CHEMISTRY LETTERS, pp. 1397-1400, 1987.

Rate of Heterogeneous Photocatalytic Oxidation of NO_2^- in Cloud Water Droplets. Estimated for Hypothetical Environmental Conditions

Yoshio HORI* and Shin SUZUKI
Department of Synthetic Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260

Rates of heterogeneous photooxidation of NO_2^- were measured in aqueous suspension of TiO_2 (anatase), TiO_2 (rutile), and ZnO under illumination. The reaction proceeds in zero order with respect to NO_2^- concentration. The rates were estimated for cloud water droplets in hypothetical environmental conditions. The rate amounts to 11% h^{-1} for cloud water content of 0.2 g m^{-3}.

Nitric acid is one of major components of acid rain water. Nitric acid is derived from nitrogen oxides in atmospheric air by some oxidation process. NO_2^- is formed in the dissolution of NO and NO_2 into water, $2NO_2 + H_2O = NO_2^- + NO_3^- + 2H^+$ and $NO + NO_2 + H_2O = 2NO_2^- + 2H^+$. However, the concentration of nitrous acid in natural rain water is much lower than that of nitric acid.[1)] NO_2^- may possibly be oxidized to NO_3^- in water droplets in the atmosphere. But the rate of oxidation of NO_2^- by O_2 in water is, as is well known, very low without any catalyst at ambient temperature.

Airborne particulate substances contain various metal oxides. Ibusuki has emphasized importance of heterogeneous reactions of air pollutants in atmospheric air.[2)] Martin evaluated the rate of oxidation of SO_2 in aqueous suspension of carbonaceous particles under hypothetical environmental conditions[3)] on the basis of the experimental results by Brodzinsky et al.[4)] Some metal oxides contained in airborne particulates are active in heterogeneous photocatalytic reactions. For example, these particulate substances obtained from some urban areas contain 1 to 4% of semiconductor particles, such as ZnO, PbO, TiO_2, and Fe_2O_3.[5)] A few papers reported heterogeneous photocatalytic reactions of air pollutants.[6)] We also indicated in previous papers that NO in gas phase and NO_2^- in water are photocatalytically oxidized in the presence of semiconductor particles under illumination.[7)] This communication briefly describes the rates of photocatalytic oxidation of NO_2^- experimentally obtained in water and an evaluation of the rate in cloud water droplets under hypothetical environmental conditions. There has been no report with respect to estimation of photocatalytic contribution to air pollution reactions under environmental conditions.

A Pyrex reactor, equipped with a quartz window (44 mm diameter), was employed for the experiments. The reactor contained 200 ml of $NaNO_2$ solution with 0.2 g of catalyst powder kept in suspension by a magnetic stirrer. The aqueous suspensions were maintained at 20 °C by circulation of water in a glass tube (8 mm i. d.) installed in the reactor from a constant temperature bath. The reactor was illuminated by a 400 W high-pressure mercury lamp (Toshiba H400). The mercury lamp, jacketed with an optical glass tube, emitted photons of wave length longer than ca. 300 nm. A gas mixture of purified N_2 (80%) and O_2 (20%) was introduced to the reactor, bubbled through the aqueous suspension. Photon intensity was measured by a chemical actinometer of iron (III) oxalate. Two milliliter aliquots of the aqueous suspensions were taken from the reactor during the reaction at appropriate time intervals. The aliquots were analyzed after filtration for the concentrations of NO_2^- and NO_3^- by an ionchromatograph (Toyo Soda). The catalyst powders employed were TiO_2 (anatase, 99.99%), TiO_2 (rutile, 99.99%), and ZnO (99.99%). They were purchased from Furuuchi Kagaku Co. Ltd. TiO_2 (rutile) purchased from Wako Junyaku Co. Ltd. was also examined. The water was doubly distilled after deionization.

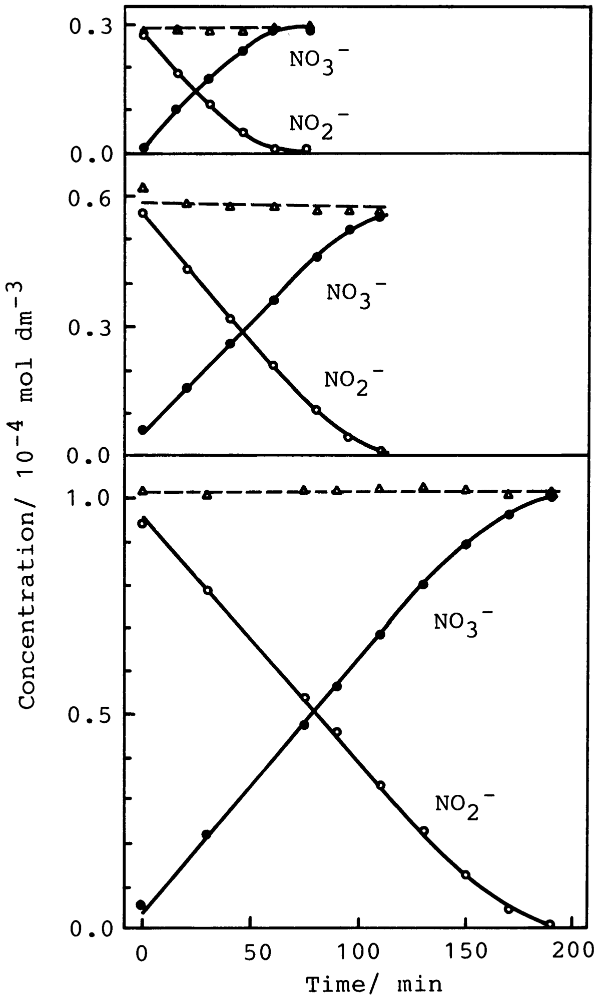

Fig. 1. Time course of heterogeneous photocatalytic oxidation of various concentrations of NO_2^- in the presence of TiO_2(anatase). The sums of NO_2^- and NO_3^- are shown (—▲——▲—).

Figure 1 illustrates time courses of photocatalytic oxidation of various concentrations of NO_2^- in aqueous suspensions of TiO_2 (anatase). NO_2^- was oxidized to NO_3^- quantitatively; the sums of NO_2^- and NO_3^- remained constant during the reaction. The rates of the reaction are nearly equal for three different initial concentrations of NO_2^-. The rates remain constant until NO_2^- concentration decreases below 0.1×10^{-4} mol dm^{-3}. These experimental facts indicate that the reaction proceeds in zero order with respect to NO_2^- concentration. The identical features were observed for ZnO and TiO_2 (rutile) from Furuuchi Kagaku, whereas TiO_2 (rutile) from Wako Junyaku did not show any photocatalytic activity. The rates of oxidation by these catalyst powders are shown in Table 1.

Electrochemical measurements were conducted with TiO_2 thin film coated electrodes prepared from the TiO_2 (anatase) powder used in the present photocatalytic reactions. The experimental results suggested that NO_2^- would be oxidized by some oxygen-containing active species such as HO_2^- and $\cdot OH$, which would be produced in oxidation of H_2O by positive holes formed in the valence band of semiconductor particles by illumination. The concentration of NO_2^- would be relatively much higher than that of HO_2^- or $\cdot OH$. Hence, the reaction will proceed in zero order with respect to the concentration of NO_2^-. O_2 will scavenge the electrons in the conduction band of semiconductor particles. The details of the electrochemical and the kinetic studies as well as the difference of the photocatalytic activities of two rutiles will be discussed elsewhere.8)

The rate does not depend upon the amount of catalyst powders over 0.15 g. Thus the incident photons to the reactor would be totally absorbed by the catalyst powders. We confirmed by using a set of color filters that the oxidation of NO_2^- in TiO_2 (anatase) and ZnO suspension proceeds with band-gap irradiation (wave length shorter than 400 nm for TiO_2 (anatase)). Photon intensity was approximately 5.8×10^{16} quanta cm^{-2} s^{-1} for wave length shorter than 525 nm under the experimental conditions.9) One can thus estimate the photon intensity effective for the excitaion of TiO_2 (the wave length shorter than 400 nm) on the basis of emission spectra of a high-pressure mercury lamp.10) The value was ca. 2.3×10^{16} quanta cm^{-2} s^{-1}, close to the solar radiation of the wave length shorter than 400 nm outside the troposphere.11) By assuming that two electrons are involved in the reaction, the quantum efficiency of 0.7% is obtained for TiO_2 (anatase). The identical procedure gives the quantum efficiency of 0.4% for ZnO.

One can evaluate the rate of photocatalytic oxidation of NO_2^- in cloud water droplets by photoactive semiconductor particles under hypothetical environmental conditions. The following conditions are assumed. The concentration of photoactive particles is x ($g\ m^{-3}$) suspended in environmental air. The particles are spherical with uniform diameter 2r (cm) and specific denstiy d ($g\ cm^{-3}$). The cross sectional area s ($cm^2\ m^{-3}$) is thus 3x/4rd for the absorption of solar radiation per unit atmospheric air. The rate of oxidation of NO_2^- is v ($mol\ cm^{-2}\ s^{-1}$) per unit cross sectional area of catalyst for irradiation. All these particles would be contained in cloud water droplets as condensation nucleus in environmental conditions. The concentration of NO_2^- in cloud water is c ($mol\ l^{-1}$), and the cloud water content is q ($g\ m^{-3}$). Thus the rate of oxidation of NO_2^-, R ($\%\ h^{-1}$), is

$$R = (sv)(3600)(100)/cq(10^{-3}) = (2.7 \times 10^8)(xv/rd)(1/cq).$$

The following values are assumed for the parameters in reference to environmental measurement data reported in literatures.1,5) The total concentration of airborne suspended substance is 1×10^{-4} $g\ m^{-3}$, in which 0.2% of TiO_2 and 1% of ZnO are contained. The diameter of particles is 0.5×10^{-6} m ($r = 0.25 \times 10^{-4}$ cm), and $c = 1 \times 10^{-4}$ $mol\ dm^{-3}$. v is calculated from the rates of NO_2^- photooxidation (Fig. 1 and so on) divided by the area of the quartz window of the reactor. For example, v is obtained for TiO_2(anatase) by using the following values; the rate of NO_2^- photooxidation as obtained from the slopes of the straight lines of Fig. 1, 0.59×10^{-6} $mol\ dm^{-3}\ min^{-1}$, the volume of the reactor 0.2 dm^3, the radius of the quartz window 2.2 cm.

$$v = (0.59 \times 10^{-6})(0.2)/(60)(3.14)(2.2)^2 = 1.29 \times 10^{-10}\ mol\ s^{-1}\ cm^{-2}.$$

R is thus numerically calculated for TiO_2 (anatase) and ZnO with q as a parameter and tabulated in Table 1. The sum of the rates due to TiO_2 and ZnO amounts to 11%

Table 1. Estimated rates of heterogeneous photocatalytic oxidation of NO_2^- in cloud water droplets by semiconductor particles contained in hypothetical airborne particulate substance

	Density, d/ g cm^{-3}	Concentration, x/ g m^{-3}	Rate per cross sectional area, v/ mol cm^{-2} s^{-1}	Cloud water content, q/ g m^{-3}	Estimated rate, R/ % h^{-1}
TiO_2 (anatase)	3.8	0.2×10^{-6}	1.29×10^{-10}	0.2	3.7
				0.5	1.5
				1.0	0.7
TiO_2 (rutile)			0.96×10^{-10}		
ZnO	5.6	1.0×10^{-6}	0.79×10^{-10}	0.2	7.6
				0.5	3.0
				1.0	1.5

Diameter of the particle: 0.5×10^{-4} cm.
Concentration of NO_2^-: 1×10^{-4} mol l^{-1}.

for cloud water content 0.2 g m^{-3}. Although the conditions are hypothetical, the values are still remarkably high for oxidation of NO_2^-. More detailed investigations with natural airborne dusts, soil, or fly ash are needed for the determination of actual contribution of this reaction to the acid rain formation.

The authors thank Mrssrs. Akira Bandoh, Yasushi Shimada, and Tohru Suganuma for their assistance in experimental works. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 60550564 from the Ministry of Education, Science and Culture.

References

1) M. Tamaki, T. Hiraki, and H. Watanabe, Taiki Osen Gakkaishi, 20, 71 (1985).
2) T. Ibusuki, Taiki Osen Gakkaishi, 22, 1 (1987).
3) L. R. Martin, "SO_2, NO, and NO_2 Oxidation Mechanisms: Atmospheric Considerations," ed by J. G. Calvert, Butterworth Publishers (1984), p.63.
4) R. Brodzinsky, S. G. Chang, S. S. Markowitz, and T. Novakov, J. Phys. Chem., 84, 3354 (1980).
5) A. Mizohata, Y. Matsuda, K. Sakamoto, and S. Kadowaki, Taiki Osen Gakkaishi, 21, 83 (1986); T. Mamuro, A. Mizohata, and T. Kubota, ibid., 14, 296 (1979); S. Iwamoto, A. Utsunomiya, R. Ishibashi, and H. Mutoh, ibid., 20, 286 (1985).
6) Summarized and reviewed by T. Ibusuki in Ref. 2.
7) Y. Hori, A. Nakatsu, and S. Suzuki, Chem. Lett., 1985, 1429; Y. Hori, K. Fujimoto, and S. Suzuki, ibid., 1986, 1845.
8) Y. Hori, A. Bandoh, A. Nakatsu, and S. Suzuki, to be published.
9) The quantum yield of the chemical actinometer was assumed to be unity for the wave length shorter than 525 nm for approximation.
10) J. F. Rabek, Experimental Methods in Photochemistry and Photophysics, Part 1, John Wiley & Sons (1982).
11) F. S. Johnson, J. Meteorol., 11, 431 (1954).

(Received March 23, 1987)