

Removal of Atmospheric pollutants

(5) Absorption of Lean NO_x in Aqueous Solutions of NaClO₂ and NaOH

Ichibei KUDO, Takashi KONDO, Eizo SADA* and Hidehiro KUMAZAWA*

大気汚染物質除去に関する研究

(5) NaClO₂, NaOH 水溶液による 希薄NO_xの吸収

工藤市兵衛・近藤高司・佐田栄三*・熊沢英博*

The absorption of such lean NO_x as encountered in flue gases in aqueous mixed solutions of NaClO₂ and NaOH was carried out using a stirred vessel with a plane interface at 25 °C and atmospheric pressure. The rate of NO₂ absorption was analyzed by the chemical absorption theory under the fast-reaction regime. The reaction prevailed was found to be the parallel reactions involving oxidation and hydrolysis, and to be second-order with respect to NO₂. The second-order rate constant for the hydrolysis was evaluated as 3.09×10^8 L/mol s. The order of reaction relative to ClO₂⁻ was derived unity for the chlorite concentration greater than 1.0 molar. The third-order rate constant for the oxidation was derived as 7.32×10^8 (L/mol)²/s at [NaOH]=0.20 molar. For the absorption of NO, there appears a gradual jump in absorption rate at the interfacial concentration of NO ranging from 5×10^{-7} to 2×10^{-6} mol/L. Above this transition region, the order of reaction in NO approaches 2, whereas below the transition region, the order of reaction becomes unity.

Introduction

More than 90 percent of the nitrogen oxides(NO_x) emitted from stationary combustion facilities is nitrogen monoxide. In order to effectively remove NO_x by wet scrubbing methods it is desirable to oxidize NO to NO₂ in either gas or liquid phase, because the physical solubility of NO in aqueous absorbent is much smaller than that of NO₂. With respect to wet scrubbing with liquid-phase oxidation, the alkaline solution of NaClO₂ as well as the alkaline solution of KMnO₄ have been found to be a practically promising absorbent for NO. not only from the standpoint of the degree of NO removal but also the chemical absorption mechanism, the process of absorption with liquid-phase oxidation has been assessed and analyzed (Teramoto et al., 1976a and 1976a, Sada et al., 1977).

In our previous paper (Sada et al., 1978a), the absorption of NO in aqueous mixed solutions of NaClO₂

and NaOH was performed using a semi-batch stirred vessel with a plane gas-liquid interface at 25°C and atmospheric pressure. The rate of absorption was analyzed on the basis of chemical absorption theory under the fast-reaction regime. The overall reaction involved was found to be second-order in NO and first-order in NaClO₂ in the range of NaClO₂ concentration greater than 0.8 molar. The reaction rate constants evaluated were exponentially decreased with the NaOH concentration and correlated by $k = k_0 \exp(-3.73 [\text{NaOH}])$.

But in our previous work, the gas-phase composition of solute gas (NO) was restricted to percent-order of magnitude. The concentration of NO in the flue gases from stationary combustion sources is generally less than several hundred ppm. Therefore, it is necessary to discuss the absorption mechanism of such lean NO by oxidative absorbents.

The present work was undertaken to establish the chemical absorption mechanism of such lean NO as encountered in the flue gases. To this end, the absorp-

This paper has been published in I & E C Proc. Des. Develop., 275, 18 (1979).

*京都大学 工学部

tion of NO in aqueous mixed solutions of NaClO₂ and NaOH was carried out using the stirred vessel with a plane gas-liquid interface. Moreover, to obtain kinetic information on the second step reaction in the reaction between NO and aqueous mixed solution of NaClO₂ and NaOH ($2\text{NO} + \text{ClO}_2^- \rightarrow 2\text{NO}_2 + \text{Cl}^-$ (I), $4\text{NO}_2 + \text{ClO}_2^- + 4\text{OH}^- \rightarrow 4\text{NO}_3^- + \text{Cl}^- + 2\text{H}_2\text{O}$ (II)), the absorption of lean NO₂ was performed into the same absorbent.

Experimental

All experimental runs were using a stirred vessel with a plane gas-liquid interface at 25°C and 1 atm. The absorber used (I.D.=80mm, Liquid volume=500cm³) is the same one as in our previous work (Sada et al., 1978a). The absorber was operated continuously with respect to the gas phase and batch-wise with respect to the liquid phase. The stirring speeds of liquid phase and gas phase stirrers were kept at 162 and 500 rpm, respectively.

Solute gas NO or NO₂ was supplied from cylinder of 1% concentrated by N₂. Both these gases were further diluted with N₂ to the desired concentration. All the inlet and outlet gas-phase compositions were determined by UV derivative spectrophotometer analyzer (Yanaco UO-1 derivative spectrophotometer). The absorption rate was calculated from the difference between inlet and outlet gas-phase composition and total flow rate.

Further details for experimental apparatus and procedure can be found elsewhere (Sada et al., 1978a).

Experimental Results and Discussion

Liquid-Side Mass Transfer Coefficient. In order to convert experimental absorption rates to the enhancement factors, the liquid-side mass transfer coefficient is required. In the previous work (Sada et al., 1978b), the liquid-side mass transfer coefficient k_L^0 was determined by the physical absorption of pure N₂ O into under various liquid-phases stirring speeds n_L and correlated to n_L as $k_L^0 = 9.89 \times 10^{-5} n_L^{0.65}$ (where n_L ranged from 60 to 280 rpm). The coefficient for NO_x, k_{L1}^0 was predicted by a correlation

$$k_{L1}^0 (D_1/D_{\text{N}_2\text{O}-\text{H}_2\text{O}})^{2/3} \quad (1)$$

as in the previous paper (Sada et al., 1978b).

The gas-phase resistance was estimated to be less than 7% of the total resistance by the empirical correlation given by Hikita et al. (1975).

NO₂-NaClO₂/NaOH System. The reaction between NO₂ and ClO₂⁻ in an alkaline solution is considered to be



and corresponds to the second-step reaction in the reaction of NO with the same liquid-reactant. The reaction involved is assumed m-th order relative to NO₂ and n-th order relative to ClO₂⁻. When the process of chemical absorption lies under the fast-reaction regime, the absorption rate NO₂ can be derived as

$$N_{A2} = \sqrt{\frac{2}{m+1}} k C_{B0} C_{A2i}^{m+1} D_{A2} \quad (2)$$

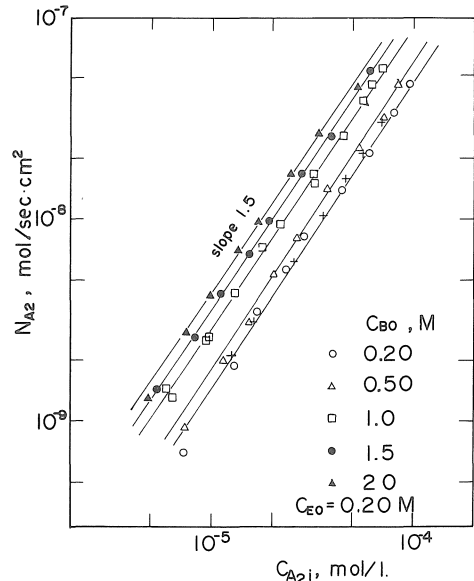


Fig. 1. Relationship between N_{A2} and C_{A2i} for NO₂-NaClO₂/NaOH system. Effect of [NaClO₂] on N_{A2} .

In Figure 1, the absorption rate of NO₂, N_{A2} , is plotted against the interfacial concentration of NO₂, C_{A2i} . The interfacial concentration of NO₂ can be converted from the physical solubility and the gas phase concentration at the interface. The physical solubility of NO₂ in aqueous mixed solutions of NaClO₂ and NaOH was calculated from the correlation (Onda et al., 1970):

$$\log(\alpha/\alpha_w) = -(K_B I_B + K_E I_E) \quad (3)$$

where K_B and K_E are the salting-out parameters for the electrolytes B (NaClO₂) and E (NaOH), respectively and depend on the ion species and gas present. The contribution of NO₂ to the salting-out parameter, however, is not available in the literature.

* The raw data on absorption rates have been stored and can be prevailed in response to request by the authors.

Here the contribution of NO_2 , X_{g_1} is assumed same as that of N_2O . The physical solubility of NO_2 in water was evaluated from the equilibrium concentration reported by Andrew and Hanson (1961). Then, the Bunsen absorption coefficient α_w of NO_2 in water was calculated to be 0.914 at 25°C .

Figure 1 shows that there is a linear relationship between $\log N_{A2}$ and C_{A21} with a slope of 1.5. The enhancement factors evaluated from the data falling on the straight lines are ranged from 60 to 450 with an increase in the chlorite concentration. Whereas the value of C_{B0}/C_{A21} is varied from 2×10^3 to 4×10^5 . So the data on the straight lines are belived

under the fast-reaction regime of pseudo-mth-order. Therefore, the order of reaction in NO_2 is determined as 2. The crosses in this figure denote data with absorption of NO_2 in water. The relationship between $\log N_{A2}$ and $\log C_{A21}$ also gives a stright line with a slope of 1.5 and the order of reaction (hydrolysis) with respect to NO_2 is determined as 2. For the hydrolysis of NO_2 ($2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$), the secondor der rate constant is derived as 3.09×10^8 L/mols from eq 2. In addition, it can be seen from the figure that for lower concentration of NaClO_2 , the hydrolysis predominates over the oxidation. Here, in order to calculate the second-order rate constant k_{hyd} from eq 2, the diffusivity of NO_2 in aqueous mixed solutions of NaClO_2 and NaOH was required. The reduction of the diffusivity of NO_2 in the aqueous mixed solutions was assumed as observed redustion in N_2O diffusivity. That is, NO_2 diffusivity under consideration was estimated by

$$(D/D_w)_{\text{NO}_2} = (D/D_w)_{\text{N}_2\text{O}} \quad (4)$$

as proposed by Joosten and Danckwerts (1972). The diffusivity of N_2O in the aqueous mixed solutions was obtained in the previous work (Sada et al., 1978c) and the diffusivity of NO_2 in water was assumed to be equal to that of N_2O_4 , which was available in the literature (Kramers et al., 1961).

The absorption of NO_2 into water has been extensively investigated (for example, Sherwood, Pigford and Wilke, 1975), but the gas-phase concentration of NO_2 has been restricted to percent-order of magnitude, so that coexisting N_2O_4 in the gas phase would have an important role in the hydrolysis of NO_2 .

In general, both the hydrolysis and the oxidation are considered to proceed in parallel and thus, eq 2 should be rewritten by

$$N_{A2} = \sqrt{\frac{2}{m+1} (k_{hyd} + kC_{B0}^m) C_{A21}^{m+1} D_{A2}} \quad (5)$$

On the basis of above experimental evidence, the dependence of C_{B0} on $N_{A2}/\sqrt{C_{A21}^3 D_{A2}}$ and $N_{A2}^2/(C_{A21}^3$

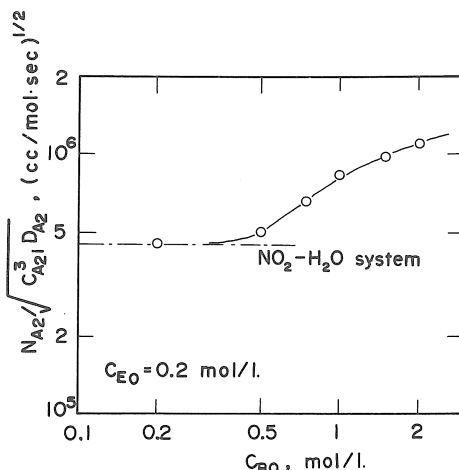


Fig. 2. Effect of $[\text{NaClO}_2]$ on $N_{A2}\sqrt{C_{A21}^3 D_{A2}}$ for NO_2 - $\text{NaClO}_2/\text{NaOH}$ system.

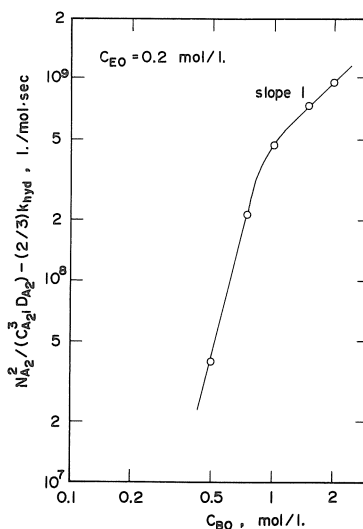


Fig. 3. Effect of $[\text{NaClO}_2]$ on $N_{A2}^2/(C_{A21}^3 D_{A2}) - (2/3)k_{hyd}$.

$D_{A2}) - (2/3) k_{hyd}$ were assessed. As a result, Figures 2 and 3 were obtained. From these figures, following information can be derived: When the chlorite concentration is lower than 0.2 molar, the accompanying reaction is dominated by the hydrolysis. In this case, the absorbent contains 0.2 molar NaOH , but the neutralization with NaOH can be neglected in comparison with the hydrolysis. Figure 3 indicates that for C_{B0} greater than 1.0 molar, there appears a linear relationship with a slope of unity. Hence for such high concentrations of NaClO_2 , the oxidation is the first-order with respect to NaClO_2 . The third-order ((2.1)th order) rate constant k can be calculated by eq 5 with an estimate of k_{hyd} . The averaged value of k was 7.32×10^8 (L/mol) $_2$ /s. For the chlorite concentration ranging from 0.5 to 1.0 molar, the dependence of C_{B0}

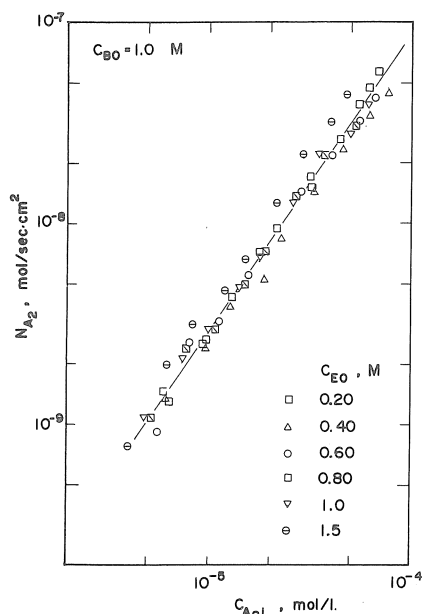


Fig. 4. Relationship between N_{A2} and C_{A2i} for NO_2 - $\text{NaClO}_2/\text{NaOH}$ system. Effect of $[\text{NaOH}]$ on N_{A2} .

on $N_{A2}^2 / (C_{A2i}^3 D_{A2}) - (2/3) k_{hyd}$ was very high and no simple relationship between these two quantities could be derived.

The influence of alkaline concentration on the rate of absorption was investigated at a constant chlorite concentration equal to 1.0 molar. The concentration of NaOH was varied from 0.2 to 1.5 molar. Experimental results were shown in Figure 4 as a plot of N_{A2} vs C_{A2i} . The second-order dependence on NO_2 (that is, slope 1.5) at different NaOH concentrations, on one hand, remains unchanged. On the other hand, apparent rate has a minimum value at a certain NaOH concentration. Assuming that the prevailing reaction is regarded as second-order in NO_2 , the effect of the NaOH

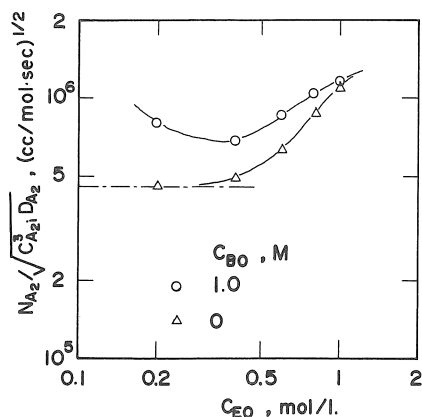
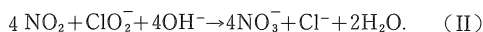
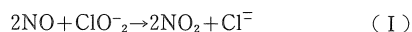


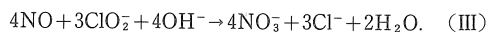
Fig. 5. Effect of $[\text{NaOH}]$ on $N_{A2} / \sqrt{C_{A2i}^3 D_{A2}}$.

concentration on the absorption rate was calculated. As a result, Figure 5 was obtained. For the sake of comparison, experimental data with NO_2 - NaOH system were plotted in the same figure. It is known that the oxidative power of the chlorite increases with decreasing the pH value of the solution (Sada et al., 1978a). For the NaOH concentration smaller than 0.4 molar, the absorption rate in Figure 4 decreases with the NaOH concentration, which corresponds to the slowing down of the rate of oxidation with increasing the NaOH concentration. Whereas it can be seen from comparison with data on NO_2 - NaOH system that the neutralization with NaOH would play an important role in the absorption for the NaOH concentration greater than 0.6 molar.

NO - $\text{NaClO}_2/\text{NaOH}$ System. The reaction NO and ClO_2^- in an alkaline solution is considered to be (Sada et al., 1978a)



The overall reaction reduces to



In our previous paper (Sada et al., 1978a), assuming that the chemical reaction is regarded as m -th order in NO and n -th order in ClO_2^- the absorption process was analyzed on the basis of the theory of absorption with (m,n) th order reaction, where the gas-phase concentration of NO , however, was restricted from 0.5 to 15 vol%. In the present experiment, such lean NO as encountered in the flue gases was absorbed into aqueous mixed solutions of NaClO_2 and NaOH . Observed absorption rate of NO , N_{A1} , was plotted against corresponding interfacial concentration of NO , C_{A1i} , in Figure 6. That concentration of NaClO_2 , C_{BO} , was varied from 0.25 to 2.0 molar, while the concentration of NaOH was maintained at 0.10 molar. A group of straight lines (lines 1-5) with slope of 1.5 in the same figure represents the experimental results for high NO concentration with percent-order of magnitude, which was obtained in the previous paper (Sada et al., 1978a). The experimental results for lower NO concentrations do not fall on extended lines from lines 1-5. When the concentration of NaClO_2 , C_{BO} , is 1.5 and 2.0 molar, the slope of the relation of $\log N_{A1}$ vs $\log C_{A1i}$ is varied from 1.5 to 1.0 with decreasing C_{A1i} . This implies that the order of reaction relative to NO changes from 2 to 1. When C_{BO} becomes lower than 1.0 molar, there appears some gradual jump in absorption rate within the interfacial concentrations ranging from 5×10^{-7} to 2×10^{-6} mol/L. Above this transition region, experimental rates gradually approach the upper lines. Below the transition region, the slope of plotted relations decreases from unity to slightly less

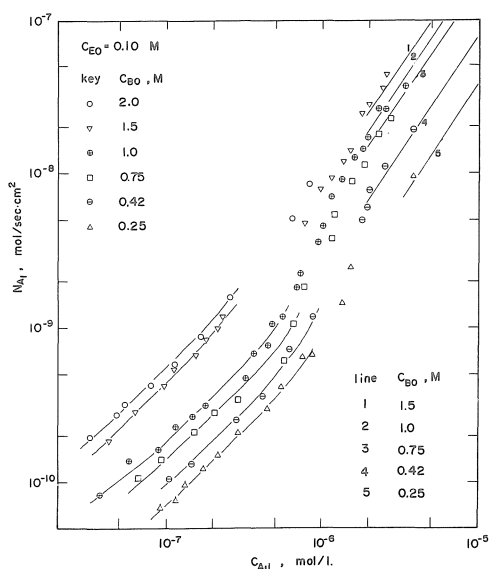


Fig. 6. Dependence of C_{A11} on N_{A1} for NO- $\text{NaClO}_2/\text{NaOH}$ system.

with decreasing C_{A11} . Therefore, the order of reaction in NO is close to unity. The increase of absorption rate in the transition region may be due to the presence of some intermediate species with more oxidative than ClO_2^- . Thus, the problem in the near future would lie in identifying the liquid-phase components.

Concluding Remarks

The absorption rate of lean NO_x in aqueous mixed solutions of NaClO_2 and NaOH was measured using a semibatch stirred vessel with a plane gas-liquid interface at 25°C and 1 atm. The rate of NO_2 absorption was interpreted under the fast reaction regime. The reaction prevailed was found to be the parallel reactions involving oxidation and hydrolysis, and to be second-order with respect to NO_2 . The second-order rate constant for the hydrolysis was evaluated as 3.09×10^8 L/mol s. The order of reaction relative to ClO_2^- was derived unity for the chlorite concentration greater than 1.0 molar. The third order rate constant for the oxidation was derived as 7.32×10^8 (L/mol)²/s at $[\text{NaOH}] = 0.2$ molar. The effect of the NaOH concentration on the absorption rate becomes significant because of the neutralization as the concentration exceeds 0.6 molar.

For the absorption of NO, there appears a gradual jump in absorption rate at the interfacial concentration of NO ranging 5×10^{-7} to 2×10^{-6} mol/L, when the chlorite concentration is lower than 1.0 molar. Above this transition region, the order of reaction in NO approaches 2 as previously derived. Below the transition region, the order of reaction in NO changes from unity to slightly less. When the chlorite concentration

is higher than 1.0 molar, the order of reaction in NO continuously varies from 2 to 1 with a decrease in the interfacial concentration of NO.

Nomenclature

- C = concentration in the liquid phase, mol/L or M
- D = diffusivity in the liquid phase, cm²/s
- I = ionic strength, g-ion/L
- K = salting-out parameter, L/g-ion
- k = second-order rate constant of hydrolysis of NO_2 , L/mol s
- k_{hyd} = second-order rate constant of hydrolysis of NO_2 , L/mol s
- k_L = liquid-side mass transfer coefficient, cm/s
- m = order of reaction relative to absorbing gas
- N = absorption rate, mol/s cm²
- n = order of reaction relative to liquid-phase reactant
- n_L = stirring speed in the liquid phase, rpm

Greek Letter

- α = Bunsen absorption coefficient, cm³-gas/cm³-solution

Subscripts

- A₁ = absorbing gas (NO)
- A₂ = absorbing gas (NO_2)
- B = liquid-phase reactant B (NaClO_2)
- E = liquid-phase reactant E (NaOH)
- i = gas-liquid interface
- w = water
- O = initial value

Superscript

- = without reaction

Literature Cited

Andrew, S.P.S., Hanson, D., Chem. Eng. Sci.,14,105 (1961).
 Hikita, H., Asai, S., Ishikawa, H., Y., Chem. Eng. Sci., 30,607 (1975) .
 Joosten, G.E.H., Danckwerts, P.V.,J.Chem. Eng. Data, 17, 452 (1972) .
 Kramers,H., Blind, M.P.P., Snoeck, E., Chem. Eng. Sci.,14, 115 (1976) .
 Onda,K., Sada, E., Kobayashi, T., Kito,S.,J. Chem. Eng. Japan, 3,137 (1970) .
 Sada, E., Kumazawa,H., Hayakawa, N., Kudo,I., Kond, T., Chem. Eng. Sci.,23, 1171 (1977) .
 Sada, E., Kumazawa,H., Kudo, I., Kondo, T., Chem. Eng. Sci.,33, 315 (1978a) .

Sada, E., Kumazawa, H., Tsuboi N., I., Kudo, T., Ind. Eng. Chem. Proc. Des. Dev., 17, 321 (1978b) .
Sada, E., Kumazawa, H., Yamanaka, Y., Kudo, I., Kondo, T., J. Chem. Eng. Japan, 11, 276 (1978c) .
Sherwood, T.K., Pigford, R-L., Wilke, C. R., "Mass Transfer" , p.354, McGraw-Hill, New York N.Y., 1975.
Teramoto, M., Ikeda, M., Teranishi, H., Kagaku

Kogaku Ronbunshu 2, 86 (1976a) .
Teramoto, M., Ikeda, M., Teranishi, H., Kagaku Kogaku Ronbunshu, 2, 637 (1976b) .
This work was supported by the Science Research Foundation of Ministry of Education, Japan, Grant No. 147099. The authors wish to acknowledge the support leading to the publication of this article.

(Received January 16, 1980)