8

CONTRIBUTION TO THE KINETICS OF GLASS FORMATION FROM SOLUTIONS

HELMUT SCHMIDT AND ALFRED KAISER
Fraunhofer-Institut für Silicatforschung,
Würzburg, West Germany

MICHAEL RUDOLPH AND AXEL LENTZ
Abteilung für Anorganische Chemie,
Universität Ulm, West Germany

INTRODUCTION

The kinetics of hydrolysis of tetraalkoxysilanes have been investigated by different authors.[1-5] Depending on reaction conditions different orders of the overall reaction were found and different mechanisms of the transition states were postulated. Generally, these papers do not take into account the possibility of different rates in the single reaction steps of the hydrolysis of the different species $(RO)_nSi(OH)_{4-n}$ ($n = 4$ to 1) for the reaction

$$(RO)_nSi(OH)_{4-n} + H_2O \rightarrow (RO)_{n-1}Si(OH)_{4-(n-1)} + ROH \qquad (1)$$

If different rate constants for the reaction with different values of n are assumed, it is unlikely that the reaction can be simply described. The results described elsewhere[6,7] show that for special reaction conditions one can describe at least the beginning of hydrolysis as first order overall kinetics. In this paper the experimental conditions of hydrolysis were varied with respect to higher and lower catalyst concentrations. Furthermore, mechanistic aspects of the hydrolysis reaction are discussed.

EXPERIMENTAL

The reaction of $Si(OR)_4$ with water was monitored by measuring the H_2O concentration via IR spectroscopy. The concentration of H_2O represents the number of unhydrolyzed OR groups exactly, as long as no condensation takes place.[6] It could be shown that in a 1:1 mixture of silane and ethanol the absorbance of water at 1650 cm^{-1} follows Lambert–Beer's law up to 8% by volume and with minor corrections up to about 10% by volume. This was valid for HCl concentrations up to 1 mmole/L and NH_3 concentrations up to 100 mmole/L. The IR data were transmitted to a data processing system, where baseline corrections and kinetics plots could be made.

Tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS) were chosen to be studied. The water to silane ratios were 1:2 to 2:1 (by moles), yielding a ratio of hydrolysable groups to water ($SiOR:H_2O$) from 8:1 to 2:1. Ethanol was used as the solvent for silane and catalyst. The volume ratio of silane: ethanol was kept at 1:1. HCl was used as catalyst in concentrations from 0.1 to 1.0 mmole/L and NH_3 in concentrations from 10 to 100 mmole/L. The high NH_3 concentrations were necessary for a reasonable reaction time. The reaction temperature was kept at 20°C (in all experiments) by use of a thermostated cell.

RESULTS AND DISCUSSION

General Considerations

Figure 8.1 shows a comparison between the hydrolysis of TMOS and TEOS with identical HCl concentrations and the NH_3 catalyzed hydrolysis of TMOS.

Generally the reaction rate of hydrolysis of TMOS is remarkably faster than that of TEOS if similar reaction conditions are used. In the case of HCl catalysis, the half life (with respect to water consumption) is about 10 to 20 times higher with TEOS than with TMOS. Further systematic experiments confirm that these results are independent of HCl concentration and of the starting amount of water which is consistent with former data. With NH_3 as a catalyst the differences between the reaction rates seem to be even higher than with HCl. However, with base catalysis condensation takes place much earlier than with acid catalysis and therefore interpretation of long-term experiments is more difficult. Another general difference between HCl and NH_3 catalysis is that NH_3-catalyzed reactions require higher catalyst concentrations for similar reaction rates. This might be due to the fact that HCl is a strong and nearly completely dissociated acid, whereas NH_3 is a weak base which remains mainly undissociated as NH_4OH in the reacting system.

Though these experiments were carried out with an understochiometric amount of water with respect to hydrolysis of all SiOR groups, hydrolysis was not complete and stopped at a residual amount of about 5–20% water. There was a tendency for residual concentrations to increase with increasing starting

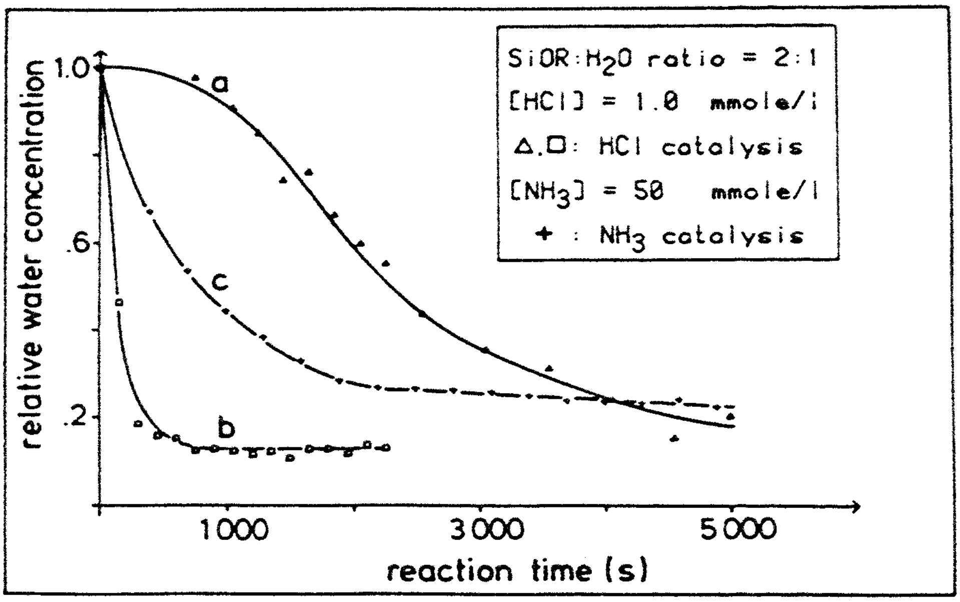


Figure 8.1 Hydrolysis of TEOS with HCl catalysis (curve *a*) and of TMOS with HCl (curve *b*) and NH_3 catalysis (curve *c*).

concentrations. With NH_3 catalysis sometimes an intermediate increase of water concentration could be observed, indicating that the condensation reaction overcomes the effect of water consumed by the hydrolysis reaction.

Kinetic Results

Hydrolysis experiments were carried out with TMOS and TEOS using HCl and NH_3 as catalysts in concentrations of 0.1 to 1.0 mmole/L (HCl) and 10 to 100 mmole/L (NH_3), which confirmed the tendencies described above. The curves obtained from reaction conditions with half lifes of less than about 500 s generally can be fitted approximately with first order kinetics according to the restrictions mentioned above. A typical example of this type of curve is shown in Fig. 8.1, curve *b*. Curves with half lifes of significantly more than 500 s show something like "inhibition phases" (curve *a*, Fig. 8.1). The hydrolysis curve of the latter type cannot be explained by a single reaction using only one reaction order and one rate constant k. As a consequence, k values computed under the assumption of a definite order of reaction should vary with turnover [k_{I}, Eq. (2) $\triangleq$ first order; k_{II}, Eq. (3) $\triangleq$ second order].

$$k_{\mathrm{I}}t = \ln \frac{1}{x} \tag{2}$$

$$k_{\mathrm{II}}t = \left(\frac{1}{a-b}\right) \ln \left(\frac{b}{a} \cdot \frac{a-x}{b-x}\right) \tag{3}$$

$$a = c_{o(\mathrm{H_2O})}; \qquad b = c_{o(\mathrm{SiOR})}; \qquad x = c_{t(\mathrm{SiOH})} = c_{o(\mathrm{H_2O})} - c_{t(\mathrm{H_2O})}$$

TABLE 8.1 Rate Constants k_I (First Order Assumption) and k_{II} (Second Order Assumption) Calculated After Different Consumption of Water

Silane	Catalyst	Catalyst Concentration (mmole/L)	SiOR:H_2O Ratio	$k_I \times 10^3$ (s^{-1}) After Water Consumption of			$k_{II} \times 10^4$ ($L \cdot mole^{-1} \cdot s^{-1}$) After Water Consumption of		
				20%	30%	50%	20%	30%	50%
TEOS	HCl	0.5	2:1	0.11	0.14	0.19	1.14	1.51	2.27
			4:1	0.39	0.42	0.49	3.97	4.35	5.29
			8:1	0.49	0.57	0.72	5.00	5.82	7.44
		0.1	2:1	0.01	0.01	0.01	0.09	0.12	0.17
			4:1	0.04	0.05	0.07	0.36	0.48	0.71
			8:1	0.06	0.08	0.11	0.62	0.80	1.10
TMOS	HCl	0.5	2:1	1.70	2.10	2.98	18.0	22.8	36.7
			4:1	2.32	3.21	4.95	23.9	33.5	53.3
			8:1	3.28	4.20	5.59	33.2	42.8	57.9
		0.1	2:1	0.27	0.30	0.39	2.9	3.2	4.5
			4:1	0.29	0.42	0.68	3.0	4.4	7.3
			8:1	0.66	0.77	0.99	6.6	7.9	10.2
TMOS	NH_3	50	2:1	1.16	1.06	0.94	12.24	11.59	10.96
			4:1	0.74	0.84	0.88	7.64	8.74	9.48
			8:1	0.47	0.62	0.92	4.71	6.31	9.58
		10	2:1	2.98	0.13	0.11	1.41	1.44	1.25
			4:1	0.10	0.13	0.17	1.04	1.32	1.81
			8:1	0.04	0.05	0.09	0.45	0.56	0.88

Table 8.1 compares turnover dependence of *k* values calculated according to assumptions of first or second order reactions.

The most important consequence of these results is that a first order assumption as suggested from earlier results cannot be maintained, if the reaction conditions are varied over a wider range. Since the type *b* curve cannot be fitted with any other reaction order, and since it is unlikely that the chemical mechanisms of the reaction change remarkably with the relatively modest change of pH and H_2O concentrations, the influence of different rates of the single reaction steps has to be considered.

Effect of Water Concentration

Regardless of the formal treatment and the rate of water turnover, Table 8.1 shows a remarkable effect of the SiOR:H_2O ratio on the reaction rate. In the case of HCl catalysis the reaction rates generally increase as the starting concentration of water decreases. Figure 8.2 shows the dependence of the relative hydrolysis rate constants of TEOS on HCl concentration and on the SiOR:H_2O

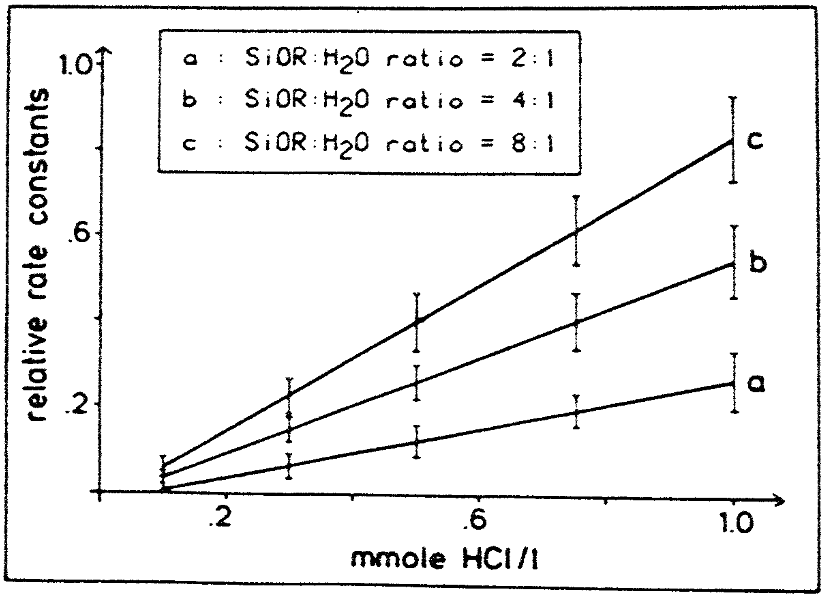


Figure 8.2 Dependence of the relative rate constants $k_1 \cdot f$ of the hydrolysis of TEOS with HCl as catalyst from the HCl concentration and from the starting SiOR : H_2O ratio. (Normalization factor $f = 500$.)

ratio. The constants are calculated from Eq. (2) after 50% consumption of the initial water. Similar results are obtained by using Eq. (3) and also for the TMOS system.

With NH_3 as catalyst the effect of the starting concentration of water on the reaction rate is less clear. If one calculates relative k values from an early state of the reaction, there often is an interference from the "inhibition phase", but later in the reaction the influence of the condensation reaction becomes stronger and can lead to errors. Therefore Fig. 8.3 shows the relative rate constants for

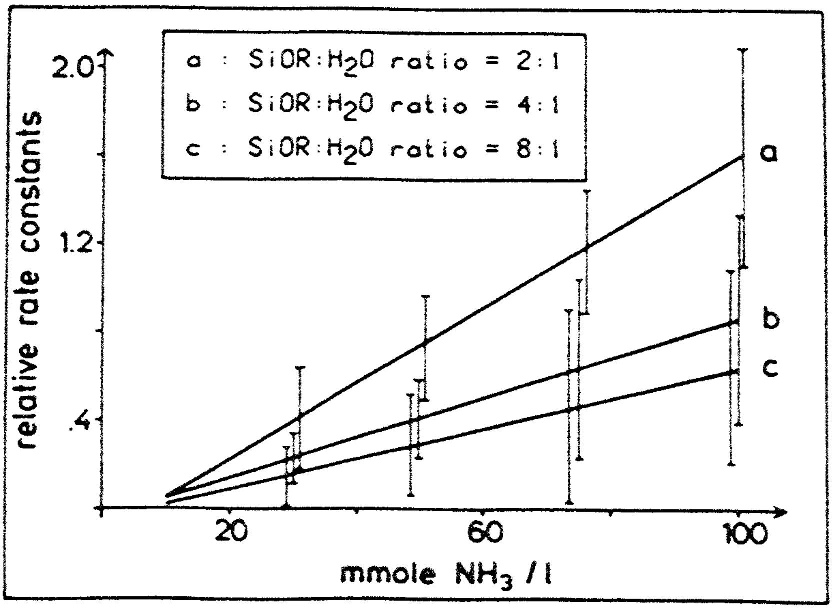


Figure 8.3 Dependence of the relative rate constants $k_1 \cdot f$ of the hydrolysis of TMOS with NH_3 catalysis from the NH_3 concentration and from the SiOR:H_2O starting ratio. (Normalization factor $f = 500$.)

$SiOR:H_2O$ starting ratios of 2:1, 4:1, and 8:1 using TMOS. Despite the scattered data the trend toward higher reaction rate constants with higher starting amounts of water becomes clear.

Mechanistic Aspects

The results of the measurements of hydrolysis reaction rates in the systems TEOS and TMOS with HCl and NH_3 as catalysts show that considering only an overall hydrolysis reaction can be misleading. Therefore the single reaction steps of Eq. (1) have to be taken into consideration. From theoretical considerations it becomes probable that the hydrolysis rate increases with an increasing number of hydrolyzed OR groups of the reacting silane due to a decrease in the stabilizing effect of alkyl groups in the transition state. In order to find out the effect on the hydrolysis reaction of this assumption, a computer simulation of the single hydrolysis steps was performed. For computing the actual concentrations of the $(RO)_nSi(OH)_{4-n}$ species first order kinetics and a ratio of 1:2:4:8 for the k values of the single steps of reaction (1) was assumed. Figure 8.4 shows the relative concentrations of each $(RO)_nSi(OH)_{4-n}$ species versus H_2O content. The resulting curve (dashed line) represents the total "activity" of hydrolysable species derived from the sum of the concentrations of each alkoxy- or hydroxysilane multiplied with its relative rate constant. This curve indicates that a maximum of "activity" occurs somewhat after the beginning of the reaction. This behavior shows an "inhibition phase" followed by a region of maximum activity where water is consumed very rapidly due to an "acceleration phase" in the H_2O consumption curve. These results however do not indicate whether the reactions of the single species follow first or second order kinetics.

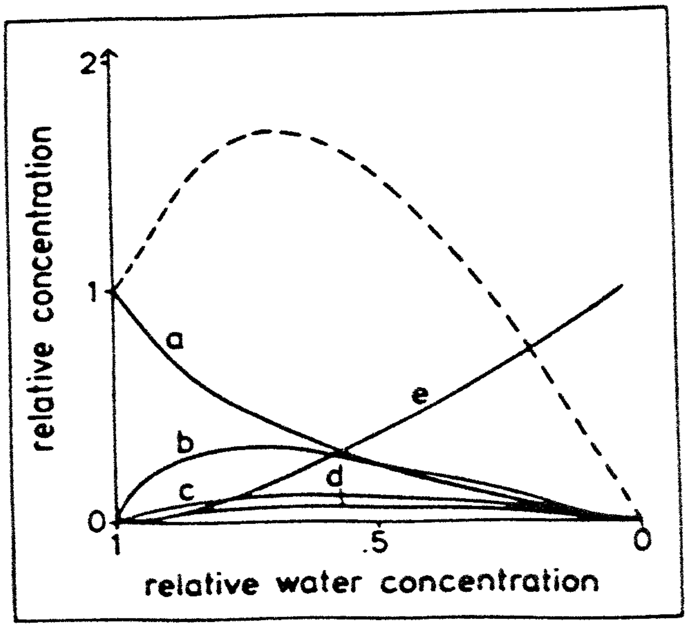
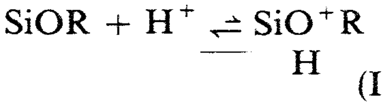


Figure 8.4 Computer simulation of the relative concentrations of the different hydrolysis intermediates [$a = (RO)_4Si$; $b = (RO)_3SiOH$; $c = (RO)_2Si(OH)_2$; $d = ROSi(OH)_3$; $e = Si(OH)_4$]. Dashed line: resulting summarized "activity" (explanation see text).

The different effects of water in acid and base catalyzed systems may be due to the fact that HCl is a strong acid which is completely dissociated. Increasing amounts of water reduce the activity of protons by hydration with respect to

$$H_2O + H^+ \rightleftharpoons H_3O^+ \tag{4}$$



$$SiOR + H^+ \rightleftharpoons Si\underset{H}{O^+}R \tag{5}$$

(I)

the formation of (I) which is considered as an important intermediate in the hydrolysis path. In the case of NH_3 as catalyst water is needed to build up the catalytically active OH^- species; so increasing amounts of water lead to higher OH^- activity:

$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^- \tag{6}$$

These mechanistic ideas have not yet been proved, but they can explain the results obtained from the experiments reported above. In order to complete the analysis more concentrations of the reaction components, especially the $SiOR:H_2O$ ratio need to be studied. More information is also expected from extended computer calculations with systematic variations of the single rate constants. Additional data also can be expected by quantitative chemical analysis of $(RO)_nSi(OH)_{4-n}$ species as a function of reaction time and by comparing the effects of different catalysts (weak acids or strong bases).

ACKNOWLEDGMENTS

The authors want to thank Prof. Dr. H. Scholze for his helpful discussions and the Bundesminister für Forschung und Technologie for financial support.

REFERENCES

1. R. Aelion, A. Loebel, and F. Eirich, *J. Am. Chem. Soc.* **72**, 5705 (1950).
2. E. Åkerman, *Acta Chem. Scand.* **10**, 298 (1956); **11**, 298 (1957).
3. C. J. Brinker, K. D. Keefer, D. W. Schaefer, R. A. Assink, B. D. Kay, and C. S. Ashley, *J. Non-Cryst. Solids* **63**, 45 (1984).
4. M. G. Voronkov, V. P. Mileshkevich, and Y. A. Yushelevskii, *The Siloxane Bond*, Plenum, New York, 1978.
5. R. E. Timms, *J. Chem. Soc. A* 1969 (1971).
6. H. Schmidt, H. Scholze, and A. Kaiser, *J. Non-Cryst. Solids* **48**, 65 (1981).
7. H. Schmidt and A. Kaiser, *Glastechn. Ber.* **54**, 338 (1981).