $^1/_3$ ml. of acid in 10 ml. of tetramer had changed but little if any in viscosity, whereas the samples with small amounts of acid had set to gel-like liquids of very high viscosity. These differences are due to chain-termination of siloxane molecules by silyl sulfate groups. Until an aqueous phase appears by silanol condensation, the concentration of such groups in the siloxane is higher with fuming acid, which dissolves initially in the siloxane, than with 98% acid, with which some aqueous phase always is present.

**Removal of Silanol Groups.**—It readily can be demonstrated that a dimethylsilanol, such as tetramethyldisiloxanediol, reacts immediately with a chlorosilane, such as dimethyldichlorosilane, at room temperature to evolve hydrogen chloride, forming a polydimethylsiloxane. It also is known that a chlorosilane will react with sulfuric acid to form hydrogen chloride and silyl sulfate groups.[11] Thus, with dimethyldichlorosilane and sulfuric acid, the silyl sulfate groups formed are similar to those formed in the reaction of tetramer with sulfuric acid. Depending on the relative amounts of chlorosilane and acid, these may be normal sulfate or acid sulfate groups.

The first experiment was to add 0.3 g. of dimethyldichlorosilane to 10 ml. of tetramer, then to add dropwise and with hard shaking 0.2 g. of fuming sulfuric acid. This mixture was heated for 10 minutes at 175°, but no obvious change in viscosity of the mixture occurred during this treatment nor

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(6) S. W. Kantor, R. C. Osthoff and W. T. Grubb, THIS JOURNAL, **76**, 5190 (1954).

(7) W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 360 (1945).

(8) M. J. Hunter, J. F. Hyde, E. L. Warrick and H. J. Fletcher, *ibid.*, **68**, 667 (1946).

(9) M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *ibid.*, **68**, 2284 (1946).

(10) D. W. Scott, *ibid.*, **68**, 2294 (1946).

(11) W. I. Patnode and F. C. Schmidt, *ibid.*, **67**, 2272 (1945).

in 24 hours subsequently at room temperature (stoppered to exclude air). When the mixture of tetramer, chlorosilane and acid was treated with a few drops of water, then heated to 175°, polymerization proceeded rapidly and the siloxane became highly viscous. It was observed that when a similar inhibited mixture was exposed in an open test-tube to room air at room temperature, an obvious polymerization of the siloxane could be observed within a few hours. This polymerization proceeded most rapidly at the surface of the siloxane in contact with air and a "skinning-over" effect was noticed.

In another experiment, 3 ml. of sulfuric acid was boiled with excess dimethyldichlorosilane until the mixture no longer evolved hydrogen chloride. This mixture contained normal silyl sulfate groups but no silanol. Addition of this material to tetramer caused no appreciable degree of siloxane rearrangement, either in 16 hours at 175° or on standing for several days at room temperature in a closed container. Exposure of the mixture to air at room temperature resulted in a polymerization and an increase in viscosity as noted before.

In a third experiment, sulfuric acid was heated with $^2/_3$ of the quantity of dimethyldichlorosilane necessary for complete elimination of the acid hydrogen. The mixture was boiled until the evolution of hydrogen chloride had ceased. A small amount of this material added to tetramer catalyzed a rapid polymerization of the siloxane both at 175° and at room temperature.

**Reaction with Nitric Acid.**—A sample of tetramer containing 2% of 90% fuming nitric acid polymerized slowly at 175° to form a thick sirup. A similar mixture, stoppered and allowed to stand at room temperature, increased slowly in viscosity; at the end of 24 hours the viscosity was twice that of the original tetramer. On prolonged standing, the siloxane eventually became a thick sirup. When a sample of tetramer together with 5% of 70% nitric acid was allowed to stand stoppered at room temperature for one week, the viscosity of the siloxane phase dropped to approximately 80% of that of the original tetramer, indicating a considerable chain-limiting effect by, presumably, silanol and silyl nitrate groups. With both fuming nitric and 70% nitric acids, the siloxane phase gradually acquired a yellow color.

**Reaction with Hydrogen Halides.**—When anhydrous hydrogen fluoride was bubbled through 20 ml. of anhydrous tetramer in a polyethylene flask, the siloxane became quite warm (50–55°), an aqueous phase appeared and steadily increased in volume while the siloxane phase slowly decreased in volume, and the presence of substantial amounts of volatile organosilicon compounds in the exit vapor from the reaction vessel could be demonstrated.[12] Within 0.5 hour, about 5 ml. of aqueous phase had appeared below the siloxane phase, and a similar volume of tetramer had disappeared since the liquid level in the flask remained almost constant. At this point, the flask was capped with a solid polyethylene cap and allowed to stand for one week at room temperature. The viscosity of the siloxane phase was found to be only half that of the original tetramer.

In a similar experiment, anhydrous hydrogen chloride was bubbled through tetramer. Only a very slight cloudiness in the siloxane suggested the appearance of an aqueous phase within 15 minutes at room temperature. The flask was stoppered and allowed to stand at room temperature for one week. At the end of this period, the siloxane had a viscosity approximately 73% of that of tetramer. A portion of this material was boiled vigorously for several minutes at 175° to remove excess hydrogen chloride, then was cooled and treated with several drops of silver nitrate solution. Shaking this mixture caused the formation of a substantial precipitate of silver chloride in the aqueous phase. A solution of tetramethyldisiloxanediol in tetramer gave negative results when tested with silver nitrate solution. In another experiment, 0.5 ml. of 35% aqueous hydrogen chloride and 5 ml. of tetramer were placed in a stoppered tube and allowed to stand for one week. At the end of this period, the viscosity of the siloxane phase was 12% higher than that of tetramer. This phase also gave a positive test for the presence of chlorosilane although much slighter in amount than that observed in the previous test. The original tetramer gave a negative test for halogen.

When anhydrous hydrogen bromide was bubbled through tetramer, the rapid appearance of cloudiness denoted the formation of an aqueous phase. After 15 minutes, the flask was sealed. After one week, the siloxane had a viscosity 2.5 times that of tetramer. A test for the presence of halogen in the siloxane, as described above, gave a strongly positive result. In a second test, a few drops of water were placed in a test-tube together with 10 ml. of tetramer, then hydrogen bromide was bubbled through the water phase and the siloxane to saturate the mixture. The tube was stoppered and allowed to stand at room temperature. Twenty-four hours later, the viscosity of the siloxane was 6.5 times that of tetramer, and 3 days later the siloxane was a thick sirup whose viscosity was too high to measure by the procedure being used. This material did not become any thicker on continued standing although when it was exposed to air, the upper surface of the siloxane rapidly became more viscous owing to loss of chain-terminating groups by the volatilization of hydrogen bromide from the mixture and the hydrolysis of silyl bromide end groups.

**Reaction with Other Acids.**—Perchloric acid was effective in causing siloxane rearrangement polymerization both at room temperature and at elevated temperatures. Pyrophosphoric acid was effective at elevated temperatures, but 85% acid (sirupy phosphoric acid) had no effect on either the boiling point or viscosity of tetramer when a sample of tetramer together with 2.5% by weight of the acid was allowed to stand for a week at room temperature. Various experiments were made in which 50-g. quantities of tetramer were heated at reflux (175°) with 0.25-g. amounts of oxalic acid, trichloroacetic acid and perfluorobutyric acid for 16-hour periods. With none of these materials was any appreciable change noted in the viscosity or boiling point of the siloxane; thus they are considered to be ineffective as siloxane rearrangement catalysts as compared with acids like sulfuric acid. This does not imply that they did not react with the siloxane.

A mixture of 60 ml. of tetramer and 0.5 ml. of trifluoroacetic acid was refluxed for 16 hours, during which the siloxane polymerized to a sirup. Various proportions of trifluoroacetic acid were added to tetramer, both in sealed tubes and in open tubes and allowed to stand at room temperature for two days. In none of these experiments could any appreciable change in the viscosity or boiling point of the siloxane–acid mixture be observed. Over a period of two weeks, a mixture of 10 ml. of tetramer and 0.5 ml. of acid in a closed bottle polymerized to a thin sirup. Infrared analysis of a similar mixture (made up at room temperature, stoppered and measured several days later; no siloxane polymerization evident from viscosity measurements) showed definite evidence for both silanol groups and the presence of Si–O–C bonds.

**Conductance Experiments.**—The conductivity cell was glass and contained two platinum electrodes 1-cm. square spaced 1-cm. apart. The voltage supply was a 90-volt battery and the meter was a 20-microampere meter. The addition of sulfuric acid or fuming sulfuric acid to tetramer in various amounts up to quantities sufficient to cause rapid gelation of the siloxane gave no observable conductivity of the siloxane phase. Bubbling any of the anhydrous hydrogen halides through tetramer likewise gave negative results. These experiments were repeated with hexamethyldisiloxane in place of the tetramer, but results similarly were negative. The addition of small quantities of siloxane to sulfuric acid or fuming acid, with 1.5 volt battery as the voltage source, produced marked increases in the conductivities of these media. This is in agreement with the results obtained by Price.[3]

When 0.5 ml. of trifluoroacetic acid was added to 10 ml. of anhydrous tetramer in the cell, the current passed by the cell was *ca.* 0.5 microampere, corresponding to a conductance of approximately $5 \times 10^{-9}$ mho.

## Discussion

In view of the experimental evidence, the most probable mechanism for acid-catalyzed rearrangement of siloxane bonds in polydimethylsiloxanes involves an equilibrium reaction in which coördination of the acid proton to the siloxane oxygen is followed by cleavage of the siloxane bond with the formation of a silanol group and a silyl ester or silyl halide group. The reversal of this process with

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[12] This ready cleavage of organosiloxanes by hydrogen fluoride has been reported previously.[6]

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.

**Acknowledgments.**—I should like to express my appreciation to Drs. R. C. Osthoff, W. T. Grubb and A. M. Bueche for interesting discussions and to Mr. C. A. Hirt for the infrared analyses.

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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.

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## 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).