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Pressure-Jump Method in Reaction of Nitric Oxide and Chlorine over Mordenite

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The catalytic reaction of nitric oxide and chlorine was investigated in the $0 \sim 40$ Torr pressure ranges over H-mordenite at 250°C. The initial rate was proportional with respect to the pressure of nitric oxide and was expressed with the Langmuir-type kinetic equation with respect to the pressure of chlorine. By applying the pressure-jump method, the rate near equilibrium was clear to be expressed as $r = \overrightarrow{k}\, P_{NO}(P_{NOCl})^{-1} - \overleftarrow{k}\, P_{NOCl}(P_{NO})^{-1}\,(P_{Cl_2})^{-1}$, and the stoichiometric number was found to be equal to unity. It was concluded that the rate-determining step of the reaction was $(NO)_a + (Cl_2)_a \rightarrow (NOCl)_a + (Cl)_a$. The reaction mechanism explained both the rates at initial and at equilibrium, and the stoichiometric number.

INTRODUCTION

The method of the determination of the stoichiometric number (*1*) for the rate determining step in a chemical reaction has given good results for the investigation of the mechanism of the heterogeneous catalysis (*2*). The principle of the method is that the stoichiometric number ν of the rate determining step can be estimated from the equilibrium constant K and the forward and backward reaction rate constant $\overrightarrow{k}$ and $\overleftarrow{k}$;

$$K^{1/\nu} = \overrightarrow{k}/\overleftarrow{k}. \tag{1}$$

In principle, a step cannot, however, be distinguished from another step with the same stoichiometric number by the method. Moreover, the method requires in advance to be given the elementary reactions which compose the overall reaction.

The chemical relaxation method (*3*) pioneered and developed by Eigen *et al.* has been extensively used for the study of rapid reactions in solutions. A great advantage of the method is that the rate constants of the forward and backward reactions can be obtained independent of the equilibrium constant. By application of the chemical relaxation method to a reaction, the plausible rate equations can be checked doubly by the examinations of the relation between the relaxation curves obtained and the rate equation applied and the consistency between the observed equilibrium constant and the equilibrium constant calculated from the rate constants by Eq. (1). To our knowledge, the method has never been applied to the heterogeneous catalysis.

The authors tried to apply the pressure-jump method to the reaction of nitric oxide and chlorine over H-mordenite.

$$2NO + Cl_2 \rightleftarrows 2NOCl. \tag{2}$$

The reaction was chosen as a model reaction for the application of the pressure-jump method for the following reasons: (i) the system of nitric oxide and chlorine does not give any products other than nitrosyl chloride in usual conditions; (ii) the equilibrium constant and the rate of the reaction can be obtained from usual pressure decreases; and (iii) the rate is moderately high.

In this paper, we described the kinetics of the catalytic reaction represented in Eq.

(2) in the following story. First, the initial rates and the relaxation times with pressure-jump were obtained. The relation between the relaxation times and the equilibrium pressures was examined by applying the plausible rate equations, and a most applicable rate equation near equilibrium and the stoichiometric number were found. Then, the reaction mechanism was proposed which explained both the rates and the stoichiometric number.

EXPERIMENTAL

The H-mordenite was prepared by ion exchange of the sodium ions of the sodium type of Zeolon (Norton Co. Ltd.) with 10% of aqueous solution of ammonium chloride and was heated at 400°C under vacuum. The percent exchange of the cation measured by flame photometry was 95%. Nitric oxide and chlorine were supplied from Nihon Sanso Co. Ltd. and purified by repeated distillations. The apparatus consists of 3000 ml Pyrex bulb equipped with a cavity for catalyst bed at the bottom, an oil manometer which is connected with the bulb through a narrow tube filled with helium in order to prevent the oil from direct contacting with the reacting gases because they may be absorbed into the oil, a gas sampling device for the gas chromatographic analyses and a gas inlet one. The stopcocks used were greaseless ones to prevent the grease from absorbing the reacting gases. The manometer oil used was a diffusion pump oil (Dow Corning, 704 diffusion pump fluid) and its vapor pressure is negligibly small. In order to measure the small change of the pressure, temperatures at the bulb were carefully kept constant during the course of the reaction. The bulb except the cavity was surrounded with a metal jacket filled with water maintained at a constant temperature (Fig. 1). Gas analyses were performed by GLC with a 3-m column of β,β'-oxydipropionitrile/cellite at room temperature. Helium was used as a carrier gas and its flow rate was about 40 cm^3/min. In order to obtain the settled activity, the mordenite was exposed to 20 Torr of nitric oxide and chlorine for 1 day at 250°C and was evacuated for 1 min at the same temperature before use. Chlorine was admitted and nitric oxide was next admitted into the vessel. Ten seconds after admission the stopcock was shut, and at one minute the first pressure reading was taken. Pressure readings were taken thereafter at convenient intervals. The readings were extrapolated graphically to time zero to get the initial pressure of the nitric oxide.

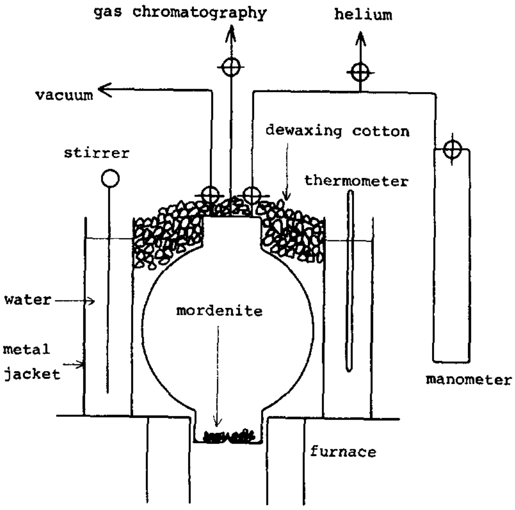

FIG. 1. Schematic of apparatus.

RESULTS

Initial Rate

A typical plot of the total pressure against time at 250°C was shown in Fig. 2. No products other than nitrosyl chloride

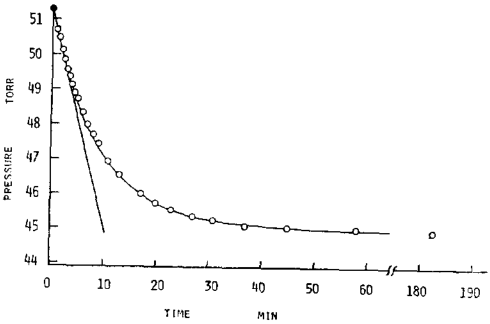

FIG. 2. The change in the total pressure as a function of time at 250°C. Initial pressure of nitric oxide: 26.40 Torr; initial pressure of chlorine: 24.91 Torr. Mordenite: 337 mg, ●: extrapolated initial total-pressure.

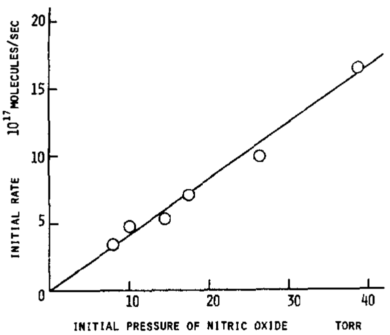

FIG. 3. Initial rate as a function of initial pressure of nitric oxide at 250°C. Initial pressure of chlorine: 20 Torr. Mordenite: 337 mg.

were detected by the gas chromatographic analyses. The initial rate was estimated from the initial slope of the pressure-time curve as drawn by straight line in Fig. 2. Without the mordenite, the initial rate was 4×10^{15} molecules/sec with 10 Torr of nitric oxide and chlorine, and was negligible in comparison with the rate with the mordenite. The initial rates under a constant initial pressure of chlorine were plotted against the initial pressure of nitric oxide as shown in Fig. 3. The initial rates obtained under a constant initial pressure of nitric oxide were plotted against the initial pressure of chlorine (Fig. 4). The initial rate in the reaction of nitric oxide and chlorine $\vec{r}_0$, therefore, was expressed as

$$\vec{r}_0 = kP_{\mathrm{NO}}(KP_{\mathrm{Cl_2}})/(1 + KP_{\mathrm{Cl_2}}) \qquad (3)$$

$$\simeq kP_{\mathrm{NO}} \qquad (P_{\mathrm{Cl_2}} \geqq 10\ \mathrm{Torr}), \qquad (4)$$

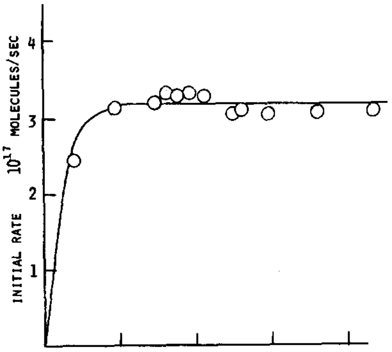

FIG. 4. Initial rate as a function of initial pressure of chlorine at 250°C. Initial pressure of nitric oxide: 10 Torr. Mordenite: 337 mg.

where k and K are constants, and P_{NO} and $P_{\mathrm{Cl_2}}$ are the pressure of nitric oxide and chlorine, respectively. The rate observed was proportional to the amount of the mordenite used and is, therefore, attributed to the surface reactions.

Pressure-Jump

The equilibrium pressures of nitric oxide, chlorine, and nitrosyl chloride ($P_{\mathrm{NO}}{}^e$, $P_{\mathrm{Cl_2}}{}^e$ and P^e_{NOCl}) were estimated from the initial pressures of nitric oxide and chlorine and the decrease of the pressure when the change of the pressure stopped. The equilibrium constant calculated from the equilibrium pressures thus obtained was in agreement with that of Dixon (*4*). Then, the perturbation from the equilibrium was accomplished by the introduction of a small amount of nitric oxide ($\Delta P_{\mathrm{NO}} \sim (1/5)P_{\mathrm{NO}}{}^e$) into the system and the relaxation to a new equilibrium state was followed. The relaxation curve is expressed as

$$P_0 - P = (P_0 - P_\infty)(1 - \exp(-t/\tau)), \qquad (5)$$

where P_0 and P_∞ are the pressures at time 0 and time ∞, respectively (Fig. 5). These procedures were repeated and the relaxation times τ were obtained in the various values of the equilibrium pressures. The equilibrium pressures of nitric oxide, chlorine, and nitrosyl chloride, and the pressures of nitric oxide introduced for the

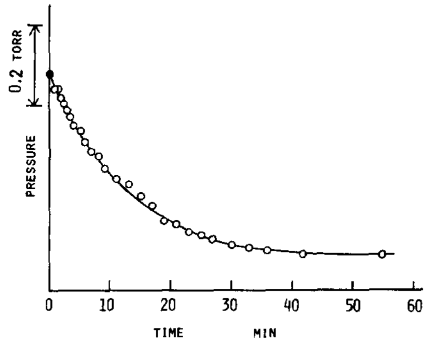

FIG. 5. Pressure-jump relaxation curve. This curve was obtained by the introduction of nitric oxide ($\Delta P_{\mathrm{NO}} = 2.07$ Torr) into the system with the equilibrium pressures of $P_{\mathrm{NO}}{}^e = 13.55$ Torr, $P_{\mathrm{Cl_2}}{}^e = 18.49$ Torr and $P^e_{\mathrm{NOCl}} = 12.85$ Torr over 337 mg of mordenite at 250°C. ●: extrapolated initial pressure.

TABLE 1

SUMMARY OF KINETIC DATA

No.	P_{NO}^e Torr	ΔP_{NO} Torr	$P_{Cl_2}^e$ Torr	P^e_{NOCl} Torr	K^a Torr^{-1}	$1/\tau$ min^{-1}	X_4^b Torr^{-1}	Y_4^b Torr min^{-1}
1	22.85	2.22	18.14	19.84	0.0416	0.0664	0.0451	0.291
2	30.37	2.55	15.90	24.30	0.0403	0.0557	0.0493	0.287
3	13.55	2.07	18.49	12.85	0.0482	0.0910	0.0436	0.264
4	15.94	2.01	20.68	14.76	0.0415	0.0790	0.0391	0.263
5	9.55	2.46	23.33	9.45	0.0440	0.1059	0.0295	0.220
6	10.07	2.51	21.69	9.30	0.0394	0.1012	0.0283	0.199

[a] $K \equiv (P^e_{NOCl})^2/(P_{NO}^e)^2 P_{Cl_2}^e$.

[b] X_4 and Y_4 are written in No. 4 of Table 3.

perturbation and the relaxation times observed were summarized in Table 1.

DISCUSSION

The Rate Equation Near Equilibrium

The relation between the relaxation times and the equilibrium pressures was examined by the application of twelve plausible rate equations with integer or half-integer order summarized in Table 2. The pressures of nitric oxide, chlorine, and nitrosyl chloride can be written as

$$\begin{aligned} P_{NO} &= P_{NO}^e + \Delta P_{NO} - 2\Delta, \\ P_{Cl_2} &= P_{Cl_2}^e - \Delta, \qquad (6) \\ P_{NOCl} &= P^e_{NOCl} + 2\Delta, \end{aligned}$$

where Δ is the pressure which decreases after the admission of nitric oxide. Substituting Eq. (6) into each of the rate equations summarized in Table 2, expanding the resulting equations (neglecting terms of higher order of Δ) and making use of Eq. (1), we obtain the following equation:

$$d\Delta/dt = -(1/\tau)(\Delta - \Delta_0), \qquad (7)$$

where Δ_0 is written as

$$\Delta_0 = \frac{2P^e_{NOCl}P_{Cl_2}^e\Delta P_{NO}}{4P^e_{NOCl}P_{Cl_2}^e + 4P_{NO}^eP_{Cl_2}^e + P_{NO}^eP^e_{NOCl}}. \qquad (8)$$

Relaxation time τ is expressed as a function of the equilibrium pressures depending on

TABLE 2

RATE EQUATIONS CONSIDERED IN THE EXPERIMENT EXPRESSED AS

$$r = \overrightarrow{k}(P_{NO})^m(P_{Cl_2})^n(P_{NOCl})^q - \overleftarrow{k}(P_{NO})^s(P_{Cl_2})^t(P_{NOCl})^u$$

AND THE STOICHIOMETRIC NUMBER ν

No.	m	n	q	s	t	u	ν
1	0	1	0	−2	0	2	1
2	1	0	0	−1	−1	2	1
3	1	0	0	0	−½	1	2
4	1	0	−1	−1	−1	1	1
5	1	0	−1	0	−½	0	2
6	1	½	0	0	0	1	2
7	1	1	−1	−1	0	1	1
8	1	1	0	−1	0	2	1
9	2	0	−1	0	−1	1	1
10	2	½	−1	0	−½	1	1
11	2	1	0	0	0	2	1
12	2	1	−1	0	0	1	1

TABLE 3

The Relation Between the Forward and Backward Reaction Rate-Constants and the Relaxation Time and the Equilibrium Pressures Written in Eq. (9). The Numbers of This Table Agree with Those of Table 2

No. i	X_i	Y_i
1	$\frac{4(P^e_{NOCl})^2}{(P_{NO}^e+\Delta P_{NO})^2}\left(\frac{1}{P_{NO}^e+\Delta P_{NO}}+\frac{1}{P^e_{NOCl}}\right)$	$\frac{1}{\tau}$
2	$\frac{(P^e_{NOCl})^2}{2(P_{NO}^e+\Delta P_{NO})P_{Cl_2}^e}\left(\frac{4}{P^e_{NOCl}}+\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{1}{P_{Cl_2}^e}\right)$	$\frac{1}{2\tau}$
3	$\frac{P^e_{NOCl}}{4(P_{Cl_2}^e)^{3/2}}+\frac{1}{(P_{Cl_2}^e)^{1/2}}$	$\frac{1}{2\tau}$
4	$\frac{(P^e_{NOCl})^2}{(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}+\frac{1}{P_{Cl_2}^e}\right)\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$	$\frac{1}{\tau}\frac{(P^e_{NOCl})}{(P_{NO}^e+\Delta P_{NO})}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$
5	$\frac{P^e_{NOCl}}{2(P_{NO}^e+\Delta P_{NO})(P_{Cl_2}^e)^{3/2}}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$	$\frac{P^e_{NOCl}}{\tau(P_{NO}^e+\Delta P_{NO})}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$
6	$2\left(2(P_{Cl_2}^e)^{1/2}+\frac{(P_{NO}^e+\Delta P_{NO})}{2(P_{Cl_2}^e)^{1/2}}\right)^{-1}$	$\frac{1}{\tau}\left(2(P_{Cl_2}^e)^{1/2}+\frac{(P_{NO}^e+\Delta P_{NO})}{2(P_{Cl_2}^e)^{1/2}}\right)^{-1}$
7	$\frac{(P^e_{NOCl})^2}{(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}+\frac{1}{P_{Cl_2}^e}\right)^{-1}$	$\frac{P^e_{NOCl}}{\tau(P_{NO}^e+\Delta P_{NO})P_{Cl_2}^e}\left(\frac{2}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}+\frac{1}{P_{Cl_2}^e}\right)^{-1}$
8	$\frac{2(P^e_{NOCl})^2+4(P^e_{NOCl})(P_{NO}^e+\Delta P_{NO})}{(P_{NO}^e+\Delta P_{NO})^2(P_{NO}^e+\Delta P_{NO}+2P_{Cl_2}^e)}$	$\frac{1}{\tau(P_{NO}^e+\Delta P_{NO}+2P_{Cl_2}^e)}$
9	$\frac{(P^e_{NOCl})^2}{(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}\left(\frac{2}{P^e_{NOCl}}+\frac{1}{P_{Cl_2}^e}\right)\left(\frac{4}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$	$\frac{P^e_{NOCl}}{\tau(P_{NO}^e+\Delta P_{NO})^2}\left(\frac{4}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}\right)^{-1}$
10	$\frac{(P^e_{NOCl})^2}{(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}\left(\frac{2}{P^e_{NOCl}}+\frac{1}{2P_{Cl_2}^e}\right)\left(\frac{4}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}+\frac{1}{2P_{Cl_2}^e}\right)^{-1}$	$\frac{P^e_{NOCl}}{\tau(P_{NO}^e+\Delta P_{NO})^2(P_{Cl}{}^e)^{1/2}}\left(\frac{4}{P_{NO}^e+\Delta P_{NO}}+\frac{2}{P^e_{NOCl}}+\frac{1}{2P_{Cl_2}^e}\right)^{-1}$
11	$\frac{4P^e_{NOCl}}{(P_{NO}^e+\Delta P_{NO})(P_{NO}^e+\Delta P_{NO}+4P_{Cl_2}^e)}$	$\frac{1}{\tau(P_{NO}^e+\Delta P_{NO})(P_{NO}^e+\Delta P_{NO}+4P_{Cl_2}^e)}$
12	$2\left(\frac{2(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}{(P^e_{NOCl})^2}+\frac{4(P_{NO}^e+\Delta P_{NO})P_{Cl_2}^e}{P^e_{NOCl}}+\frac{(P_{NO}^e+\Delta P_{NO})^2}{P^e_{NOCl}}\right)^{-1}$	$\frac{1}{\tau}\left(\frac{2(P_{NO}^e+\Delta P_{NO})^2P_{Cl_2}^e}{(P^e_{NOCl})^2}+\frac{4(P_{NO}^e+\Delta P_{NO})P_{Cl_2}^e}{P^e_{NOCl}}+\frac{(P_{NO}^e+\Delta P_{NO})^2}{P^e_{NOCl}}\right)^{-1}$

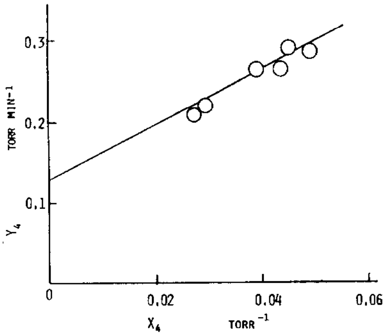

FIG. 6. Linear plot of Eq. (9). X_4 and Y_4 written in No. 4 of Table 3.

the rate equation applied, and which is modified to the following equation:

$$Y_i = \overrightarrow{k} + \overleftarrow{k} X_i. \qquad (9)$$

X_i and Y_i are, therefore, expressed as a function of the relaxation time and the equilibrium pressures depending on the rate equation applied, and are summarized in Table 3. Integration of Eq. (7) gives

$$\Delta = \Delta_0(1 - \exp(-t/\tau)). \qquad (10)$$

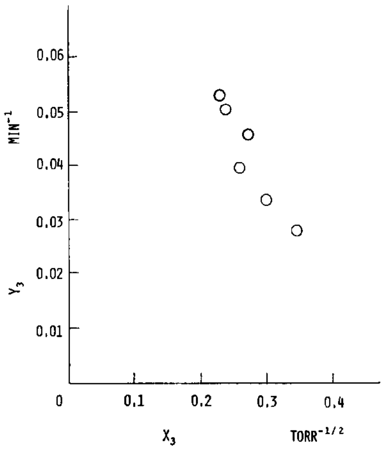

FIG. 8. Plot of kinetic data according to Eq. (9). X_3 and Y_3 are written in No. 3 of Table 3.

Equation (10) is equal to Eq. (5) since Δ and Δ_0 are equal to $P_0 - P$ and $P_0 - P_\infty$, respectively, and gives a relaxation curve as shown in Fig. 5. The only rate equation expressed in No. 4 in Table 2 was concluded to be applicable to the reaction near equilibrium by the examination of the relation between the relaxation times and the equilibrium pressures for the twelve rate equations summarized in Table 2. We got a straight line by plotting of Y_4 against X_4 as shown in Fig. 6. The ratio of the intercept $\overrightarrow{k}$ to the slope $\overleftarrow{k}$ must be equal to the equilibrium constant (stoichiometric number $\nu = 1$). The observed ratio, $\overrightarrow{k}/\overleftarrow{k} = 0.038$ Torr^{-1}, was nearly equal to the equilibrium constant observed, $K = 0.043$ Torr^{-1}. Such unity is not a mere accident. The plottings of the experimental data according to the equations summarized in Table 3 showed that the rate equations except the equation expressed in No. 4 of Table 2 cannot be applied to the reaction. Some of the plottings of the Y_i against the X_i are shown in Figs. 7–9. If the rate equation expressed

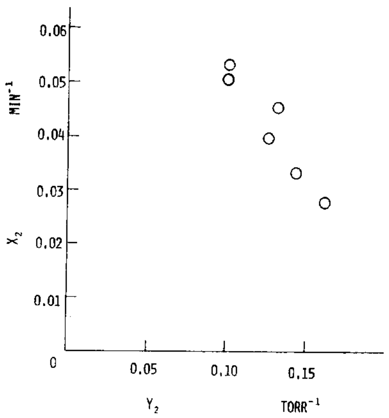

FIG. 7. Plot of kinetic data according to Eq. 9). X_2 and Y_2 are written in No. 2 of Table 3.

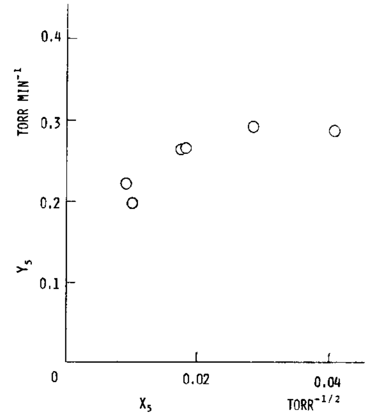

FIG. 9. Plot of kinetic data according to Eq. (9). X_5 and Y_5 are written in No. 5 of Table 3.

in No. 2 of Table 2 is applicable to the reaction near equilibrium, a straight line ought to be gotten by plotting Y_2 against X_2, and the ratio of the intercept to the slope gives the equilibrium constant K in Fig. 7. If the rate equation expressed in No. 3 or No. 5 of Table 2 is applicable to the reaction near equilibrium, a straight line ought be gotten by plotting Y_3 or Y_5 against X_3 or X_5, respectively, and the ratio of the intercept to the slope gives the square root of the equilibrium constant, $K^{1/2}$ in Fig. 8 or Fig. 9, respectively. It is clearly shown that the rate equation expressed in Nos. 2, 3 and 5 in Table 2 cannot be applied to the reaction.

The Reaction Mechanism

The initial rate expressed in Eqs. (3) or (4) and the rate equation near equilibrium expressed in No. 4 of Table 2 was derived if the following reaction steps were postulated.

$$\mathrm{NO + S(1) \underset{k_2}{\overset{k_1}{\rightleftarrows}} NOS(1),} \qquad \text{(i)}$$

$$\mathrm{Cl_2 + S(2) \underset{k_4}{\overset{k_3}{\rightleftarrows}} Cl_2S(2),} \qquad \text{(ii)}$$

$$\mathrm{NOS(1) + Cl_2S(2) \underset{k_6}{\overset{k_5}{\rightleftarrows}} NOClS(1) + ClS(2),} \qquad \text{(iii)}$$

$$\mathrm{ClS(2) + NOS(1) \underset{k_8}{\overset{k_7}{\rightleftarrows}} NOClS(1) + S(2),} \qquad \text{(iv)}$$

$$\mathrm{NOClS(1) \underset{k_{10}}{\overset{k_9}{\rightleftarrows}} NOCl + S(1),} \qquad \text{(v)}$$

where k_1–k_{10} represent the rate constants of the reaction steps (i)–(v), and S(1) and S(2) the different vacant surface sites, and NOS(1), $\mathrm{Cl_2S(2)}$, NOClS(1), and ClS(2) represent the adsorbed species. The rate equation expressed in Eqs. (3) and (4), and No. 4 of Table 2 could not be explained by other mechanisms such as

$$\left.\begin{aligned} \mathrm{NO} &\rightleftarrows \mathrm{NO(a)}, \\ \mathrm{Cl_2} &\rightleftarrows \mathrm{2Cl(a)}, \\ \mathrm{NO(a) + Cl(a)} &\rightleftarrows \mathrm{NOCl(a)}, \\ \mathrm{NOCl(a)} &\rightleftarrows \mathrm{NOCl}. \end{aligned}\right\} \qquad (11)$$

If the step (iii) is the rate-determining one, the overall reaction rate is expressed as follows.

$$r = \frac{k_1k_3k_5}{k_2k_4} P_{\mathrm{NO}}P_{\mathrm{Cl_2}}\{\mathrm{S(1)}\}\{\mathrm{S(2)}\} - \frac{k_2k_6k_8}{k_1k_7}\left(\frac{k_{10}}{k_9}\right)^2 \frac{(P_{\mathrm{NOCl}})^2}{P_{\mathrm{NO}}}\{\mathrm{S(1)}\}\{\mathrm{S(2)}\}, \qquad (12)$$

where $\{\mathrm{S(1)}\}$ and $\{\mathrm{S(2)}\}$ are the concentrations of the surface vacant sites of site 1 and site 2, respectively, and they are written as

$$\{\mathrm{S(1)}\} = \frac{\{\mathrm{S(1)}\}_0}{1 + (k_1/k_2)P_{\mathrm{NO}} + (k_{10}/k_9)P_{\mathrm{NOCl}}}, \qquad (13)$$

$$\{\mathrm{S(2)}\} = \frac{\{\mathrm{S(2)}\}_0}{1 + (k_3/k_4)P_{\mathrm{Cl_2}} + (k_2k_8k_{10}/k_1k_7k_9)(P_{\mathrm{NOCl}}/P_{\mathrm{NO}})}, \qquad (14)$$

where $\{\mathrm{S(1)}\}_0$ and $\{\mathrm{S(2)}\}_0$ are the total concentrations of site 1 and site 2, respectively. At high pressures of nitrosyl chloride and chlorine $((k_{10}/k_9)P_{\mathrm{NOCl}} \gg 1 + (k_1/k_2)P_{\mathrm{NO}},\ (k_3/k_4)P_{\mathrm{Cl_2}} \gg 1 + (k_2k_8k_{10}/k_1k_7k_9)\ (P_{\mathrm{NOCl}}/P_{\mathrm{NO}}))$, Eqs. (13) and (14) can be modified to

$$\{\mathrm{S(1)}\} = (k_9/k_{10})(1/P_{\mathrm{NOCl}})\{\mathrm{S(1)}\}_0, \qquad (15)$$

$$\{\mathrm{S(2)}\} = (k_4/k_3)(1/P_{\mathrm{Cl_2}})\{\mathrm{S(2)}\}_0. \qquad (16)$$

Substituting Eqs. (15) and (16) into Eq. (12), we get

$$r = \frac{k_1k_5k_9}{k_2k_{10}} \frac{P_{\mathrm{NO}}}{P_{\mathrm{NOCl}}}\{\mathrm{S(1)}\}_0\{\mathrm{S(2)}\}_0 - \frac{k_2k_4k_6k_8k_{10}}{k_1k_3k_7k_9} \frac{P_{\mathrm{NOCl}}}{P_{\mathrm{NO}}P_{\mathrm{Cl_2}}}\{\mathrm{S(1)}\}_0\{\mathrm{S(2)}\}_0. \qquad (17)$$

This equation is equal to the rate equation expressed in No. 4 of Table 2 if $\vec{k}$ and $\overleftarrow{k}$ are equal to $(k_1k_5k_9/k_2k_{10})\{\mathrm{S}(1)\}_0\{\mathrm{S}(2)\}_0$ and $(k_2k_4k_6k_8k_{10}/k_1k_3k_7k_9)\{\mathrm{S}(1)\}_0\{\mathrm{S}(2)\}_0$, respectively.

At the initial stage of the reaction of nitric oxide and chlorine, the second term is negligible to the first term in Eq. (12). The third terms of the denominators of Eqs. (13) and (14) are also negligible to the sums of the first and second terms. We get, therefore, as the initial rate of the forward reaction represented in Eq. (2)

$$\vec{r}_0 = \frac{k_5(k_1/k_2)P_{\mathrm{NO}}}{1 + (k_1/k_2)P_{\mathrm{NO}}} \frac{(k_3/k_4)P_{\mathrm{Cl_2}}}{1 + (k_3/k_4)P_{\mathrm{Cl_2}}} \{\mathrm{S}(1)\}_0\{\mathrm{S}(2)\}_0. \tag{18}$$

The observed initial rate expressed in Eq. (3) agrees with Eq. (18) at low pressure of nitric oxide $((k_1/k_2)P_{\mathrm{NO}} \ll 1)$.

At the initial stage of the decomposition of nitrosyl chloride, the first term is negligible to the second term in Eq. (12). The second term is negligible to the sum of the first and the third terms in the denominator of Eq. (13), and the sum of the first and second terms are negligible to the third term in the denominator in Eq. (14). We get, therefore, as the initial rate of the backward reaction represented in Eq. (2)

$$\overleftarrow{r}_0 = k_6 \frac{(k_{10}/k_9)P_{\mathrm{NOCl}}}{1 + (k_{10}/k_9)P_{\mathrm{NOCl}}} \{\mathrm{S}(1)\}_0\{\mathrm{S}(2)\}_0. \tag{19}$$

If the second term is negligible to the first term in the denominator of Eq. (19) in the system of nitrosyl chloride over Pyrex glass, Eq. (19) agrees with an experimental result obtained by Spencer and Ashmore (*5*) that the rate of the heterogeneous decomposition of nitrosyl chloride was proportional to the pressure of nitrosyl chloride.

We considered only the rate equations with integer or half-integer orders for the rate equations near equilibrium and not considered the Langmuir-type kinetic equations. The application of the Langmuir-type kinetic equations to the examination of the pressure-jump relaxation curves increases the complication of the mathematical manipulations. It is one of the disadvantages of the pressure-jump method for applying to the heterogeneous catalysis. In this case, it may be satisfied to treat the pressure-jump relaxation curves with the rate equations with integer or half-integer orders in the following reason. The initial rate in the pressure range summarized in Table 1 was expressed in Eq. (4) and the initial rate of the heterogeneous decomposition of nitrosyl chloride over Pyrex glass was proportional to the pressure of nitrosyl chloride (*5*). These rates were expressed with integer orders. In general, the rate equation with integer or half-integer orders may be a limiting form of a complicated Langmuir-type kinetic equation. The rate equation expressed in No. 4 of Table 2 is a limiting form of the Langmuir-type kinetic Eq. (12) in this case.

The reaction of nitric oxide and chlorine over H-mordenite was a model reaction to apply the pressure-jump method. The pressure-jump method has provided useful information for establishing the reaction mechanism. The method has been applied to the catalytic dehydrogenation of propane over alumina-chromia and the study will be reported elsewhere.

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