be a function of the rapidity of heating if this could be varied significantly.

Nevertheless, it is apparent that the molecular processes responsible for the glass transition must necessarily be partly responsible for the increase in the dielectric loss. We picture these processes as occurring in the amorphous region of the polymer where, with rise of temperature, the viscosity of this region falls to a value low enough for the observed phenomena to occur.

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EVANSTON, ILLINOIS

NOTES

Studies of Zirconium Tetramandelate[1]

BY RICHARD B. HAHN AND LEON WEBER[2]

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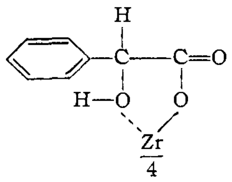
In studying the reactions of various organic acids with zirconyl ions, Kumins[3] observed that a precipitate was formed when a zirconyl chloride solution was treated with a solution of *d,l*-mandelic acid (phenylglycolic acid). The precipitate was shown to be zirconium tetramandelate, $Zr(C_8H_7O_3)_4$. Using mandelic acid as a reagent, Kumins developed an analytical method for the determination of zirconium in the presence of various other ions. Hahn[4] found that quantitative precipitation of zirconium tetramandelate occurs even in strongly acid solution and that hafnium was also precipitated by mandelic acid.

Kumins considered the zirconium tetramandelate precipitate as a simple salt, $Zr(C_8H_7O_3)_4$, whereas Feigl[5] postulated a chelate type structure



Kumins observed that zirconium tetramandelate dissolves in aqueous ammonia. This he attributed to the formation of a soluble complex with ammonia, although no experiments were made to substantiate this. The solvent action displayed by ammonia on zirconium tetramandelate was explained by Feigl as being due to the presence of acidic (OH) groups in zirconium tetramandelate. The acidity of the weakly acidic alcoholic (OH) group of mandelic acid is enhanced by the coördination of the zirconium with the oxygen atom of an (OH) group as shown in the above structure. The binding of the hydrogen atom is loosened and hence it becomes more mobile, or more acidic. If all four mandelate groups are linked to zirconium in this inner complex manner, one can assume that all four hydrogen atoms could be replaced by ammonia; however, if only two molecules of mandelic acid are so linked and two bound normally, then only two hydrogen atoms would be replaced by ammonia. The first condition would assign zirconium the coördination number of 8, which is quite rare, and the second would assign the more common value of 6. In order to clarify the structure and the reactions of zirconium tetramandelate the following investigations were made.

Experimental

Reagents.—Chemically pure zirconyl chloride, $ZrOCl_2 \cdot 8H_2O$ (Fisher Scientific Co.), was used in all experiments. This was checked spectrographically and found to be free of impurities except for a small amount of hafnium. A solution was prepared by dissolving the salt in water. This solution was standardized by precipitation with mandelic acid.

d,l-Mandelic acid (Eastman Kodak Co. No. 722 melting point 119–121°) was used. A saturated aqueous solution (about 15%) was used in all experiments.

Sodium mandelate (Mallinckrodt) was purified by several recrystallizations from 95% ethyl alcohol. The final salt was assumed to be $NaC_8H_7O_3$.[6]

Reaction of Zirconyl Ions with *d,l*-Mandelic Acid.—When a solution containing zirconyl ions is treated with mandelic acid a precipitate does not form immediately. A clear solution is obtained which persists for a moment or two even when a large excess of mandelic acid is present. If the mandelic acid is added dropwise, a precipitate does not form until almost equivalent amounts are mixed. It was considered that an intermediate soluble complex may be formed first which then reacts with more mandelic acid to form a precipitate. In order to check this hypothesis a conductometric titration was carried out. Standard solutions of zirconyl chloride and sodium mandelate were prepared. The zirconyl chloride was titrated with the standard sodium mandelate solution using the apparatus described by Willard, Merritt and Dean.[7] The results are shown in Fig. 1.

50.0 ml. of 0.0163 *M* zirconyl chloride was found to react with 1.9 ml. of 1 *M* sodium mandelate. This indicates that approximately 2.3 moles of sodium mandelate react with 1 mole of zirconyl ion to form a soluble complex. The reaction might be formulated as

$$ZrO^{++} + 2HC_8H_7O_3 \longrightarrow ZrO(C_8H_7O_3)_2 + 2H^+$$

When an excess of mandelate ion is added a precipitate of zirconium tetramandelate results

$$ZrO(C_8H_7O_3)_2 + 2HC_8H_7O_3 \longrightarrow Zr(C_8H_7O_3)_4 + H_2O$$

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[1] This study was supported in part by a grant from the Atomic Energy Commission, AT(11-1)213.

[2] Submitted as a thesis by Leon Weber in partial fulfillment for M.S. degree in chemistry, Wayne University.

[3] C. A. Kumins, *Anal. Chem.*, **19**, 376 (1947).

[4] R. B. Hahn, *ibid.*, **21**, 1579 (1949).

[5] F. Feigl, "Chemistry of Specific, Sensitive, and Selective Reactions," Academic Press, Inc., New York, N. Y., 1949.

[6] J. D. M. Ross and R. J. Morrison, *J. Chem. Soc.*, 1016 (1933).

[7] H. H. Willard, L. L. Merritt and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Co., New York, N. Y., 1951, p. 224.

The first reaction takes place rapidly whereas the second reaction proceeds slowly. This is indicated by the fact that no break in the conductometric titration curve is obtained when precipitation takes place.

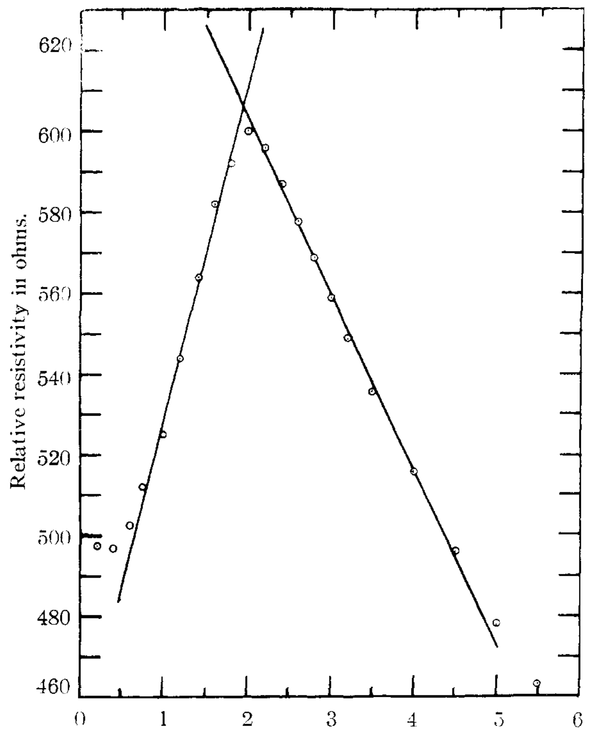

Fig. 1.—Conductometric titration of 50 ml. of 0.0653 *N* zirconyl chloride with 1.00 *N* sodium mandelate.

Preparation of Zirconium Tetramandelate.—Chemically pure zirconyl chloride octahydrate was dissolved in a solution containing three parts by volume of water and one part by volume of concentrated hydrochloric acid. The resulting solution was heated to 80° and a 15% solution of *d,l*-mandelic acid was added dropwise with stirring until precipitation was complete. The precipitate was filtered and washed three times with acetone and two times with ether then dried at 110°. Analysis of the precipitate gave the following percentages.

Anal. Calcd. for $Zr(C_8H_7O_3)_4$: C, 55.24; H, 4.06; ZrO_2, 17.71. Found: C, 55.28; H, 4.15; ZrO_2, 17.80.

Reaction of Zirconium Tetramandelate with Ammonia.—Weighed amounts of zirconium tetramandelate were suspended in about 25 ml. of water in glass-stoppered flasks. An amount of standard ammonia solution sufficient to dissolve about one-half of the zirconium tetramandelate was pipetted into each flask. The flasks were stoppered then shaken in a mechanical shaker for two hours. After reaching equilibrium, the undissolved zirconium tetramandelate precipitate was filtered off then dried and weighed. Analysis showed there was no change in the composition of the undissolved precipitate.

The remaining solution was acidified with hydrochloric acid. Mandelic acid was added which caused the reprecipitation of zirconium tetramandelate. The amount of zirconium tetramandelate recovered agreed exactly with the amount dissolved by the ammonia. The molar relationship of the zirconium tetramandelate to the ammonium hydroxide was 1 to 3 (one mole of zirconium tetramandelate reacts with three moles of ammonia). These data are shown in Table I (samples a and b).

TABLE I

DISSOLUTION OF ZIRCONIUM TETRAMANDELATE IN AMMONIA AND ETHYLENEDIAMINE

Sample	Wt. of $Zr(C_8H_7O_3)_4$ (g.)	0.1157 *N* ammonia added, ml.	0.1509 *N* HCl for back titration, ml.	Wt. of residue (g.)	Molar ratio $\frac{\text{base}}{Zr(C_8H_7O_3)_4}$
a	0.4789	10.00	...	0.2212	3.01
b	1.0393	25.00	...	.3656	2.98
c	0.4051	50.00	25.02	....	3.45
d	0.3676	50.00	26.15	....	3.48
e[a]	0.3237	50.00[a]	25.60	....	1.76[a]

[a] 0.1106 *N* ethylenediamine used in this experiment.

The reaction of zirconium tetramandelate with an excess of ammonia was also studied. A weighed amount of zirconium tetramandelate was dissolved in excess standard ammonia solution. The excess ammonia was titrated with standard hydrochloric acid using a glass electrode as indicator (Beckman *p*H meter model H-2). The results shown in Table I (samples c and d), indicate that about 3.5 moles of ammonia react with one mole of zirconium tetramandelate. Ethylenediamine was substituted for ammonia and the above experiment repeated. Sample (e) in Table I shows the same relationship holds also for ethylenediamine. A typical titration curve is given in Fig. 2.

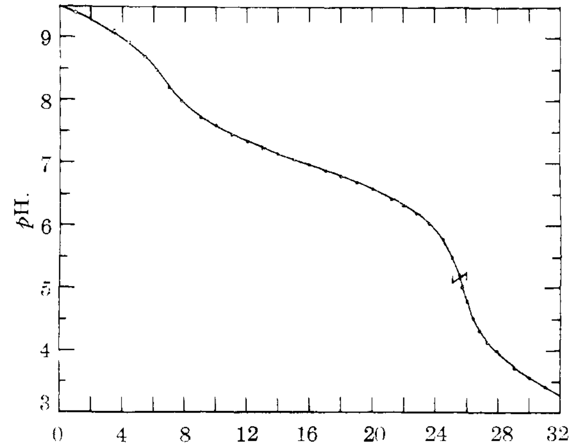

Fig. 2.—Potentiometric titration of excess 0.1106 *N* ethylenediamine with 0.1509 *N* hydrochloric acid.

Reaction of Zirconium Tetramandelate with Sodium Bicarbonate and Sodium Carbonate.—When solid zirconium tetramandelate is treated with a solution of sodium bicarbonate, the solid slowly dissolves accompanied by the evolution of carbon dioxide gas. A clear solution is obtained finally. Upon longer standing, this solution gradually becomes turbid due to the formation of a precipitate of zirconium hydroxide. If an excess of mandelate ion is present, however, no precipitate is formed. The same phenomena are observed when zirconium tetramandelate is treated with sodium carbonate. The formation of carbon dioxide gas in this reaction indicates definitely that zirconium tetramandelate has acidic properties.

The weight of carbon dioxide formed by treating known amounts of zirconium tetramandelate with an excess of sodium bicarbonate solution were determined. Erratic and non-stoichiometric results were obtained. This was caused probably by partial hydrolysis of the zirconium tetramandelate molecule.

Reaction of Zirconium Tetramandelate with Other Solvents.—Other weakly basic solvents: methylamine, ethylamine, dimethylamine and other primary and secondary amines dissolved zirconium tetramandelate in the same manner as ammonia. These substances do not act as true solvents but rather as bases which react with the weakly acidic hydroxyl groups of zirconium tetramandelate to form soluble salts.

Zirconium tetramandelate is insoluble in acetone, ethyl alcohol, ethyl ether, chloroform and benzene.

X-Ray Diffraction Studies.—X-Ray diffraction patterns (powder method) were made on zirconium tetramandelate, ammonium mandelate, ammonium zirconium mandelate, sodium zirconium mandelate and sodium mandelate. In each case a separate distinct pattern was obtained. This indicates that in the reaction of zirconium tetramandelate with ammonia and sodium bicarbonate, no extensive hydrolysis takes place but a new salt-like compound is formed.

These studies show that zirconium tetramandelate must be a chelate type compound as postulated by Feigl. The reaction of ammonia with an excess of zirconium tetramandelate can be formulated

$$H_4Zr(C_8H_6O_3)_4 + 3NH_4OH \longrightarrow (NH_4)_3HZr(C_8H_6O_3)_4 + 3H_2O$$

An alternate explanation would be that three molecules of mandelic acid form a chelate ring with zirconium whereas the fourth molecule of mandelic acid forms a simple salt-like linkage. This would require that zirconium have a coördination number of 7, which is unlikely.

When an excess of ammonia is added, some of the tetrabasic salt $(NH_4)_4Zr(C_8H_6O_3)_4$ is formed. The reaction, however, is not stoichiometric as indicated by the molar ratio 1:3.5 of zirconium tetramandelate to ammonia. With other weak bases and basic salts, like sodium carbonate, corresponding reactions take place. With strong bases, however, hydrolysis takes place and zirconium hydroxide is precipitated. Because of the lack of stoichiometry the above reactions are not suitable as analytical methods.

CHEMISTRY DEPARTMENT
WAYNE UNIVERSITY
DETROIT, MICHIGAN

Oxygen Exchange in the Hydrothermal Growth of Quartz[1]

BY RICHARD G. YALMAN, JAMES F. CORWIN, GWILYM E. OWEN AND NEIL FETTER

RECEIVED MAY 5, 1955

During investigation of the mechanism of the isothermal formation of α-quartz at 400° and 340 atm. in sodium fluoride solutions, several oxygen exchange experiments were performed. By assuming that all of the oxygen atoms were equivalent and that the exchange was controlled by a homogeneous phase reaction between dissolved silica and water, complete isotopic exchange was observed.[2] On the basis of similar assumptions it has recently been shown that at 750° and at 960° the exchange reaction follows first-order kinetics.[3] In the latter experiments, however, the product was not identified and the degree of oxygen exchange per mole of silica was not determined.

The purpose of this note is to report some additional experiments on the exchange of oxygen in the silica–water system in the absence of fluoride ion.[4] Two sets of results were obtained. In the first of these all of the silica reacting was in the water phase, *i.e.*, dissolved, during all or most of the reaction time of 48 to 144 hours, and complete isotopic exchange was observed. On the other hand in those experiments where silica glass was converted into α-quartz, only partial isotopic exchange was observed.

Three different nutrient solutions prepared with water having a sevenfold O^{18} enrichment were used. These were 2 *M* sodium carbonate, 0.025 *M* sodium hydroxide and 0.025 *M* sodium chloride adjusted to a *p*H of 10 with sodium hydroxide. In the isothermal experiments using the sodium hydroxide and sodium chloride solutions the autoclaves and control equipment, the experimental procedure for the hydrothermal conversion of silica glass to α-quartz, the method of analysis for O^{18} and the procedure for calculating the degree of oxygen exchange were the same as those described previously.[2,5]

In the two experiments made with the 2 *M* sodium carbonate solutions, the gradient method of Nacken[6] was used, *i.e.*, the top and the bottom of the autoclaves were maintained at 380 ± 5° and 360 ± 5°, respectively, for 144 hours. In one of these experiments (No. 869) using 30 g. of α-quartz as the source of silica, 13.6 g. of the silica was found as an alkali soluble sludge in the bottom of the autoclave. In the second experiment (No. 872) using 30 g. of silica glass, 14 g. of the source material was found as an alkali-soluble sludge while the remainder was converted into α-quartz. The silica found in the sludge corresponds to the solubility of α-quartz in sodium carbonate solutions at 350–400°[7] and was probably present as soluble silica during the experiment.[6,7]

In order to calculate the degree of oxygen exchange in the gradient runs it was first necessary to determine the degree of exchange between water and sodium carbonate and between water and soluble silica under the conditions of our experiments. Accordingly separate runs were made with sodium carbonate and with disodium dihydrogen silicate solutions. As a further check on the procedure, additional experiments were also made using sodium sulfate solutions. The results of these various experiments are listed in Table I and indicate that complete oxygen exchange should occur in both the water-carbonate and the water-soluble silica systems during the gradient runs. This was confirmed in experiment no. 869 in which α-quartz was used as the source of the silica (see Table II). In the second gradient experiment in which silica glass was converted into α-quartz the degree of oxygen exchange was calculated by assuming that complete oxygen exchange occurred between the carbonate initially present and the silica ultimately found in the sludge. The results of this experiment are included in Table II.

The results of the isotopic exchange experiments in which silica glass was completely converted into α-quartz under isothermal conditions at 400° and 340 atm. using the sodium hydroxide and the sodium chloride solutions are summarized in Table III.

The complete isotopic exchange which is reported in Table I for the water–dihydrogen silicate system at 100° and in Table II for experiment No. 869 indicates that during the course of these experiments equilibria involving monomeric[8] silica had

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(1) The results and interpretations presented here are derived from work supported on contract between Antioch College and the U. S. Army Signal Corps through its Signal Corps Engineering Laboratories at Fort Monmouth, New Jersey.

(2) J. F. Corwin, R. G. Yalman and G. E. Owen, THIS JOURNAL, **75**, 1581 (1953).

(3) D. A. Hutchinson, *J. Chem. Phys.*, **22**, 758 (1954).

(4) The function of fluoride ion and the effect of *p*H on the hydrothermal formation of quartz is currently being investigated in this Laboratory. The results of this work will appear in a forthcoming publication.

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(6) R. Nacken, Report on Research Contract for Synthesis of Oscillator Crystals. U. S. Army Signal Corps, Interrogations (1946).

(7) I. I. Friedman, THIS JOURNAL, **70**, 2009 (1948).

(8) E. L. Brady, *J. Phys. Chem.*, **57**, 706 (1953).