

KINETIC STUDIES OF THE REACTION OF PROPYLENE OXIDE
ONTO SILICA GEL BY MEANS OF POTENTIOMETRY

Katsumichi ONO, Kazuhisa OKURA, and Kenkichi MURAKAMI
Chemical Research Institute of Non-Aqueous Solutions,
Tohoku University, Katahira, Sendai 980

Propylene oxide was found to react easily with silica gel surfaces in the presence of water. The reaction obeyed second order kinetics with respect to the concentration of proton. Kinetic data suggested that propylene oxide was chemisorbed on the silica gel surfaces with ring opening.

Silica gel surfaces are well known for the ability to react with various organic substances by virtue of their silanol groups.¹⁾ The structure and properties of silanol groups have been studied in detail by many workers and a weakly acidic character of these groups is considered to be responsible for the high reactivity of silica gel surfaces. One of the most famous reactions with organic substances is probably the esterification of silanol groups with alcohols.²⁾ This reaction, however, requires relatively severe conditions such as high temperatures or high pressures to obtain the products in satisfactory yields.

Deuel and others³⁾ reported that propylene oxide reacted easily with montmorillonite and that it was chemically bonded to the surface of montmorillonite. Although detailed description was not given, the reaction was fast even at room temperature.

It seems interesting to apply this reaction to the surface modification of silica gel, since both montmorillonite and silica gel have the same surface silanol groups. If these groups are associated with the reaction, the detailed studies of the reaction would give a basis for development of a simple method to prepare organic derivatives of silica gel.

It has been found in the present study that propylene oxide also reacts easily with silica gel surfaces under a mild condition. Preliminary results on kinetic studies by means of potentiometry will be briefly described in this article.

Aerosil 200 silica (Degussa) was used throughout this study. Specific surface area determined by BET method was about 180 m²/g. The density of silanol groups on the surface was estimated to be about 1.75 silanols/100 Å² by means of the chlorination with thionyl chloride.⁴⁾ First, the reaction of propylene oxide (PO) with silica gel was carried out in the presence of water at the reflux temperature of PO (35°C) for 1 hour. Reaction products were centrifuged, washed repeatedly with acetone and benzene, and then dried in vacuo. Carbon contents of PO treated silica gel are shown in Fig. 1 as a function of the amount of water. Evidently,

the reaction is accelerated by the addition of a small amount of water, and silica gel surfaces are covered with organic groups which cannot be extracted by organic solvents. The presence of water seems to be essential for the reaction, since the yield is remarkably reduced in the absence of water. The yield is also reduced in higher water contents, because of the partial hydrolysis of once formed PO derivatives of silica gel. In order to confirm the chemisorption of PO, the PO treated silica gel was hydrolyzed completely by dilute sodium hydroxide solution and the products were extracted with ether. Gas chromatographic analysis of the extracts revealed the formation of propylene glycol. The result indicates the formation of chemisorbed species such as structure (I) on the silica gel surfaces.

In order to obtain further information about the mechanism of the reaction of PO with silica gel, kinetic measurements were carried out. As has been well known, silica gel behaves weakly acidic when suspended in aqueous media. As the reaction with PO proceeds, the acidic character of the silica gel suspension should be weakened. Thus the reaction can be monitored by recording the electromotive force (emf) of a pH sensitive glass electrode. The measurements were carried out by connecting the reaction mixture with a reference electrode by means of an extra KNO_3 bridge.

The emf of a glass electrode should be represented by Nernst equation,

$$E = E_A + E_J + (RT/F) \ln a_{\text{H}^+}, \quad (1)$$

where E_A and E_J are asymmetric and diffusion potentials, R is gas constant, T is absolute temperature, and F is Faraday constant. The activity of proton a_{H^+} can be replaced by proton concentration c_{H^+} without serious error. Assuming the sum $E_A + E_J$ is constant throughout a run, equation (1) results in the equation that,

$$\frac{1}{c_{\text{H}^+}} = \frac{A}{\exp\{FE(t)/RT\}} \quad (2)$$

where $A = \exp\{F(E_A + E_J)/RT\}$. The rate of chemisorption can be estimated by the elemental analysis of PO treated silica gel, sampled at appropriate time intervals. It was found that a linear relationship holds approximately between the amount of reacted PO and $\exp\{FE(t)/RT\}$. The chemisorption process may be represented,

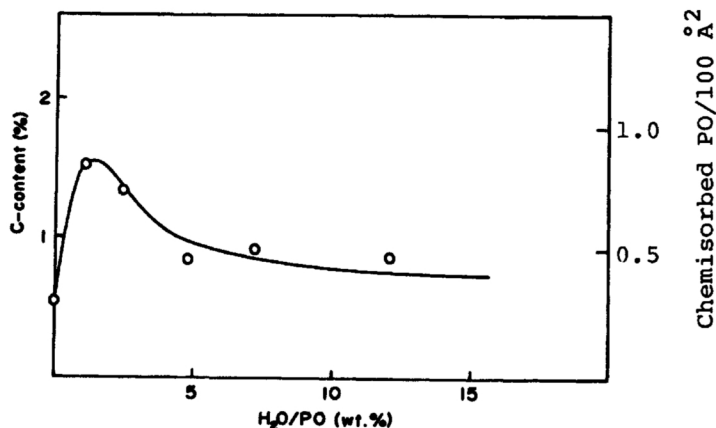
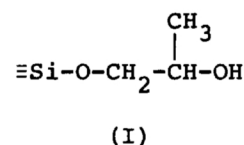


Fig. 1. Carbon contents of PO treated silica gel. 0.5g of silica gel was allowed to react with the total amount of 50ml of PO and water at 35°C for 1 hour.



therefore, by the same kinetic expression as the decrease in proton concentration. Second order kinetics leads to equation (3), by applying equation (2),

$$\frac{1}{\exp\{FE(t)/RT\} - \exp\{FE(\infty)/RT\}} - \frac{1}{\exp\{FE(0)/RT\} - \exp\{FE(\infty)/RT\}} = k_2 t/A, \quad (3)$$

where k_2 is a second order rate constant and $E(0)$ and $E(\infty)$ are emfs at $t=0$ and $t=\infty$, respectively. The equation requires the linear relationship between $[\exp\{FE(t)/RT\} - \exp\{FE(\infty)/RT\}]^{-1}$ and time.

Figure 2 shows an example of this type of plot obtained for the reaction of PO with silica gel in acetone solution. The plot was sufficiently linear over the wide range of time, indicating the second order decrease in proton concentration. The slope $k_2' = k_2/A$ is the experimental rate constant of this reaction. Second order rate constant k_2 cannot be determined, unless the term A is estimated. This is difficult because this term includes the diffusion potential E_J which cannot be readily estimated especially for non-aqueous solutions.

According to the current theory of diffusion potential, the term FE_J/RT in the parenthesis of term A is the function of transference numbers of ions, moving across the liquid junction. Since the transference numbers are generally independent of temperature,⁵⁾ the term FE_J/RT is also regarded to be independent of temperature. Provided that E_A is far smaller than E_J , and this is the case for the present experiment, term A is almost insensitive to the change of temperature. Then the activation energy of the reaction can be calculated simply from the slope of Arrhenius plot of the experimental rate constant k_2' . The value of 10.0 kcal/mole was obtained (Fig. 3).

It has been generally accepted that the activation energy for physical adsorption is less than 5 kcal/mole. A fairly high value of activation energy exclude the possibility that the above described process is the physical adsorption of PO onto silica gel. Moreover, it cannot be expected that the specific chemical interaction such as hydrogen bonding exists between the oxygen atom of PO and silanol, because the amount of reacted PO on the silica gel diminished markedly in the absence of water. Hence, above kinetic results give strong evidence in support of the chemisorption of PO with silica gel surfaces.

Another evidence supporting the chemisorption of PO was given by the deuterium isotope effect on the reaction which was measured by replacing water

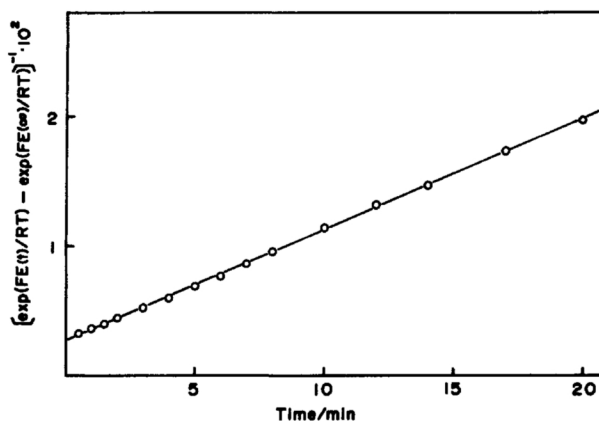
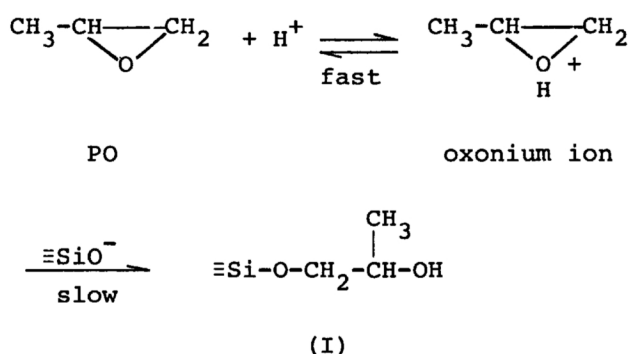


Fig. 2. Second order plot of emf versus time. 0.4g of silica gel was allowed to react with 25ml of 8% acetone solution of PO containing 2% of water at 15°C.

with deuterium oxide. The ratio of experimental rate constant k_D'/k_H' was about 2.3 at 20°C in 8% acetone solution. This value well corresponds to the one reported for acid-catalyzed ring opening of ethylene oxide.⁶⁾ The effect has been generally interpreted in terms of the difference in the stability of the intermediate oxonium ions.⁶⁾ Thus the chemisorption of PO onto silica gel may be also accounted by the following scheme, being typical of acid-catalyzed ring opening of epoxides.



Further works are in progress on the kinetics and on the application of this reaction.

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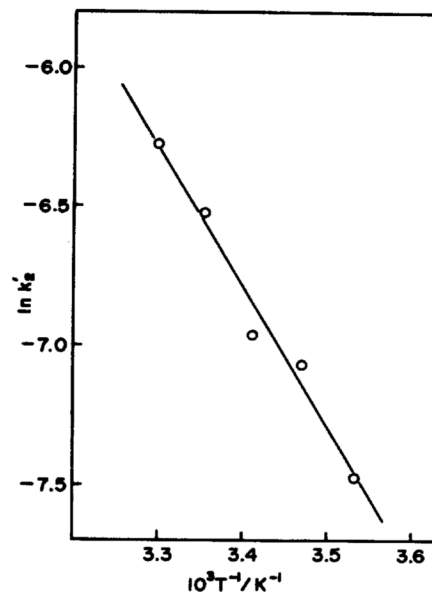


Fig. 3. Arrhenius plot of experimental second order rate constant k_2' ($l \cdot M^{-1} \cdot \text{min}^{-1}$).

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