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Liquid-Phase Oxidation of Diethanolamine on a Pd-Al_2O_3 Catalyst. I.[1] Kinetic Studies

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Diethanolamine was oxidized by gaseous oxygen to N-(2-hydroxyethyl)glycine in an aqueous solution containing sodium hydroxide over a 0.5% Pd-alumina catalyst in the temperature range of 50—80 °C and at ambient pressure in a slurry reactor, and the kinetics was investigated. Under the present experimental conditions, all mass transfer resistances were assumed to be insignificant. The catalyst was very active but its activity decreased rapidly while it was in contact with oxygen.

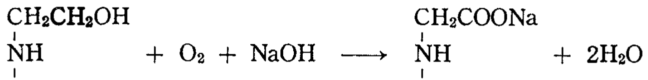
A power-law model was assumed for this reaction. The reaction order was estimated to be 0.37 with respect to diethanolamine concentration and 0.64 with respect to oxygen concentration. The rate was analyzed according to the Hougen-Watson model. It is concluded that the oxidation is mainly controlled by the surface reaction between adsorbed diethanolamine and oxygen in the liquid phase. This reaction is an excellent model for studies of three-phase reaction systems (gas-liquid-solid).

Keywords——liquid-phase oxidation; diethanolamine; palladium on aluminium oxide catalyst; reaction kinetics; slurry reactor; deactivation of catalyst

The liquid-phase oxidation of polyols with oxygen is of great interest to both chemists and pharmacists, as the products can be widely used in the synthesis of medicines and surfactants. Usually the reaction is carried out over a noble metal catalyst in the presence of alkali. Many patents have been claimed on this process,[2] but there is little information on the kinetics of the reaction.

This reaction is an excellent example of a three-phase reactor system. In three-phase reactors, various physical and chemical processes are involved, such as gas-liquid mass transfer, liquid-solid mass transfer, intraparticle diffusion, adsorption, surface reaction and desorption. All of these steps can influence the performance of three-phase reactors.

In this paper, the kinetics of the liquid-phase oxidation of diethanolamine to N-(2-hydroxyethyl)glycine was studied in the presence of sodium hydroxide over a 0.5% Pd-alumina catalyst.



$$\begin{matrix}CH_2CH_2OH\\ |\\ NH\\ |\\ CH_2CH_2OH\end{matrix} + O_2 + NaOH \longrightarrow \begin{matrix}CH_2COONa\\ |\\ NH\\ |\\ CH_2CH_2OH\end{matrix} + 2H_2O \qquad (1)$$

All experiments were carried out in a slurry reactor. To obtain intrinsic kinetics, it is necessary to plan experiments in the absence of mass transfer resistances. This can be achieved by performing experiments with sufficiently small particles and at a high agitating speed in a slurry reactor.[3]

In the following paper,[4] the effect of mass transfer resistances on the global rate of reaction in a packed-bed reactor will be presented.

Experimental

Chemicals——Reagent grade diethanolamine and sodium hydroxide (stated purity of 95%) were used as supplied. For catalyst preparation, reagent grade palladium chloride and γ-alumina particles (KHD, 2—4 mm, Sumitomo Chemical Inc.) were used. Commercial hydrogen, oxygen and nitrogen gases were used without further purification.

Catalyst Preparation——Evacuated alumina particles (24—42 mesh) were soaked in an aqueous hydrogen chloride solution of palladium chloride for 8 hours. The solution was evaporated off, and after thorough drying, the particles were reduced at 400 °C for 4 hours in a Pyrex glass tube through which hydrogen was flowing. The particles were crushed and sieved (smaller than 250 mesh). The catalyst used in this study contained 0.5 wt% palladium.

Apparatus and Operating Procedure——The reactor was a glass container with 7.0 cm inner diameter and 9.2 cm long. Four evenly spaced vertical baffles, 9.0 cm high and 0.7 cm wide, were fitted to the wall of the reactor. Agitation was done with a 6 blade turbine, 3.0 cm in diameter. The gas mixture (oxygen and nitrogen) was sparged into the liquid-phase continuously during the reaction, that is, the gas-phase was a flow system.

The reactor was charged with an aqueous solution of diethanolamine and sodium hydroxide. The powder catalyst was added after the temperature and the concentration of oxygen had become constant, and samples of about 2 cm³ were taken periodically at intervals of 10—20 min. Operating conditions are shown in Table I.

TABLE I. Experimental Conditions

Reaction temperature, °C	50—80
Catalyst 0.5 wt% Pd–Alumina (smaller than 250 mesh)	
Catalyst loading, g/cm³	0.5×10^{-2}—3.0×10^{-2}
Concentration of diethanolamine, mol/cm³	3.9×10^{-5}—29.8×10^{-5}
Concentration of sodium hydroxide, mol/cm³	5.0×10^{-5}—40.2×10^{-5}
Concentration of oxygen, mol/cm³	0.6×10^{-7}—2.45×10^{-7}
Gas flow rate, cm³/min	200
Agitating speed, rpm	1200

Identification and Analysis——The produced N-(2-hydroxyethyl)glycine was isolated by treating the reaction mixture with cation exchange resin, and recrystallized from ethanol–water solution (mp 182—184 °C). The product was identified by comparing its infrared spectrum with that of an authentic sample.[5]

The selectivity for N-(2-hydroxyethyl)glycine was about 95% under our experimental conditions. The concentration of produced N-(2-hydroxyethyl)glycine was estimated by titration, and from this amount the conversion of diethanolamine and the rate of reaction were calculated.

Results and Discussion

The dependence of the initial rate of reaction, r_{A0} [mol/(cm³·s)], on the catalyst loading, m [g/cm³], is shown in Fig. 1. C_A, C_B and C_N [mol/cm³] are the concentrations of diethanolamine, oxygen and sodium hydroxide, respectively. The linearity of this plot shows that gas-liquid mass transfer is insignificant.

An Arrhenius plot of r_{A0} in the temperature range from 50 to 80 °C is shown in Fig. 2. Activation energy is estimated to be 16 kcal/mol, and this value is considered to represent the activation energy for the intrinsic reaction.

Based on these observations (Figs. 1 and 2), it can be assumed that the reaction is kinetically controlled under present conditions. A modelling of the reaction in the kinetic region was therefore attempted.

The effect of sodium hydroxide concentration on the rate of reaction is illustrated in Fig. 3. The data suggest that the reaction order with respect to sodium hydroxide is 1.0 in the con-

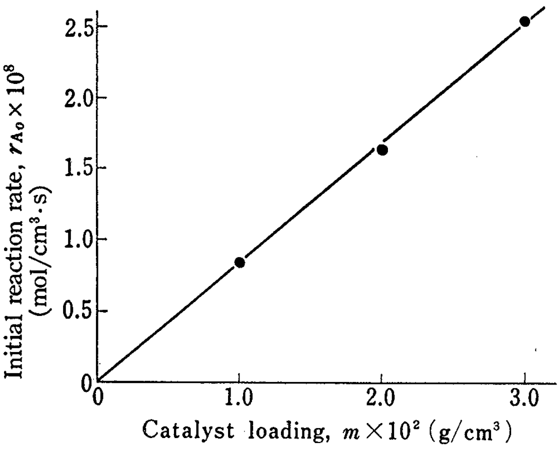


Fig. 1. Effect of Catalyst Loading on the Rate of Reaction

Reaction temperature: 55°C. $C_A=1.00\times10^{-4}$ mol/cm^3, $C_B=1.47\times10^{-7}$ mol/cm^3, $C_N=1.02\times10^{-4}$ mol/cm^3.

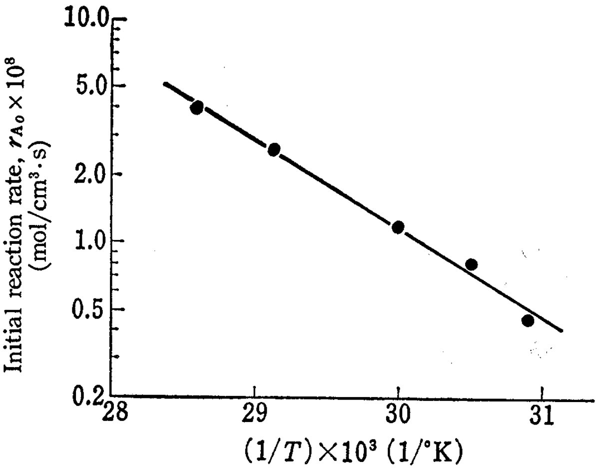


Fig. 2. Arrhenius Plot of Initial Rate of Reaction

$m=1.0\times10^{-2}$ g/cm^3, $C_A=1.00\times10^{-4}$ mol/cm^3, $C_B=1.47\times10^{-7}$ mol/cm^3, $C_N=1.02\times10^{-4}$ mol/cm^3.

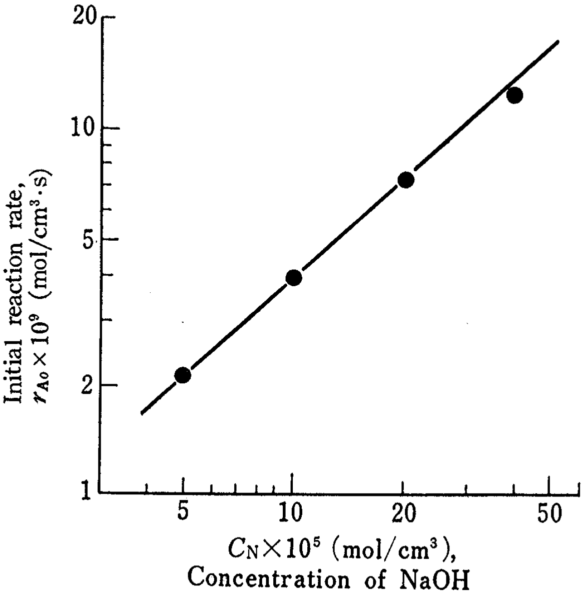


Fig. 3. Effect of Sodium Hydroxide Concentration on the Rate of Reaction

Reaction temperature: 55°C. $m=0.5\times10^{-2}$ g/cm^3, $C_A=1.00\times10^{-4}$ mol/cm^3, $C_B=1.47\times10^{-7}$ mol/cm^3.

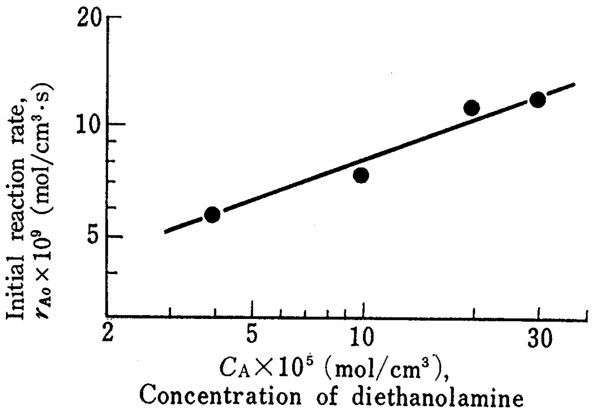


Fig. 4. Effect of Diethanolamine Concentration on the Rate of Reaction

Reaction temperature: 55°C. $m=0.5\times10^{-2}$ g/cm^3, $C_N=2.0\times10^{-4}$ mol/cm^3, $C_B=1.47\times10^{-7}$ mol/cm^3.

centration range from 5.02×10^{-5} to 4.02×10^{-4} [mol/cm^3]. Fig. 4 shows the influence of diethanolamine concentration on the rate of reaction. From these results, the reaction order with respect to diethanolamine was calculated as 0.37.

Figure 5 shows diethanolamine conversion with time, t, at various oxygen concentrations. Since the initial reaction rate decreases with increase in oxygen concentration, the order with respect to oxygen is apparently negative. However, the catalyst activity was greatly influenced by oxygen. It was observed that the reaction did not proceed with the catalyst which had already been treated with oxygen-saturated solution. In the case of pure oxygen as a gas feed, the catalyst became whitish and its activity decreased rapidly. In the low oxygen concentration range the catalyst remained active and retained the original color. It is, therefore, difficult to estimate the order with respect to oxygen in this type of batch system.

From the flow system data, the reaction order with respect to oxygen was estimated to be 0.64, as described in the next paper.[4]

From these results, a power law kinetic model can be assumed as follows:

$$r_A = -\frac{dC_A}{dt} = k \cdot m \cdot C_A^{0.37} \cdot C_B^{0.64} \cdot C_N \cdot f(C_B, t) \qquad (2)$$

where k is the rate constant and $f\ (C_B,\ t)$ is the catalyst activity as a function of C_B and t (the activity of fresh catalyst is assumed to be unity). Under the experimental conditions mentioned in Fig. 5, C_N can be considered equal to C_A, since the initial concentrations of diethanolamine and sodium hydroxide are equal and the reaction is equimolar with respect to them. Therefore, eq. (2) can be simplified to

$$-\frac{dC_A}{dt} = k \cdot m \cdot C_A^{1.37} \cdot C_B^{0.64} \cdot f(C_B, t) \qquad (3)$$

As mentioned in the experimental section, the gas-phase is a flow system, and the mass transfer resistances are negligible. Thus, during each run the concentration of oxygen can be assumed to be constant and in equilibrium with the flowing gas. With the initial condition

$$\text{at } t = 0;\ C_A = C_{A_0} \qquad (4)$$

integration of eq. (3) gives

$$Y = k \cdot F(C_B, t) \qquad (5)$$

where,

$$Y = \frac{(1-x_A)^{-0.37}-1}{0.37 \cdot C_{A_0}^{0.37} \cdot C_B^{0.64} \cdot m} \qquad (6)$$

$$F(C_B, t) = \int f(C_B, t)dt - \left[\int f(C_B, t)dt\right]_{t=0} \qquad (7)$$

$$x_A = (C_{A_0} - C_A)/C_{A_0} \qquad (8)$$

In Fig. 6, the calculated values of Y from the experimental data are plotted against time, t. The relationship is linear. The slopes of these lines vary linrearly with $1/C_B$ as shown in Fig. 7. Therefore, $F(C_B,\ t)$ can be expressed as

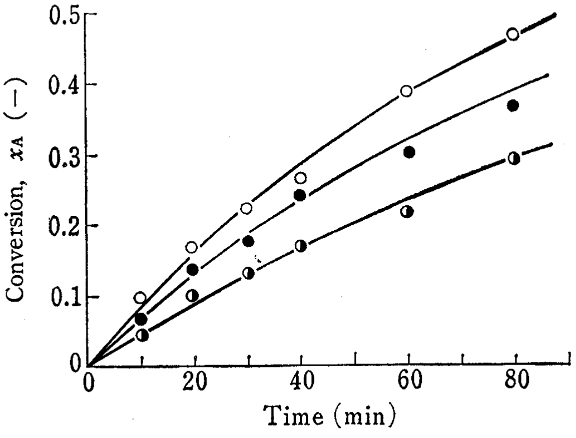


Fig. 5. Effect of Oxygen Concentration on Diethanolamine Conversion

○, $C_B=0.603\times10^{-7}$ mol/cm^3; ●, $C_B=1.47\times10^{-7}$ mol/cm^3; ◑, $C_B=2.45\times10^{-7}$ mol/cm^3.
Reaction temperature: 60°C. $m=1.0\times10^{-2}$ g/cm^3, $C_{A_0}=1.00\times10^{-4}$ mol/cm^3, $C_{N_0}=1.00\times10^{-4}$ mol/cm^3.

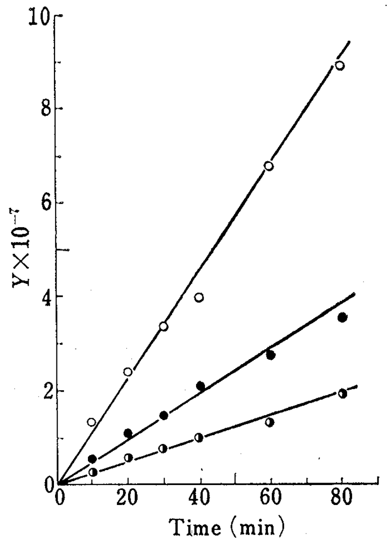


Fig. 6. Y *vs.* Time

○, $C_B=0.603\times10^{-7}$ mol/cm^3; ●, $C_B=1.47\times10^{-7}$ mol/cm^3; ◑, $C_B=2.45\times10^{-7}$ mol/cm^3.

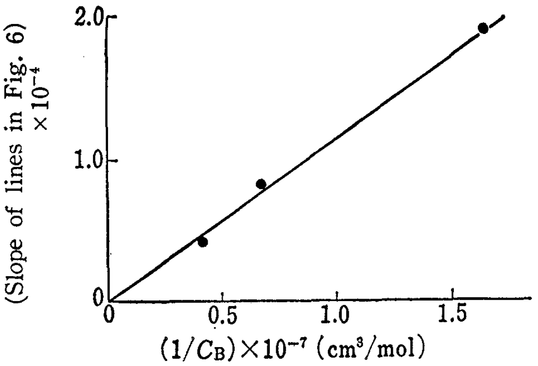


Fig. 7. Slope of the Lines in Fig. 6 *vs.* $1/C_B$

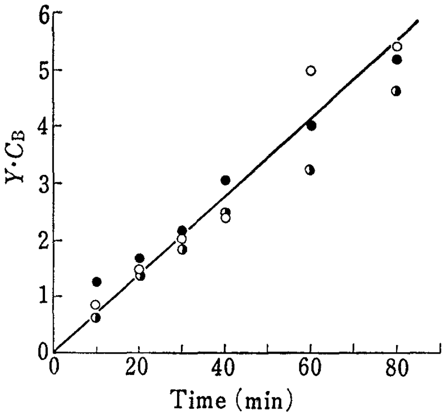


Fig. 8. $Y.\ C_B$ *vs.* Time

○, $C_B=0.603\times10^{-7}$ mol/cm^3; ●, $C_B=1.47\times10^{-7}$ mol/cm^3; ◑, $C_B=2.45\times10^{-7}$ mol/cm^3.

$$F(C_B, t) = \alpha(t/C_B) \tag{9}$$

and

$$f(C_B, t) = \alpha(1/C_B) \tag{10}$$

where, α is a constant.

Equation (10) can be explained in terms of the following scheme:

$$\sigma + O_2 \overset{K_P}{\rightleftarrows} \sigma_P \tag{11}$$

The active site, σ, is deactivated to σ_P on adsorption of oxygen. If this adsorption is in equilibrium, the fraction of active site, θ_a, may be expressed as

$$\theta_a = \frac{1}{1+K_PC_B} \tag{12}$$

where K_P is the equilibrium constant. Assuming a very strong adsorption ($K_PC_B \gg 1$), θ_a may be given by

$$\theta_a = 1/K_PC_B \tag{13}$$

Equation (13) is the same as eq. (10).

$$f(C_B, t) = 1/K_PC_B \tag{14}$$

Combining eqs. (5) and (14), the following relationship can be obtained.

$$Y\cdot C_B = \frac{k}{K_P}t \tag{15}$$

A plot of all calculated values of YC_B against time t gave essentially a straight line, as shown in Fig. 8, and k/K_P was calculated from the slope of this line.

$$k/K_P = 1.251\times10^{-3}$$

Based on this activity variation model, the rate of reaction can be analyzed according to the Hougen-Watson model.⁶⁾ Although the Hougen-Watson model contains implausible assumptions, the model is useful in considering the reaction mechanism and has been used by many investigators. Several Hougen-Watson models were compared with experimental data, and the following model was assumed for this oxidation reaction.

$$\text{diethanolamine} + \sigma \overset{K_A}{\rightleftarrows} (A)_{ad} \tag{16}$$

$$O_2 + \sigma \overset{K_B}{\rightleftarrows} (B)_{ad} \tag{17}$$

$$(A)_{ad} + O_2 \xrightarrow[\text{NaOH}]{K_A} \text{carboxylic acid} \tag{18}$$

where ($)_{ad}$ indicates an adsorbed molecule. It is assumed that diethanolamine and oxygen are adsorbed competitively on the active sites and that these adsorptions are in equilibrium. The oxidation is assumed to proceed by reaction between the adsorbed diethanolamine and oxygen in the liquid-phase (Rideal-Eley mechanism) and this step is assumed to be rate-controlling. Another type of adsorption, already indicated in eq. (11), is also assumed.

From this model, the reaction rate can be expressed as

$$\begin{aligned} -\frac{dC_A}{dt} &= \frac{k_A K_A C_A C_B C_N m}{1+K_A C_A + K_B C_B} \frac{1}{K_P C_B} \\ &= \frac{k_A K_A C_A C_N m}{K_P(1+K_A C_A + K_B C_B)} \end{aligned} \tag{20}$$

where k_A is the rate constant, and K_A and K_B are the equilibrium constants for diethanolamine and oxygen. Ruether *et al.*[7] obtained almost the same type of rate equation for ethanol oxidation over a Pd-alumina catalyst. The differences are, the dependence of the rate of reaction on alkali concentration, and the term $1/K_P C_B$. In eq. (20), C_N is almost equal to C_A as mentioned before, so this equation can be simplified to

$$-\frac{dC_A}{dt} = \frac{(k_A K_A/K_P) C_A^2 m}{1+K_A C_A + K_B C_B} \tag{21}$$

eq. (21) can be integrated to eq. (22).

$$\beta \frac{x_A}{1-x_A} - \gamma \ln(1-x_A) = t \tag{22}$$

where,

$$\beta = \frac{K_P(1+K_B C_B)}{k_A K_A C_{A0} m} \tag{23}$$

$$\gamma = K_P/k_A m \tag{24}$$

By means of the regression method, β and γ were estimated from the data, and the values are shown in Table II. The calculated values of γ are constant regardless of oxygen concentration, and a linear relationship between β and C_B was obtained, as shown in Fig. 9. From these results, the parameter values were calculated to be as follows,

$k_A/K_P = 2.88 \times 10^{-2}$ cm^3/(s·g)
$K_A = 3.21 \times 10^4$ cm^3/mol
$K_B = 2.70 \times 10^7$ cm^3/mol

Table II. Calculated Values of β and γ

C_B	β	γ
0.603×10^{-7}	2.95×10^3	3.53×10^3
1.47×10^{-7}	4.93×10^3	3.35×10^3
2.45×10^{-7}	8.55×10^3	3.54×10^3

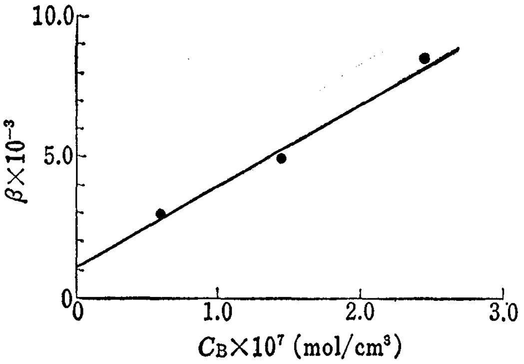


Fig. 9. β *vs.* C_B

The calculated curves based on these values agree well with the experimental data, as shown in Fig. 5. Therefore the assumed model is adequate for this reaction.

Conclusion

The Pd-alumina catalyst is very active for the oxidation of diethanolamine, but its activity decreases due to strong and nearly irreversible adsorption of oxygen, as indicated in eq. (11).

From the kinetic analysis, it is concluded that this reaction is controlled by the reaction between adsorbed diethanolamine and oxygen in the liquid-phase. Our experimental results are well interpreted by the rate eq. (2) and (14), or by eq. (20).

In this study, the role of sodium hydroxide has not been considered in detail. Further studies are planned on this point, and we also hope to develop a more stable catalyst.

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