[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, PHYSICS AND GEOLOGY, ANTIOCH COLLEGE[1]]

The Formation and Growth of Quartz in Sodium Fluoride Solutions under Isothermal Conditions

BY JAMES F. CORWIN, RICHARD YALMAN, G. E. OWEN AND A. C. SWINNERTON[2]

RECEIVED AUGUST 18, 1952

The investigation of one method of growing α-quartz under isothermal conditions has been completed under controlled conditions and the mechanism of devitrification of quartz glass and its transformation to crystalline quartz is proposed. Chemical analysis of residual solutions, X-ray analysis of the solids and isotope tracer experiments containing O^{18} were used. Complete oxygen exchange was exhibited between the water and crystalline solid formed. A relationship between laboratory and natural quartz formation is suggested.

The conditions for hydrothermal conversion of silica glass to quartz and its transfer to a seed plate of α-quartz by alkali halide solutions have been reported recently.[3,4] Since the most rapid and prolonged growth was obtained using sodium fluoride solutions and since this system was uncomplicated by other additives and temperature differentials, it was selected for determination of the mechanism by which fused silica is converted into quartz.

Experimental

Chemical Analysis and X-Ray Studies.—The apparatus and control equipment have been described in a previous publication.[4] Because of the difficulty of making any sort of instrumental measurements at 400° and 340 atmospheres pressure except temperature and pressure, a series of growth reactions were conducted under controlled conditions and the contents of the autoclave were analyzed by chemical and X-ray methods.

The conditions for maximum growth and transformation determined previously[3] were used. Some slight modifications were made to ensure constant conditions in the system. The 250-ml., stainless steel autoclaves were cleaned with strong alkali after each run to remove quartz that usually adhered to the inner surface, and then were heated with water and a standard buffer solution until neutrality was achieved. The autoclave was then loaded with 125 ml. of 0.025 *N* sodium fluoride solution and 20 g. of clear vitreous silica in the form of solid rod having approximately the same surface exposed for each run. The autoclave was then heated to 400° for periods of time ranging from 3 to 48 hours. After a run the *p*H of the liquid contents was measured and analysis for the ratio of NaF to Na_2SiF_6 was performed by the method of Geffcken and Hamann.[5] The solid material which adhered to the sides of the autoclave, the glass devitrified *in situ*, and suspended solids filtered from solution were analyzed by X-ray methods.

Experimental Results

The results of the closely controlled runs for chemical analysis are found in Table I.

TABLE I

*p*H 6.4, 400°, 48 hr., 340 atm., 125 ml. soln., 20 g. fused, clear silica; initial fluoride content 0.0575 g.

Final *p*H	NaF as fluoride, g.	Na_2SiF_6 as fluoride, g.	Total fluoride, g.	Difference fluoride final − initial g.
5.7	0.0053	0.0524	0.0577	+0.0002
9.0	.0093	.0510	.0603	+ .0028
10.0	.0049	.0570	.0619	+ .0044
7.6	.0062	.0520	.0582	+ .0007
7.4	.0064	.0492	.0556	− .0019
7.4	.0051	.0578	.0529	− .0046
9.1	.0020	.0542	.0562	− .0013

In all experiments approximately 2% of the silica was transferred to the seed where it grew as α-quartz. The remainder of the glass was either deposited on the sides of the autoclave as crystalline α-quartz or crystallized *in situ* to α-quartz. X-Ray[6] examination of material taken from all three locations confirmed microscopic identification of this material.

The crystallization of the silica glass to quartz depends upon the length of time that the experiment is continued (Table II). Up to 18 hours, a portion of the glass remains; after 18 hours, the conversion of glass to quartz is complete.

The final *p*H of single runs varied greatly even though constant conditions were maintained. However, an initial rise to a *p*H value above the original and a crystallization range of *p*H 7–10 in the early stages is indicated.

TABLE II

0.025 *N* NaF, initial *p*H 6.4, 340 atm. 400°, 125 ml. soln., 20 g., fused clear silica source.

Number of experiments	Final *p*H range	Quartz growth on seed, average mg.	Hours at temp.
14	7.3–10.4	5	<5 min.
4	7.1– 8.4	43	3
8	7.4–10.0	82	6
5	5.5– 7.8	346	18
7	5.5– 9.5	353	48

Experimental

Oxygen Exchange Studies.—Three experiments were conducted in which the solutions were made using water containing 1.5% H_2O^{18}. The density of the heavy water was determined using an Ainsworth Keyboard type balance significant to four decimal places. The solutions were then made and the experiments conducted using the same conditions as those mentioned in the previous section except all were continued 48 hours so that complete conversion of the silica glass to quartz was accomplished and larger amounts of glass were used to ensure a large change in density of the water. After completion of the experiments the solution was distilled to remove the water. The density of the water was again determined as above. All precautions suggested by Smith and Wojciechowski[7] were observed in making the density determinations.

---

(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, N. J.

(2) Deceased.

(3) J. F. Corwin and A. C. Swinnerton, THIS JOURNAL, **73**, 3598 (1951).

(4) A. C. Swinnerton, G. E. Owen and J. F. Corwin, *Discussions Faraday Soc.*, **5**, 172 (1949).

(5) W. Geffcken and H. Hamann, *Z. anal. Chem.*, **114**, 15 (1938).

(6) The authors wish to acknowledge the valuable assistance of the Central Research Laboratory of the Monsanto Chemical Co., Dayton, Ohio, for the use of their X-ray and spectrographic equipment and to I. B. Johns and A. H. Herzog for preparation and evaluation of the analyses.

(7) E. R. Smith and M. Wojciechowski, *Bull. Soc. Acad. Pol.*, **A1**, (1936).

Theory of Oxygen Exchange

Since the amount of the transformation of glass to quartz depends upon time and since the solubility of silica glass is relatively small in these solutions, the assumption is made that the transformation from solid glass to solid quartz is by the action of the solution and that the oxygen concentration of the solution at any time remains constant. However the ratio of O^{16} to O^{18} in the quartz glass transformed to crystalline quartz will depend on the O^{16} to O^{18} ratio in the solution at the instant of transformation. The change of the O^{18} concentration as a function of the silica can be represented by the equation

$$dF/d\mathrm{SiO_2} = -kF \qquad (1)$$

where SiO_2 is the quantity of glass converted to quartz and F is the mole fraction of O^{18} in the solution. The observed density of the solution is a linear function of the mole fraction of O^{18} present.

$$D_{\mathrm{obsd}} = FD_{\mathrm{H_2O^{18}}} + (1 - F)D_{\mathrm{H_2O^{16}}} \qquad (2)$$

and

$$F = \frac{D_{\mathrm{obsd}} - D_{\mathrm{H_2O^{16}}}}{D_{\mathrm{H_2O^{18}}} - D_{\mathrm{H_2O^{16}}}} \qquad (3)$$

From equation (3) we can obtain the change in the mole fraction of O^{18} as a function of the change in density of the solutions.

$$\Delta F = \frac{1}{D_{\mathrm{H_2O^{18}}} - D_{\mathrm{H_2O^{16}}}}\,\delta d D_{\mathrm{obsd}} \qquad (4)$$

If all of the oxygen in the silica glass is available for exchange with the solution during the conversion to quartz and since the total amount of oxygen in the solution remains constant, then it is convenient to express the silica in equation (1) as the fraction of oxygen made available by the silica to that present in the water itself.

$$\mathrm{SiO_2} = \frac{2 \times W_{\mathrm{SiO_2}}/\mathrm{M.W._{SiO_2}}}{W_{\mathrm{H_2O}}/\mathrm{M.W._{H_2O}}} = \frac{\text{moles O in silica}}{\text{moles O in solution}} \qquad (5)$$

Upon substituting equations (3), (4) and (5) into equation (1) and integrating, equation (6) is obtained.

$$\ln\frac{(D_i - D_0)}{(D_{\mathrm{obsd}} - D_0)} = k\,\frac{\text{moles O in SiO}_2}{\text{moles O in H}_2\text{O}} \qquad (6)$$

where D_i is the initial density of the enriched water and D_0 is the density of ordinary water. k is a proportionality constant which represents the ability of the oxygen from the water to exchange with the SiO_2 glass as it is transformed into quartz. If the SiO_2 is converted without reaction with the solvent, then $k = 0$ and no density change would be observed. If the reaction occurs and the tetrahedral nature of silicon compounds is considered, then

$$k = 2n + 2/(3n + 1) \qquad (7)$$

where n is the number of silicon atoms in the dissolved silicon species. A bridged Si–O–Si bond is indicated for n greater than one. Table III contains the values of k for several types of silicon species.

TABLE III

Formula of dissolved species	n	k
SiO_3	1	1.0
SiO_4	1	1.0
Si_2O_7	2	0.86
Si_nO_{3n+1}	∞	0.66

Experimental Results

Table IV records the data from the oxygen enriched water experiments along with the calculated values of the terms in equation (6).

TABLE IV

0.025 *N* NaF, 48 hr., 340 atm., 400°, fused clear silica glass

Wt. SiO_2 glass, g.	Wt. H_2O, g.	Ratio $\frac{\text{Oxygen-SiO}_2}{\text{Oxygen-H}_2\text{O}}$	$\ln\frac{(D_i - D_0)}{(D_{\mathrm{obsd}} - D_0)}$	k
60.0	125.0	0.288	0.283	0.98
60.0	125.0	.288	.271	0.94
60.0	125.0	.288	.291	1.01
			Av.	0.98

Discussion

Since no quartz growth and little devitrification is possible in neutral or acid solutions,[3,8,9] the following mechanism for the devitrification of the silica glass is proposed. The first reaction is represented by equation (a)

$$6F^- + SiO_2 + 2H_2O = SiF_6^{--} + 4OH^- \qquad (a)$$

which produces sufficient OH ions to provide for several possible reactions

$$2OH^- + SiO_2 = SiO_2(OH)_2^{--} \qquad (b)$$

$$OH^- + H_2O + SiO_2 = SiO(OH)_3^- \qquad (c)$$

$$OH^- + SiO_2 = SiO_2(OH)^- \qquad (d)$$

$$xOH^- + ySiO_2 + zH_2O = Si_y\,O_{(3y+1)}\,H_{(2y+2-xOH^-)} \qquad (e)$$

The results of the analyses for the NaF and Na_2SiF_6 remaining in the autoclave after a growth run, recorded in Table I, show that equation (a) is not a complete reaction but reaches equilibrium when about 90% of the fluoride has been converted to SiF_6^{--}. The OH^- ion thus formed would be enough to produce approximately *p*H 12; however, the reactions of devitrification (b, c, d and e) would be using it up almost as as fast as it is formed. The devitrification reactions would soon deplete the OH^- ion in solution if it were not for the formation of α-quartz which would be the reverse of the devitrification reaction and the return of the OH^- ions to the solution. The *p*H measurements recorded in Table II show that reaction (a) is almost immediate and probably begins in the warm-up period. The reactions then proceed with the devitrification and quartz formation until 18 hours has passed and no more glass apparently remains. An extension of the experiment to 48 hours does little to change the situation since all of the solid contents are now α-quartz and no solubility difference exists. The presence of residual silicates in solution can be shown by the formation of the silica–molybdic acid complex, and would account for the final *p*H of the growth runs.

The results of the experiments (Table IV) using water enriched with O^{18} in which an equilibrium distribution of the heavy oxygen between the solution and crystallized solid is indicated, favors reactions (b, c and d) since a mechanism corresponding to reaction (e) would result in silica complexes containing bridge oxygens, which would result in incomplete oxygen exchange with the solvent. Mechanism (d) also would not seem possible if the

---

[8] W. A. Wooster and N. Wooster, *Nature*, **157**, 297 (1946).

[9] G. Van Praagh, *Discussions Faraday Soc.*, No. 5, 338 (1949); G. Van Praagh, *Research* (*London*), **1**, 458 (1948).

tetrahedral nature of silicon and the plentiful supply of coördination ions and molecules is considered. Then of the theoretically possible quartz species listed in Table III, SiO_3, Si_2O_7 and Si_nO_{3n+1} where n is greater than 2, would be eliminated from consideration. SiO_4 formed by either reaction (b) or (c) could account for all of the variables tested experimentally. The reversal of equation (a) could also account for all of the variables. However, since crystallization and growth can be accomplished by reaction (b) or (c) in systems (3) not containing F^- or SiF_6^{--}, reaction (a) is necessary only to provide the hydroxide ions in order that the silica may be converted to α-quartz *via* reactions (b) or (c).

Weitz, Franck and Schuchard[10] have reported that orthosilicic acid occurs in river water up to 50 p.p.m. and in hot springs and geysers of New Zealand up to 1000 p.p.m. because of the high temperatures. The above suggested mechanisms postulating salts of orthosilicic acid as the interim compound between glass and α-quartz suggests that natural quartz may be formed by the same mechanism.

Acknowledgments.—The authors wish to acknowledge the help of David R. Swaney and Neil R. Fetter, who acted as technical assistants in this program.

[10] E. Weitz, H. Franck and M. Schuchard, *Chem.-Ztg.*, **74**, 256 (1951).

YELLOW SPRINGS, OHIO

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

The Preparation and Characterization of Some Pure Organobromosilanes

BY PATRICK A. MCCUSKER AND EDWARD L. REILLY

RECEIVED DECEMBER 8, 1952

Phenyldibromosilane, phenylbromosilane and *p*-methoxyphenyltribromosilane, previously unreported, have been prepared, purified and characterized. Ethyltribromosilane and diethyldibromosilane have been purified and characterized, and some other organobromosilanes further characterized. A new reaction in silicon chemistry has been observed in the preparation of triphenylbromosilane by the reaction of silicon tetrabromide with triphenylsilanol. Replacement of chlorine by bromine, accompanied by extensive cleavage of the silicon-to-carbon bond, was observed to occur by the reaction of aluminum bromide on organochlorosilanes. With hydrogen bromide alone no replacement was observed.

For the purpose of obtaining electric moment data, which are to be reported in another paper,[1] a number of pure organobromosilanes were required. Some of the compounds obtained are new and further physical data were obtained for several others. In the present paper the new data are reported and some reactions of organohalogenosilanes are discussed.

Experimental

Trimethylchlorosilane, dimethyldichlorosilane, diethyldichlorosilane from the Dow Corning Corporation, diphenyldichlorosilane from Anderson Laboratories, Inc., Adrian, Michigan, phenyltrichlorosilane and hexamethyldisiloxane from the Linde Air Products Company, and *p*-bromanisole from the Matheson Company, were used as received without further purification. Triphenylchlorosilane from Anderson Laboratories, Inc., was vacuum distilled before use. Silicon tetrabromide was prepared and purified as previously described.[2]

The refractive indices of the compounds were measured with a calibrated Abbé refractometer at 25.0°. The densities were determined in an 8-ml. Ostwald pycnometer. Melting points, below room temperature, were determined in an apparatus previously described by Kennard and McCusker.[2]

The reaction apparatus consisted of a 3-necked flask equipped with sealed stirrer and reflux condenser and protected from atmospheric moisture. The products, with the exception of triphenylbromosilane, were purified by repeated fractional distillations through a 53″ glass-helix packed column of about 15 theoretical plates. Small middle cuts were used for measurements. Analyses were carried out by titrating aqueous suspensions of the organobromosilanes with standard base. Molar refractions were calculated from the data of Warrick.[3] The purity of the fractions used for measurements of physical constants was established by constancy of boiling point and melting point.

Methyltribromosilane, Dimethylbromosilane, Ethyltribromosilane and *p*-Methoxyphenyltribromosilane.—These compounds were prepared by the dropwise addition of an ether solution of 1 mole of Grignard reagent to an ether solution containing a 5% excess of silicon tetrabromide, at a rate sufficient to maintain reflux. After the reaction was complete separation into two layers occurred. The lower layer consisted essentially of magnesium bromide etherate and was discarded. Distillation of the upper layers was complicated by the separation of large quantities of solid magnesium bromide etherate after the ether had been distilled off. In later preparations this mechanical difficulty was greatly reduced by the addition of dry carbon tetrachloride to the liquid mixture, to cause precipitation of solid magnesium bromide etherate. The liquid was then decanted and fractionally distilled. Data on purified fractions are listed in Table I.

Diethyldibromosilane, Triethylbromosilane, Phenyltribromosilane and Diphenyldibromosilane.—These compounds were prepared in one mole quantities by the bromination of partially substituted silanes obtained by the reduction of the chloro compounds with lithium aluminum hydride.

The reductions of diethyldichlorosilane and triethylchlorosilane were performed according to the procedure described by Finholt, *et al.*,[4] for the reduction of diethyldichlorosilane. The reductions of phenyltrichlorosilane and diphenyldichlorosilane were performed according to the procedure described by Benkeser, Landesman and Foster.[5] The brominations were carried out according to the procedure described by Kraus and Nelson[6] for the bromination of triethylsilane and by Nebergall[7] for the bromination of phenylsilane. Properties of purified samples of these compounds are listed in Table I.

Phenylbromosilane and Phenyldibromosilane.—To 0.3 mole of phenylsilane dissolved in 120 ml. of ethyl bromide was added dropwise over a two-hour period a solution of 0.9 gram atoms of bromine in 120 ml. of ethyl bromide. The

---

[1] E. L. Reilly, C. Curran and P. A. McCusker, THIS JOURNAL, to be published.

[2] M. S. Kennard and P. A. McCusker, *ibid.*, **70**, 1039 (1948).

[3] E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[4] A. E. Finholt, A. C. Bond, K. E. Wilzbach and H. I. Schlesinger, *ibid.*, **69**, 2696 (1947).

[5] R. A. Benkeser, H. Landesman and D. J. Foster, *ibid.*, **74**, 648 (1952).

[6] C. A. Kraus and W. K. Nelson, *ibid.*, **56**, 195 (1934).

[7] W. H. Nebergall, *ibid.*, **72**, 4702 (1950).