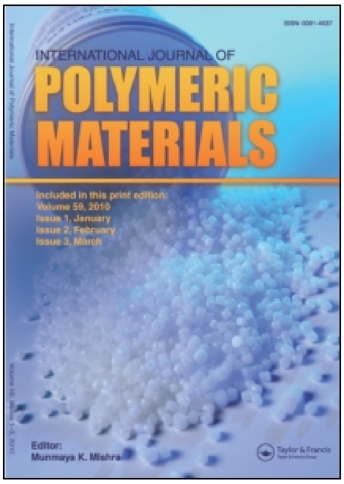

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Girgvliani, D. A. , Khananashvili, L. M. , Davtian, S. P. , Khachatrian, A. R. , Tsomaia, N. I. and Tonoian, A. O.(1994) 'The Kinetics and Interaction Mechanism of 1,4-bis(Dimethylsilyl)benzene with Allylglycidyl Ester in the Presence of Speier Catalyst', International Journal of Polymeric Materials, 25: 1, 65 — 76

To link to this Article: DOI: 10.1080/00914039408028578

URL: http://dx.doi.org/10.1080/00914039408028578

Intern. J. Polymeric Mater., 1994, Vol. 25, pp. 65–76
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Printed in Malaysia

The Kinetics and Interaction Mechanism of 1,4-bis(Dimethylsilyl)benzene with Allylglycidyl Ester in the Presence of Speier Catalyst

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The kinetics and interaction mechanism of 1,4-bis(dimethylsilyl)benzene with allylglycidyl ester in the presence of Speier catalyst is studied. Analyzing the dependence of the induction period, initial, maximal and current rates of reaction on the initial concentrations of reactants, the reaction rate constants are determined.

KEY WORDS 1,4-bis(Dimethylsilyl)benzol, allylglycidyl ester, kinetics

EXPERIMENTAL

The kinetics of the reaction was studied using the isometric differential calorimeter DAK-1-1. The heat change was measured by the registration of electromotive force using thermobatteries. The calorimeter constants were $P/g = (6.3)10^{-2}–(6.8)10^{-2}$ J/mole sec, $M/g = 9.4–11.3$ J/mole.

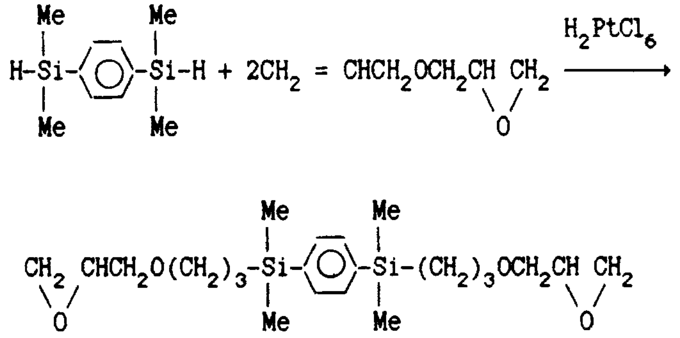
The reaction was carried out in a 50 mm length and 8.6 mm diameter glass tube, where the cycle and the solvent were loaded (40% solution). In addition a thin-wall glass ball with 1,4-bis(dimethylsilyl)benzene was fastened to a special calorimeter syringe. This syringe is put into the glass tube containing the allylglycidyl ester and the Speier catalyst H_2PtCl_6.

The syringe, with a long pivot, is located out of the calorimeter, which allows us to break the glass ball after the temperature program is set and the calorimeter is in the working range. This allows us to fix the exact start of reaction.

The synthesis was carried out in a three-necked flask at 40°C.

RESULTS AND DISCUSSION

By the interaction of 1,4-bis(dimethylsilyl)benzene with allyglycidyl ester in the presence of a Speier catalyst the silicon-containing diglycidyl ester was obtained:



(1)

The infrared spectra of the investigated substances was obtained both in the solid (with KBr) and in the liquid states by apparatus UR-10.

In the infrared spectra of the obtained diglycidyl ester the adsorption bands at 1280–1250 cm^{-1} and 820–800 cm^{-1} correspond to Si—CH$_3$, the adsorption bands at 1429, 1130, and 720 cm^{-1} correspond to Si—Ph, and the band at 920 cm^{-1} to the epoxy group. In the infrared spectra the adsorption band at 720 cm^{-1}, characteristic of secondary alcohols, is missing. This fact proves, that the reaction (1) proceeds through the double bond and without epoxy ring opening.

The kinetics and mechanism of reaction (1) was studied using the method of isothermal calorimetry at 40°C.[1]

The kinetic curve of heat change for the reaction of 1,4-bis(dimethylsilyl)benzene with allylglycidyl ester is given in Figure 1(a). In order to determine the heat of reaction during the reaction, as well as at the end of each experiment, the quantities of unreacted double bonds were determined.

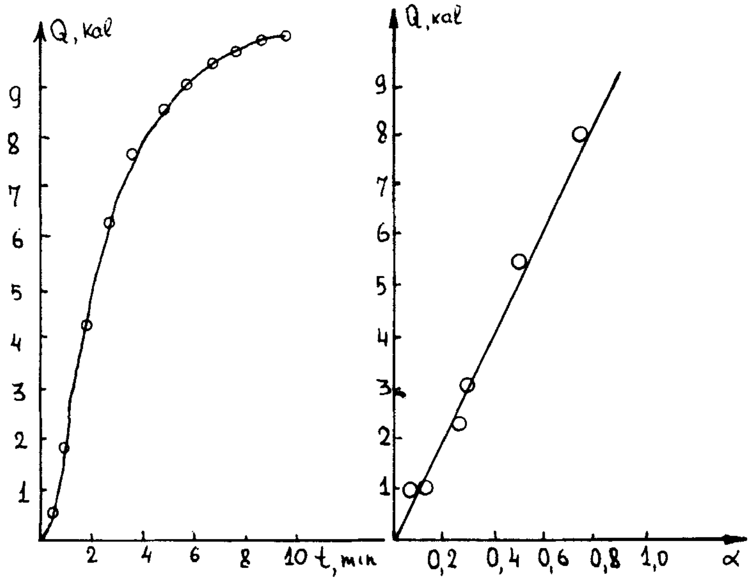


FIGURE 1 The heat change kinetics (a) and the dependence of heat change from the quantities of reacted double bonds (b).

The heat change Q of reaction (1) can be expressed as:

$$Q = q\alpha E_0 \tag{2}$$

where q is the heat of reaction and $\alpha = (E_0 - E)/E_0$ is the degree of conversion. E_0 and E are the initial and current concentrations of allylglycidyl ester. As seen from Figure 1(b), the heat change Q of reaction (1) in the variables of Equation (2) is linear.

Using the values of q, the experimentally obtained curves of heat change were

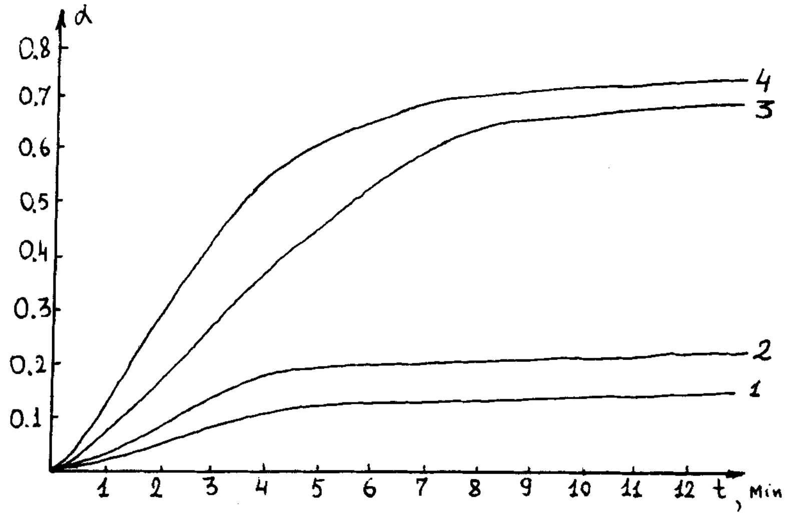


FIGURE 2 The dependence of degree of conversion versus time for K_0 = 0.06 mole/l, E_0 = 4.6 mole/l, T = 313 K and Si_0 = (1) 0.42, (2) 0.84, (3) 1.68, (4) 2.52 mole/l.

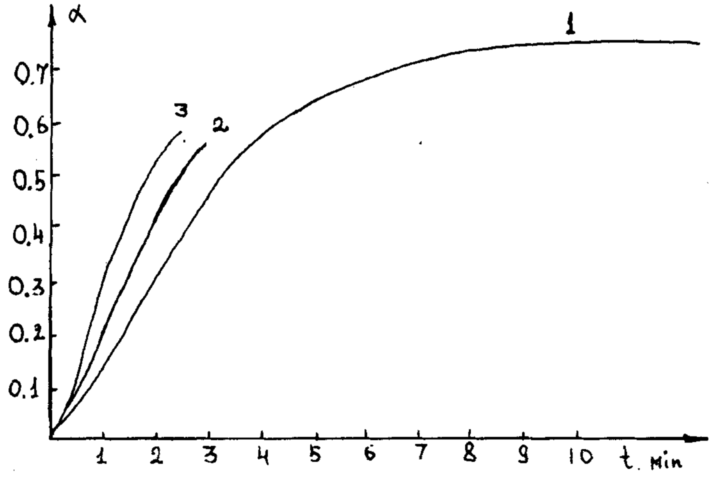


FIGURE 3 The dependence of degree of conversion versus time for E_0 = 4.6 mole/l, T = 313 K, Si_0 = 2.52 mole/l, and K_0 = (1) 0.06, (2) 0.09, (3) 0.12 mole/l.

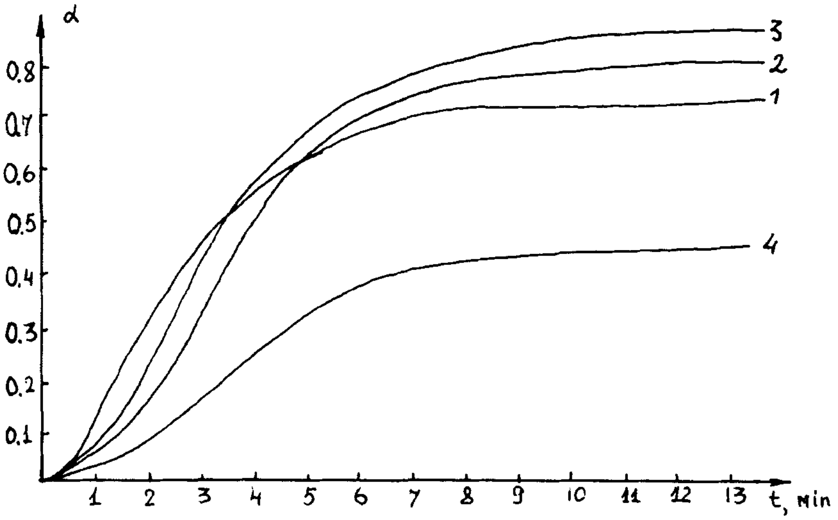


FIGURE 4 The dependence of degree of conversion versus time for T = 313 K, K_0 = 0.06 mole/l, Si_0 = 2.52 mole/l, E_0 = (1) 4.6, (2) 3, (3) 2.2, (4) 0.8 mole/l.

transferred into a dependence of the degree of conversion versus time, for different initial concentrations of E_0, Si_0 and K_0. The obtined kinetic curves are given in Figures 2–4.

As seen from Figures 2–4, the kinetic curves for the reaction of 1,4-bis(dimethylsilyl)benzene with allylglycidyl ester have a clearly expressed *S*-form. From Figures 2 and 3 one can see, that the increase of K_0 and Si_0 leads to an increase of initial and maximal reaction rates and degree of conversion. As for the induction period, it does not change.

Figure 4 shows that the change of concentration E_0 does not affect the initial reaction rate, and that the induction period is proportional to $1/E_0$.

From Figures 2–4 it can be seen, that the increase of concentration K_0 leads to the increase of the limit of degree of conversion. The increase of initial concentration Si_0 also leads to an increase of the limit of the degree of conversion, but in this case there exists the critical value of Si_0, which leads to a sharp increase in the limit of the degree of conversion.

The dependence of the initial reaction rate on Si_0 shows that the order of reaction varies from 1 (for low concentrations of Si_0) to 0 (for high concentrations of Si_0). As for the order of reaction by K_0, it is equal to one.

Using the obtained facts, the mechanism of reaction can be expressed by the following kinetic scheme:

$$Si + K \overset{k_1}{\rightleftarrows} (SiK) \tag{3}$$

$$(SiK) + E \xrightarrow{k_1} Si_1 + K \tag{4}$$

$$\mathrm{Si}_1 + \mathrm{E} \xrightarrow{k_2} \mathrm{Pr} \tag{5}$$

$$(\mathrm{SiK}) \xrightarrow{k_p} \mathrm{A} \tag{6}$$

In (3)–(6) the following notations were used:

Si—is the concentration of 1,4-bis(dimethylsilyl)benzene,
K—is the concentration of Speier catalyst,
(SiK)—is the concentration of 1,4-bis(dimethylsilyl)benzene and Speier catalyst complex,
Si_1—is the intermediate product,
E—is the concentration of allylglycidyl ester,
Pr—is the reaction product,
A—is the deactivated form of (SiK).

During the interaction of 1,4-bis(dimethylsilyl)benzene with allylglycidyl ester the hydrogen atom may split from Si.

The equations describing the change of concentrations Si, Si_1, Pr can be written as

$$\frac{d\mathrm{E}}{dt} = -k_1(\mathrm{SiK})\mathrm{E} - k_2\mathrm{Si}_1\mathrm{E} \tag{7}$$

$$\frac{d\mathrm{Si}_1}{dt} = k(\mathrm{SiK})\mathrm{E} - k_2\mathrm{Si}_1\mathrm{E} \tag{8}$$

$$\frac{d\mathrm{Pr}}{dt} = k_2\mathrm{Si}_1\mathrm{E} \tag{9}$$

For the kinetic Equations (7), (8) and (9) the balance equation is:

$$\frac{d(\mathrm{E} + \mathrm{Si}_1 + 2\mathrm{Pr})}{dt} = 0$$

or

$$\mathrm{E} + \mathrm{Si}_1 + 2\mathrm{Pr} = \mathrm{const}$$

For the initial conditions, i.e., $t = 0$, $\mathrm{E} = \mathrm{E}_0$, $\mathrm{Si}_1 = 0$, $\mathrm{Pr} = 0$ we have

$$\mathrm{Si}_1 = \mathrm{E}_0 - \mathrm{E} - 2\mathrm{Pr}$$

For the concentration (SiK) one can obtain

$$\frac{d(\mathrm{SiK})}{dt} = k_r^+(\mathrm{SiK}) - k_r^-(\mathrm{SiK}) - k_p'(\mathrm{SiK})$$

where k_r^+ means the formation of (SiK), and k_r^- is the destruction of it.

From Equations (7), (8) and (9) we have $K = K_0 - (SiK) - A$. Using the principle of quasistationary concentrations in the case of $Si_0 >> K_0$ for (SiK) we will have

$$(SiK) = \frac{k_p Si_0(K_0 - A)}{1 + k_p + k_1 Si_0} \tag{10}$$

where $K_r = k_r^+/k_r^-$; $k_p = k_r'/k_r^-$.

Using the Equation (10), the kinetic equation for A can be written as:

$$\frac{dA}{dt} = k_p' \,(SiK) = k_p' \frac{k_r Si_0(K_0 - A)}{1 + k_p + k_r Si_0} \tag{11}$$

the solution of Equation (11) is:

$$A = K_0 \left(1 - e^{-k_p' \frac{k_r Si_0}{1 + K_p + k_r Si_0} t}\right) \tag{12}$$

Using Equation (10), from Equation (7) we can get

$$\frac{d\alpha}{dt} = k_1 \frac{k_r Si_0(k_0 - A)}{1 + k_p + K_r Si_0} (1 - \alpha) + k_2(\alpha E_0 - 2Pr)(1 - \alpha) \tag{13}$$

where $\alpha = (E_0 - E)/E_0$.

Taking into account, that when $t = 0$, $\alpha = 0$, $A = 0$, $Pr = 0$ we will have:

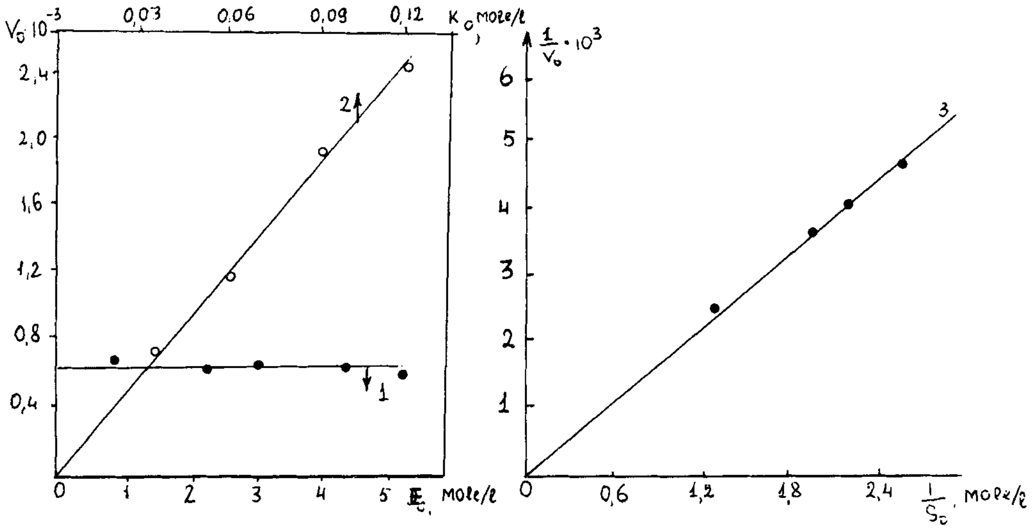
$$\left(\frac{d\alpha}{dt}\right)_{t=0} = V_0 = k_1 \frac{k_r Si_0 k_0}{1 + k_p + K_r Si_0} \tag{14}$$

Equation (14) is in good correspondence with experimental data given Figure 5. From Equation (14) it can be seen that the initial reaction rate is linearly dependent as K_0 (as for curve 3 of Figure 5) and does not depend on E_0 (as for curve 2 of Figure 5). The order of reaction by Si_0 varies from 1 (for low Si_0) to zero (for high Si_0).

Let us rewrite Equation (14) in the following form:

$$\frac{1}{V_0} = \frac{1 + k_2}{k_1 k_r k_0} \frac{1}{Si_0} + \frac{1}{k_1 k_0} \tag{15}$$

It is easy to see, that Equation (15) is in good correspondence with the experimental data given by curve 1 on Figure 5.



(a) (b)

FIGURE 5 The dependence of concentration K_0 (curve 2) and E_0 (curve 3) on the initial reaction rate and the dependence of $1/v_0$ from $1/Si_0$ (curve 1).

Comparing the data obtained from Figure 5, with Equations (14) and (15), for the reaction rate constants one can get:

$$k_1 = (6.7)\,10^{-2}\,\frac{1}{\text{mole sec}};\quad \frac{1 + k_r}{k_r} = 6.2 \pm 0.2$$

Let us find now the dependence of the induction period on the initial constants E_0, Si_0 and K_0.

Using Equation (10) and the fact that $\alpha = (E_0 - E)/E_0$, we can rewrite Equation (8) in the following form:

$$\frac{dSi_1}{dt} = k_1\,\frac{k_r Si_0(k_0 - A)}{1 + k_p + k_r Si_0}\,E_0(1 - \alpha) - k_2(\alpha E_0 - 2Pr)(1 - \alpha)E_0 \qquad (16)$$

Taking into account that during the induction period the concentration A and degree of conversion α are negligibly small (i.e., $A = 0$ and $\alpha = 0$), Equation (16) can be rewritten as:

$$\frac{dSi_1}{dt} = k_2E_0\left(\frac{k_1}{k_2}\,\frac{k_r Si_0 k_0}{1 + k_p + k_r Si_0} - Si_1\right)$$

The solution of this equation is:

$$Si = \frac{k_1}{k_2}\,\frac{k_r Si_0 k_0}{1 + k_p + k_r Si_0}\,(1 - e^{-k_2E_0t}) \qquad (17)$$

Using Equation (17), from Equation (13) we can get:

$$\frac{d\alpha}{dt} = \frac{k_1 k_r \mathrm{Si}_0 k_0}{1 + k_p + k_r \mathrm{Si}_0}\left(2 - e^{-k_2 \mathrm{E}_0 t}\right)$$

the solution of which is:

$$\alpha = 2k_1 \frac{k_r \mathrm{Si}_0 k_0}{1 + k_p + k_r \mathrm{Si}_0} t - \frac{k_1}{k_2 \mathrm{E}_0} \frac{k_r \mathrm{Si}_0 \mathrm{k}_0}{1 + k_p + k_r \mathrm{Si}_0}\left(1 - e^{-k_2 \mathrm{E}_0 t}\right) \qquad (18)$$

From Equation (18) for the induction period we will have:

$$\tau_{\text{ind}} = \frac{1}{2k_2 \mathrm{E}_0} \qquad (19)$$

The comparison of Equation (19) with Figure 6 shows that theoretical results coincide with experimental data: τ_{ind} does not depend on Si_0 and K_0 (curves 1 and 2) and is inversely proportional to E_0 (curve 3).

The value of the reaction rate constant k_2 is:

$$k_2 = (1.09 \pm 0.05)10^{-2} \frac{1}{\text{mole sec}}$$

Let us investigate now the dependence of the maximal reaction rate on the initial

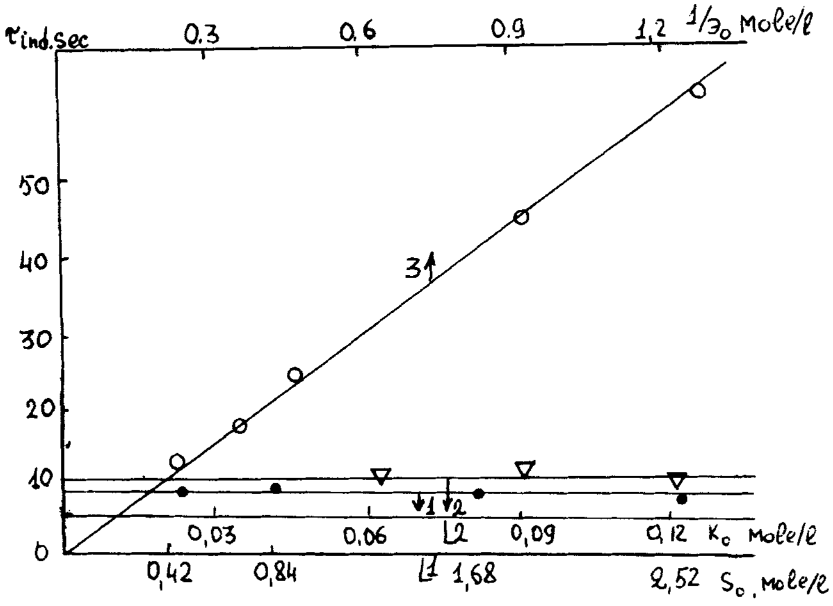


FIGURE 6 The dependence of concentration Si_0 (curve 1), K_0 (curve 2) and $1/\mathrm{E}_0$ (curve 3) from induction period.

concentrations E_0, K_0 and Si_0. Taking into account that when maximal reaction rate is reached, the concentration A is negligible, we can rewrite the equation describing the change of α in time in the following way:

$$\frac{d\alpha}{dt} = \frac{k_1 k_r \mathrm{Si}_0 k_0}{1 + k_p + k_r \mathrm{Si}_0} - \frac{k_1 k_r \mathrm{Si}_0 k_0}{1 + k_p + k_r \mathrm{Si}_0}\alpha + k_2 \mathrm{E}_0 \alpha - 2k_2 \mathrm{Pr} - k_2 \mathrm{E}_0 \alpha^2 + 2k_2 \mathrm{Pr}\alpha \qquad (20)$$

Setting the second derivative of α to zero, for maximal reaction rate W_m one gets:

$$W_m = \frac{2k_2 \mathrm{E}_0 (1 - \alpha_m)^2 \mathrm{Si}_1^m}{\mathrm{E}_0(1 - \alpha_m) - \mathrm{Si}_1^m - \dfrac{k_1}{k_2}\dfrac{k_r \mathrm{Si}_0 k_0}{1 + k_p + k_r \mathrm{Si}_0}}$$

To find Si_1^m and α_m, let us write the equation describing the change of α and Si_1 in general form:

$$\left.\begin{aligned} \frac{d\alpha}{dt} &= k_1(\mathrm{SiK})(1 - \alpha) + k_2 \mathrm{Si}_1(1 - \alpha) \\ \frac{d\mathrm{Si}_1}{dt} &= k_1(\mathrm{SiK})(1 - \alpha)\mathrm{E}_0 - k_2 \mathrm{Si}_1(1 - \alpha)\mathrm{E}_0 \end{aligned}\right. \qquad (21)$$

From Equation (21) for α_m we get:

$$\alpha_m = \frac{2k_1(\mathrm{SiK})}{k_2 \mathrm{E}_0} \ln \frac{k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) - k_2 \mathrm{Si}_1} - \frac{1}{\mathrm{E}_0}\mathrm{Si}_1 \qquad (22)$$

Using Equation (22) we will have:

$$\frac{d\mathrm{Si}_1}{dt} = k_1(\mathrm{SiK})\left[\mathrm{E}_0 - \frac{2k_1(\mathrm{SiK})}{k_2} \ln \frac{k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) - k_2 \mathrm{Si}_1} + \mathrm{Si}_1\right] - k_2 \mathrm{Si}_1 \left[\mathrm{E}_0 - \frac{2k_1(\mathrm{SiK})}{k_2} \ln \frac{k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) - k_2 \mathrm{Si}_1} + \mathrm{Si}_1\right]$$

Assuming, that

$$\frac{2k_1(\mathrm{SiK})}{k_2} \ln \frac{k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) - k_2 \mathrm{Si}_1} << \mathrm{E}_0 + \mathrm{Si},$$

we will obtain:

$$\frac{d\mathrm{Si}_1}{dt} = (\mathrm{E}_0 + \mathrm{Si}_1)[k_1(\mathrm{SiK}) - k_2\mathrm{Si}_1]$$

The solution of this equation is:

$$\mathrm{Si}_1 = \frac{\mathrm{E}_0 k_1(\mathrm{SiK})e^{(k_2\mathrm{E}_0 + k_1(\mathrm{SiK}))t_m} - \mathrm{E}_0 k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) + k_2\mathrm{E}_0 e^{(k_2\mathrm{E}_0 + k_1(\mathrm{SiK}))t_m}}$$

For the case of $k_2\mathrm{E}_0 >> k_1(\mathrm{SiK})$ this equation takes the form:

$$\mathrm{Si}_1 = \frac{\mathrm{E}_0 k_1(\mathrm{SiK})e^{k_2\mathrm{E}_0 t_m} - \mathrm{E}_0 k_1(\mathrm{SiK})}{k_1(\mathrm{SiK}) + k_2\mathrm{E}_0 e^{k_2\mathrm{E}_0 t_m}} \tag{24}$$

Using Equations (22) and (24) for the maximal reaction rate we will obtain:

$$W_m = \frac{2k_2\mathrm{E}_0(1 - \alpha_m)^2 k_1(\mathrm{SiK})(e^{k_2\mathrm{E}_0 t_m} - 1)}{[k_2\mathrm{E}_0(1 - \alpha_m) - k_1(\mathrm{SiK})]e^{k_2\mathrm{E}_0 t_m} - k_1(\mathrm{SiK})(e^{k_2\mathrm{E}_0 t_m} - 1)} \tag{25}$$

The estimates show that $e^{k_2\mathrm{E}_0 t_m} >> 1$. Using this fact Equation (25) can be rewritten as:

$$\frac{(1 - \alpha_m)^2}{W_m} = \frac{1 + k_p + k_r\mathrm{Si}_0}{2k_1k_r\mathrm{Si}_0}\,\frac{1 - \alpha_m}{k_0} - \frac{1}{k_2\mathrm{E}_0} \tag{26}$$

or

$$\frac{1 - \alpha_m}{W_m} + \frac{1}{2k_2\mathrm{E}_0(1 - \alpha_m)} = \frac{1 + k_r}{2k_1k_rk_0\mathrm{Si}_0} + \frac{1}{2k_1k_0} \tag{27}$$

From Equations (26) and (27) it is easy to see that the dependence on the variables are linear, which is in complete agreement with the experiment. Comparing Equations (26) and (27) with the curves of Figure 7, we obtain:

$$k_1 = (6.9)10^{-2}\,\frac{1}{\text{mole sec}}\,; \quad k_2 = (9.06)10^{-3}\,\frac{1}{\text{mole sec}}\,; \quad \frac{1 + k_p}{k_r} = 5.8 \pm 0.05$$

These values are in quite good agreement with the values of the same constants obtained from Equations (14), (15) and (19).

From Equation (13), using the fact that not far from the beginning of the reaction $\mathrm{Si}_1 << \mathrm{Pr}$, we can get:

$$\frac{d\alpha}{dt} = \frac{1}{1 - \alpha} - k_2\alpha\mathrm{E}_0 = k_1\,\frac{k_r\mathrm{Si}_0\left[k_0 e^{-k_p' \frac{k_r\mathrm{Si}_0}{1 + k_p + k_r\mathrm{Si}_0}}\right]}{1 + k_p + k_r\mathrm{Si}_0} \tag{28}$$

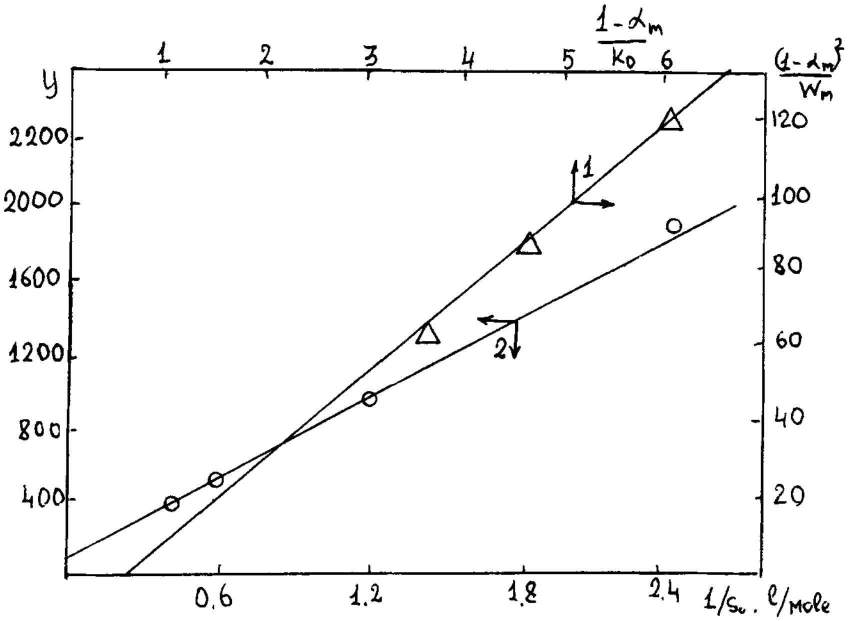


FIGURE 7 The dependence obtained in co-ordinates of Equations (26) (curve 1) and (27) (curve 2).

To compare Equation (28) with experimental data let us rewrite it in the following way:

$$\ln \frac{1-\alpha}{W} = \ln \frac{1 + k_p + k_r\mathrm{Si}_0}{k_1 k_r \mathrm{Si}_0 k_0} + k_p' \frac{k_r\mathrm{Si}_0}{1 + k_p + k_r\mathrm{Si}_0} t \tag{29}$$

where $W = d\alpha/dt$ is the current reaction rate.

The results of Equation (29) coincide completely with experimental data (see curves on Figure 8).

Comparing Equation (29) with the curves of Figure 8, we get:

$$k_p' = 0.01 \frac{1}{\text{mole sec}}; \quad \frac{1 + k_p}{k_r} = 5.7 \pm 0.4$$

These values are in quite good agreement with the values of the same constants obtained by experiment.

The kinetic scheme presented in (3)–(6) describes well the experimentally obtained general regularities of the investigated reaction. The values of the reaction rate constants calculated in the present paper are in good correspondence with experimental data.

It must be noted, that the obtained values of the reaction rate constants ($k_1 > k_2$) does not reflect the self accelerating character of this process. This seeming

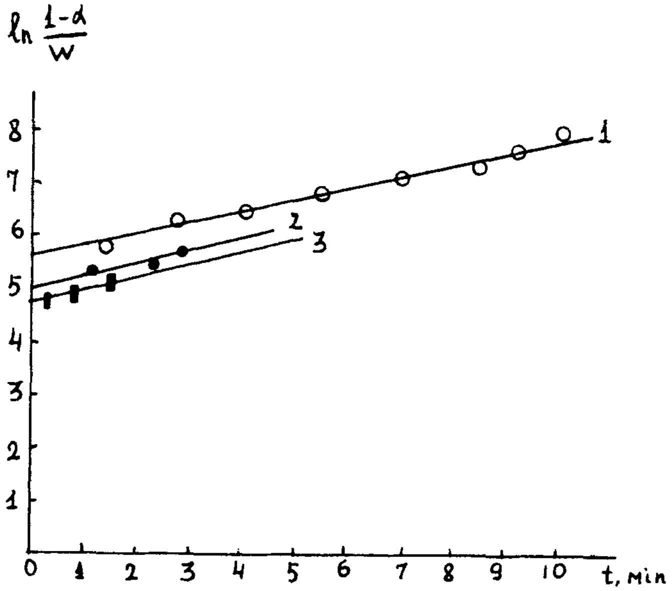


FIGURE 8 The linear dependence obtained in co-ordinates of Equation (29) for Si_0 = 2.52 mole/l, E_0 = 4.6 mole/l, T = 313 K and K_0 = (1) 0.06, (2) 0.09, (3) 0.12 mole/l.

contradiction can be easily removed, if the condition $Si_1 \gg 6(SiK)$ is taken into account. This condition is quite real, because of the very low concentration of (SiK).

Reference

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