Removal of Atomospheric Pollutants

(3) Removal of NO by Aqueous Mixed Solutions of $NaClO_2$ and NaOH

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大気汚染物質除去に関する研究

（3） $NaClO_2$, NaOH 混合水溶液による脱硝

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Abstract—The absorption of NO in aqueous mixed solutions of $NaClO_2$ and NaOH was carried out using a semi-batch stirred vessel with a plain gas-liquid interface at 25°C. The rate of absorption was discussed on the basis of chemical absorption theory under the fast-reaction regime. The overall reaction involved was presented by

$$4NO + 3NaClO_2 + 4NaOH = 4NaNO_3 + 3NaCl + 2H_2O$$

and was found to be second-order with respect to NO and first-order with respect to $NaClO_2$ in the range of $NaClO_2$ concentration greater than 0.8 molar. The reaction rate constants evaluated were exponentially decreased with the NaOH concentration and correlated by $k = k_0 \exp(-3.73C_{E0})$.

Among the nitrogen oxides (NO_x) emitted from stationary combustion sources, more than 90% of NO_x is inactive NO. In the removal of NO_x by wet scrubbing processes, it is desirable to oxidize NO to NO_2 in either or liquid phase. Several technologies by absorption of NO with liquid-phase oxidation have been under development and some of them have been in the improvement stage for practical application.
However, a target of intensive investigations lies in the degree of elimination of NO but does not lie in the analysis of chemical absorption mechanism and reaction kinetics.

In the previous work[1], the process of simultaneous absorption and oxidation in aqueous solutions of $KMnO_4$ and mixed aqueous solutions of $KMnO_4$and NaOH was discussed on the standpoint of chemical absorption. The reaction between NO and aqueous solutions of $KMnO_4$ was found to be first-order with respect to NO and first-order with respect to $KMnO_4$. The reaction rate constants evaluated were given as a function of NaOH concentration. The alkaline solution of $KMnO_4$ was found to be a promising absorbent for NO. For the time being, it appears that an alkaline solution of $NaClO_2$ is also promising because of high absorption rate, easiness in waste water treatment and low cost. Recently, Teramoto *et al*[2]. experimentally investigated the effect of various operating conditions on the rates of NO absorption in aqueous mixed solutions of $NaClO_2$ and NaOH. But the kinetics of the chemical reaction prevailing in the absorption was not clarified. In the present work, the absorption of NO by alkaline solutions of $NaClO_2$ was performed and discussed from the standpoint of chemical absorption to clarify the reaction kinetics.

EXPERIMENTAL

All experimental runs for chemical absorption were made using a stirred vessel with a plain gas-liquid interface. The absorber was batch wise with respect to the liquid. The absorber used differed considerably from one used in the previous work[1]. The vessel and the impeller in gas and liquid phases were sketched in Fig. 1. The absorption vessel was of 8.0cm i.d. with four symetrically located baffles. Two stirrers were used for agitation in gas and liquid phases, and were driven by two separate motors. The liquid stirrer was a fan turbine with eight blades and was placed at half of the liquid depth. The gas stirrer was also a fan turbine with four blades and was mounted in the center of the gas phase. The stirring speeds of the liquid phase and gas phase stirrers were kept constant at 162 and 500rpm, respectively. A circulating water jacket was attached to the outside of the vessel, and the temperature of the vessel was main-

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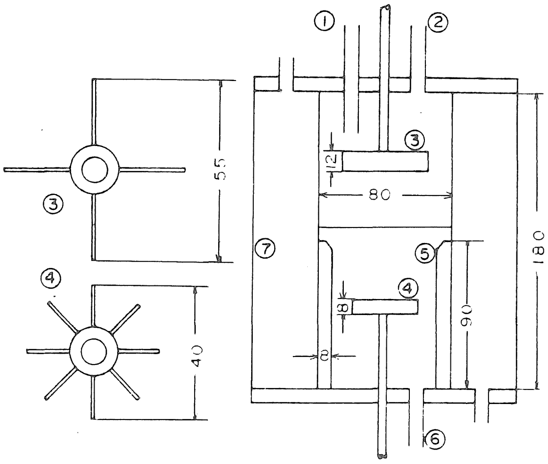

Fig. 1. Stirred vessel and impellers. 1, gas inlet; 2, gas outlet; 3, gas phase stirrer; 4, liquid phase stirrer; 5, baffle; 6, liquid inlet and oulet; 7, water jacket.

tained at 25°C.

Solute gas NO was diluted by N_2, saturated with water vapour at the temperature of the apparatus and fed into the absorber. The liquid absorbent was aqueous mixed solutions of $NaClO_2$ and NaOH, and the amount of liquid absorbent was 500cm^3. The purity of $NaClO_2$ reagent used was 85-88%. The concentration of $NaClO_2$ in the aqueous solution was determined by chemical analysis. The concentration of $NaClO_2$ and NaOH in the absorbent ranged from 0.21 to 1.50 mole/l. and from 0.05 to 0.50mole/l., respectively. The concentration of NO in the gas stream ranged from 0.8 to 15vol%. The composition of NO in the gas phase into and from the absorber was determined by gas chromatography. A molecular sieve 13 × column (1.5m long) at 28°C gave a good separation of NO and N_2 after elimination of water vapour. The gas phase compositions of NO along with the total gas flow rate enable one to calculate the rate of NO absorption.

In order to compare experimental results for chemical absorption with the theoretical solution based on film theory, the liquid-side mass transfer coefficient under physical conditions which is included in enhancement factor and reaction-diffusion modulus is required. Then, the physical absorption of pure CO_2 into water at 25°C was preliminarily performed with the same equipment in batch operation with respect to both gas and liquid phases. Agitator impeller speed in the liquid phase was varied from 60 to 280rpm. Whereas the gas phase was not agitated. Absorption rates were determined with a soap film meter.

For the evaluation of the order of reaction and the reaction rate constant, the values of diffusivity and physical solubility of NO in aqueous mixed solutions of $NaClO_2$ and NaOH are required. However, because of the occurrence of chemical reaction between nitric oxide and the mixed salt solution, the diffusivity was deduced from the corresponding value of nitrous oxide. The diffusivities of nitrous oxide were measured from the physical rates in the laminar liquid-jet. The values of nitric oxide solubilities in the mixed solutions were evaluated using a correlation of solubility of gases in aqueous solutions of mixed electrolyte salts presented by Onda *et al.*[3]. However, the value of the contribution of anion, ClO_2^-, to the salting-out parameter was not available in the literature. Then, the solubility of nitrous oxide in aqueous solutions was measured with the same apparatus as Onda *et al.*[4].

EXPERIMENTAL RESULTS AND DISCUSSION

Physico-chemical properties

By plotting the solubility of nitrous oxide in aqueous solutions of sodium chlorite in the form of log (α_w/α) against chlorite concentration, the salting-out parameter, *K*, defined by eqn (1) can be evaluated.

$$\log(\alpha/\alpha_w) = -KC_{Bo} \tag{1}$$

$$K = x_g + x_a + x_c \tag{2}$$

where K depends on the ion and gas present and x refers to the contribution of various species. The values of x_g and x_c were available in the literature[4] to be -0.2141 and 0.0183, respectively. Therefore, the value of x_a for ClO_2^- was determined to be 0.3497. The solubility of nitric oxide in aqueous solution of $NaClO_2$ and NaOH was calculated using the correlation of solubility of gases in aqueous solutions of mixed salts[3] with estimates of x_{NO} $(= -0.1825)$, x_{OH^-} $(= 0.3875)$ and x_{Na^+} $(= 0.0183)$ taken from previous works[1,4] as well as $x_{ClO_2^-}$ $(= 0.3497)$.

From the physical absorption data in the laminar liquid-jet, diffusivities of nitrous oxide in the aqueous mixed solutions were calculated by the penetration theory solution:

$$Q_A = 4C_{Ai}\sqrt{(D_A v h)}. \tag{3}$$

The reaction of the diffusivity of nitric oxide in the aqueous mixed solutions was assumed same as observed reduction in nitrous oxide diffusivity. The nitric oxide diffusivity under consideration was estimated by

$$(D_A/D_{Aw})_{NO} = (D_A/D_{Aw})_{N_2O} \tag{4}$$

as proposed by Joosten and Danckwerts [5]. Here the value of D_{Aw} is available in the literature [6].

The liquid-side mass transfer coefficient, k_L°, was determined by measuring the rate of physical absorption water at 25°C and correlated to the liquid into phase stirring speed as $k_L^\circ = 9.41 \times 10^{-5} n^{0.65}$

The liquid-side mass transfer coefficient of nitric oxide k_{LA}° was predicted by a correlation

$$k_{LA}^\circ = k_{LCO_2\text{-}H_2O}^\circ (D_A/D_{CO_2\text{-}H_2O})^{2/3} \tag{5}$$

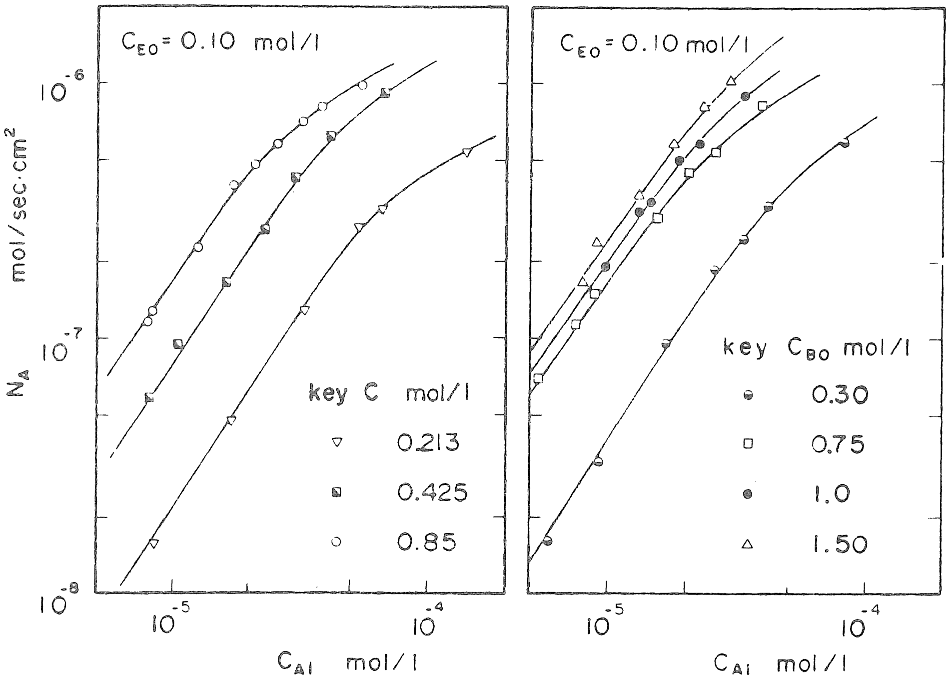

Fig. 2. Relationship between N_A and C_{Ai} as parameter of C_{BO} for $C_{EO} = 0.10$ molar.

as in previous paper [1], and was used in the evaluation of enhancement factor.

The gas-phase resistance was estimated to be less than 4% of the total resistance by the empirical correlation presented by Hikita *et al.* [7].

Reaction kinetics

The influence of chlorite concentration on the nitric oxide absorption rate was studied at a constant sodium hydroxide concentration. Experimental results were shown in Fig. 2 as a plot of the absorption rate of nitric oxide, N_A, against the interfacial concentration of nitric oxide in the liquid phase, C_{Ai}, on logarithmic coordinates. The concentration of sodium cholrite was varied from 0.213 to 1.50 molar with keeping concentration of sodium hydroxide constant to be 0.10 molar. The reaction between nitric oxide and chlorite ion in an alkaline solution is considered to be

$$2NO + ClO_2^- = 2NO_2 + Cl^- \qquad (\mathrm{I})$$

$$4NO_2 + ClO_2^- + 4OH^- = 4NO_3^- + Cl^- + 2H_2O \ (\mathrm{II})$$

The rate of chemical reaction here is regarded as the mth order relative to nitric oxide and the nth order relative to chlorite ion. Then, the order of reaction relative to nitric oxide can be calculated from the slope $(m+1)/2$ of logarithmic plot, when the process of chemical absorption lies under the fast-reaction regime and hence the rate of nitric oxide absorption can be expressed by

$$N_A = \sqrt{\left(\frac{2}{m+1} k C_{BO}^{n} C_{Ai}^{m+1} D_A\right)} \qquad (6)$$

In Fig. 2, there is a linear relationship between log N_A and log C_{Ai} for $C_{Ai} < 2 \times 10^{-5}$ molar. Slopes of linear portions of these lines predict the second-order reaction in nitric oxide. The second-order dependence on nitric oxide suggests that the elementary steps of the reaction (I) are

$$2NO = (NO)_2$$

$$\text{and } (NO)_2 + ClO_2^- = 2NO_2 + Cl^-.$$

Equation (6) suggests that the order of reaction in chlorite ion can be deduced from the slope of the logarithmic plot of $N_A/\sqrt{D_A}$ vs C_{BO} as a parameter of C_{Ai} or $N_A/C_{Ai}\sqrt{(C_{Ai}D_A)}$ vs C_{BO}. Figure 3 shows the relationship $N_A/\sqrt{(D_A)}$ and C_{BO} for $C_{Ai} = 10^{-5}$ and 2×10^{-5} molar, which are obtained by interpolating experimental values. The relationships between $N_A/C_{Ai}\sqrt{(C_{Ai}D_A)}$ and C_{BO} is also shown in the same figure. Only for C_{BO} greater than 0.8 molar, a linear relationship with the slope of 1/2 is appeared. So the order of reaction in chlorite can be determined as unity. Thus the rate of the chemical reaction of nitric oxide with aqueous alkaline solutions of sodium chlorite can be expressed in terms of second-order with respect to nitric oxide and first-order with respect to sodium chlorite for the alkaline concentration greater than 0.8 molar, and the absorption rate under the fast-reaction regime can be expressed by

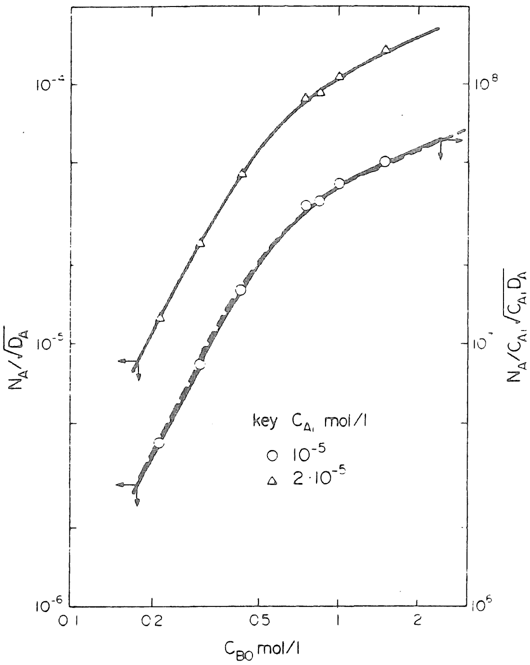

Fig. 3. Effect of C_{BO} on $N_A/\sqrt{(D_A)}$ and $N_A/C_{Ai}\sqrt{(C_{Ai}D_A)}$.

$$N_A=\sqrt{\left(\frac{2}{3}kC_{BO}C_{Ai}^3D_A\right)} \qquad (7)$$

An averaged value of reaction rate constant determined from experimental points falling on the linear portions of the lines in Fig.2 is 2.45 × 10^{12}(l/mole)^2/sec. The enhancement factors evaluated from the data falling on the straight lines in Fig. 2 are ranged from 670 to 10900 with an increase in the chlorite concentration, but are about ten times less than the values of C_{BO}/C_{Ai} under the corresponding conditions. So the data falling on the straight lines are believed under the fast-reaction regime. At higher values of C_{Ai}, the relationship deviates from the straight line because some depletion of the liquid reactant has occurred in the vicinity of the gas-liquid interface. Figure 4 shows the comparison of the enhancement factors from experimental points falling in a depletion region with the film-theory predictions. The agreement is rather good.

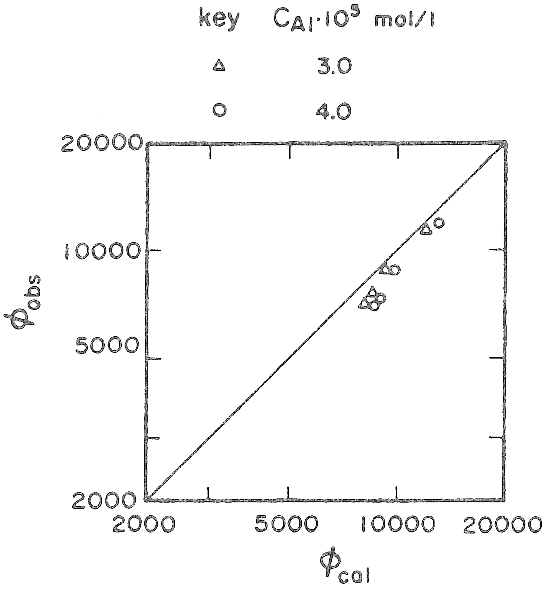

Fig. 4. Comparison of observed and predicted enhancement factor.

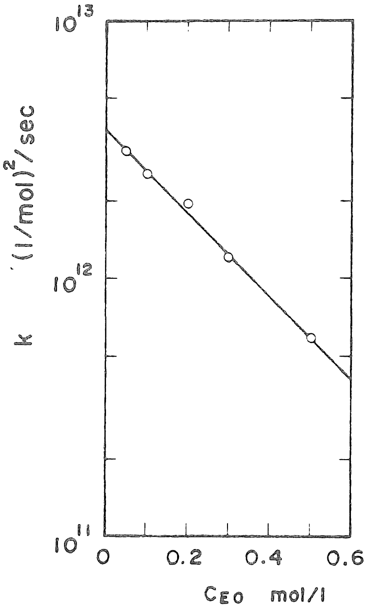

Fig. 5. Effect of NaOH concentration on reaction rate constant.

It is known that the oxidative power of the sodium chlorite increases with a decrease in pH value of the solution. Hence the rate of the reaction with nitric oxide is higher in an aqueous solution of sodium chlorite without adding sodium hydroxide than with adding sodium hydroxide. However as suggested in the reaction (I), in the removal of NO by the solution without containing sodium hydroxide, the reaction product, NO_2, is evolved. Thus, the addition of OH^- to the absorbent is required in order to fix gaseous product, NO_2,as nitrate ion. In order to evaluate the retardation effect of OH^- added, the influence of alkaline concentration on the rate of nitric oxide absorption was investigated at a constant sodium chlorite concentration equal to 1.0 molar. The concentration of sodium hydroxide was varied from 0.05 to 0.50 molar. Experimental results were analyzed using the chemical reaction mechanism derived above. Evaluated rate constant of (2,1)-order reaction are plotted against the sodium hydroxide concentration in Fig. 5. The reaction rate constant is expoentiajly decreasead with sodium hydroxide concentration and empirically correlated by $k = k_0 \exp(-3.73\ C_{EO})$.

CONCLUSION

The absorption rate of nitric oxide in aqueous mixed solutions of sodium chlorite and sodium hydroxide was measured using a semi-batch stirred tank absorber with a plain gas-liquid interface. The rate of nitric oxide absorption was interpreted under the fast-reaction regime. The reaction involved was found to be second-order in nitric oxide and first-order in sodium chlorite for the chlorite concentration greater than 0.8 molar. The reaction rate constants evaluated were exponentially decreased with the sodium hydroxide concentration.

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NOTATION

C	concentration in liquid phase, mole/l.
D	diffusivity in liquid phase, cm^2/sec
h	length of liquid-jet, cm
K	salting-out parameter, l./mole
k	rate constant of (m,n)-order reaction, $(l./mole)^{m+n-1}$/sec
m	order of reaction relative to absobing componet
N	absoption rate, mole/sec cm^2
n	order of reaction relative to liquid-phase reactant
x_g, x_a, x_c	contribution of gas, anion and cation to K, respectively, l./mole
v	liquid flow rate, cm^3/sec

Greek symbols

α	Bunsen absorption coefficient, cm^3 of gas/cm^3 of solution
ϕ	enhancement factor

Subscripts

A	absorbing gas A (NO)
B	liquid-phase reactant B ($NaClO_2$)
E	liquid-phase reactant E (NaOH)
i	gas-liquid interface
w	water
O	initial value

Superscript

$^\circ$	without reaction

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