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Reactivity of Electrons Produced in Gamma-Irradiated Zeolite Toward Several Electron Scavengers

Chiyoko NAKAZATO* and Takahiro MASUDA
Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Fukasawa, Setagaya-ku, Tokyo 158
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Relative rates of reaction of electrons produced in gamma-irradiated zeolite (Molecular Sieve 13X) with several electron scavengers were determined by competition kinetics using dinitrogen monoxide as a reference compound. A part of the electrons produced in irradiated zeolite have been disclosed to be quasi-free from the feature of their reactivity toward electron scavengers that the reactivity is similar to that of quasi-free electrons found in irradiated liquid 2,2-dimethylpropane. An analysis based on competition kinetics has provided a value 9.8×10^{12} dm^3 mol^{-1} s^{-1} as the lower limit on the rate constant for the reaction of quasi-free electrons with positive holes produced in irradiated zeolite.

A compound adsorbed on the surface of a solid is radiolyzed through a reaction induced by excitation energy transferred from an irradiated solid[1-6] and formation of electron and positive hole has been investigated by ESR or product analysis using electron or hole scavengers.[7-15] A synthesized zeolite, Molecular Sieve 13X, is an interesting adsorbent because of its highly ordered structure and large capacity of adsorption. The solid can be taken as an immobile solvent if the size of an adsorbate is small enough to enter a supercavity of zeolite. Reactions occurring in the system are considered approximately as those in solution, and kinetics used for reactions in solution will be applicable. The property of electrons produced in a solid insulator such as zeolite is interesting in connection with its reactivity. The present study was carried out to clarify the property and reactivity of electrons generated in irradiated zeolite. By using several electron scavengers and adopting kinetics for reactions in solution, it has been found that at least two kinds of electrons react with adsorbates, one showing a reactivity toward a series of electron scavengers similar to that of quasi-free electrons produced in liquid 2,2-dimethylpropane.[16,17]

Experimental

Zeolite (Molecular Sieve 13X; abbreviated to MS) was obtained from Nippon Kuromatokogyo K. K. The specific surface area is 1030 m^2 g^{-1}. Dinitrogen monoxide, sulfur hexafluoride, and methyl chloride were purchased from Takachiho Kagakukogyo K. K. Carbon tetrachloride and trichloroethylene were of spectrograde from Merck. Ethyl bromide was obtained from B. D. H.

About 12 g of MS was degassed in a quartz vessel at 600 °C for 24 h under a pressure below 10^{-3} Pa and divided to six ampules attached to the vessel in ca. 2 g each. A scavenger was introduced into the ampules through breakable seals with a vacuum line. After standing for 24 h, the ampules were irradiated by ^{60}Co gamma rays to a total dose of 1.34×10^4 Gy. The amount of molecular nitrogen formed from dinitrogen monoxide was determined by gas chromatography. Calculation for kinetic analysis was carried out with the aid of microcomputer PC-8001 (Nippon Electric Co.).

Results and Discussion

Formation of Molecular Nitrogen from MS–N_2O System. As shown in Fig. 1a, the G-value for formation of molecular nitrogen, $G(N_2)$, increases with increasing amount of N_2O introduced into an ampule and approaches a limiting value 2.8 at approximately 5×10^{-5} mol of N_2O per g of MS. The nitrogen formation is explained in terms of the reactions

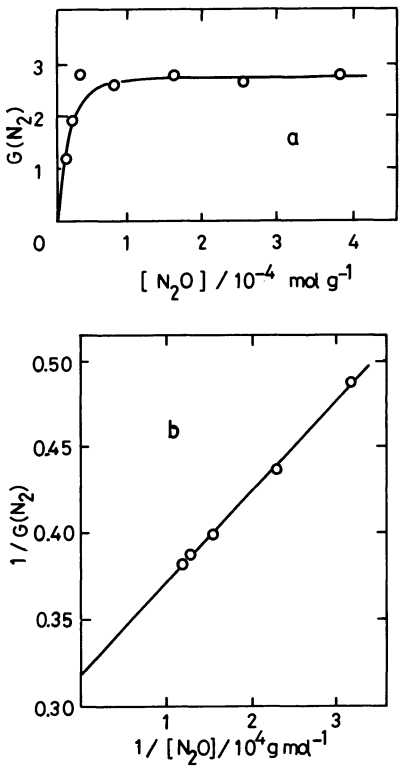

Fig. 1. a. Dependence of $G(N_2)$ on adsorbed amount of N_2O. Dose, 1.34×10^4 Gy. b. Competition plots of $1/G(N_2)$ vs. $1/[N_2O]$.

$$MS \rightsquigarrow MS^+ + e^-, \quad (1)$$

$$e^- + MS^+ \longrightarrow MS^*, \quad (2)$$

$$e^- + N_2O \longrightarrow N_2 + O^-_{ad}, \quad (3)$$

where MS^+ denotes a positive hole produced in γ-irradiated MS. From these reactions, we have

$$1/G(N_2) = 1/G_e(1+k_2[MS^+]/k_3[N_2O]). \quad (I)$$

Plotting $1/G(N_2)$ vs. $1/[N_2O]$ gave a straight line as shown in Fig. 1b, for which the observed values in Fig. 1a were not used for the plotting but the values obtained from the curve were used. Thus, a slope of 5.30×10^{-6} and an intercept of 0.32 were obtained with a correlation coefficient of 0.9988. G_e can be calculated from the intercept as 3.1, which agrees with the limiting $G(N_2)$, 2.8, within an experimental error. The slope will give k_2/k_3 if $[MS^+]$ can be estimated properly. Essentially the concentration of positive hole, $[MS^+]$, should be expressed by a steady state concentration but the estimation is very difficult. A lower limit of k_2/k_3, however, can be evaluated if the total concentration of positive hole produced in MS during irradiation is used as $[MS^+]$ instead of the steady state concentration. The total concentration of MS^+ can be calculated from G_e and the total dose by assuming $G_e=G(MS^+)$. In the present experimental conditions, it is 3.9×10^{-6} mol g^{-1} and hence 4.2 is obtained as k_2/k_3. If it is assumed that the rate constant for the reaction of quasi-free electron with N_2O in liquid 2,2-dimethylpropane, 2.3×10^{12} dm^3 mol^{-1} s^{-1}, is applicable to k_3, the lower limit of the rate constant for the reaction of electron with positive hole in MS is 9.8×10^{12} dm^3 $mol^{-1}s^{-1}$. Sulfur hexafluoride is known to react with quasi-free electron with the rate constant of 1.98×10^{14} dm^3 mol^{-1} s^{-1} in liquid 2,2-dimethylpropane[17] and the electron produced in γ-irradiated MS was found to react with SF_6 85 times as fast as with N_2O, as described below. The positive hole in MS is thought to have at least the same reactivity as SF_6. The steady state concentration of MS^+, therefore, would be less than 1.9×10^{-7} mol g^{-1}.

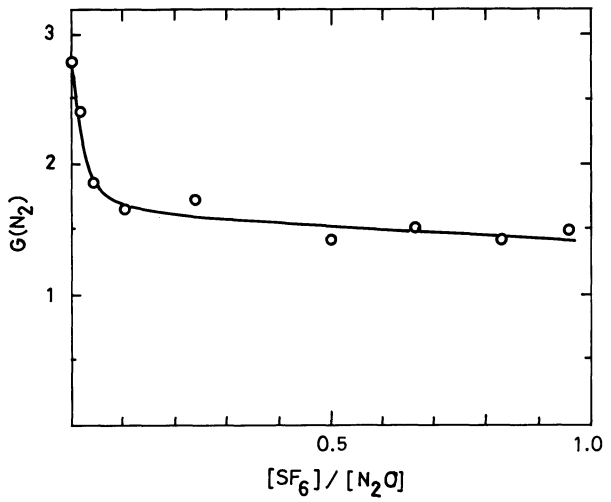

Fig. 2. Decrease in $G(N_2)$ in the presence of SF_6. $[N_2O]$, 4×10^{-4} mol g^{-1}.

Competition between N_2O and a Second Scavenger toward Electron Produced in MS. Addition of a second scavenger gives rise to decrease in the yield of molecular nitrogen formed from N_2O in irradiated MS. In Fig. 2, an effect of SF_6 on $G(N_2)$ is shown. The decrease in $G(N_2)$ is understood in terms of the competition between Reactions 3 and 4:

$$e^- + S \longrightarrow S^- \text{ or product(s)}, \quad (4)$$

where S denotes an electron scavenger added to the system as a competitor of N_2O such as SF_6. The competition kinetics is expressed by

$$1/\Delta G(N_2) = 1/G_e(1+k_3[N_2O]/k_4[S]), \quad (II)$$

where $\Delta G(N_2)$ is the difference of $G(N_2)$ between those observed in the absence and presence of the second scavenger, and G_e is the primary yield of electrons for which N_2O and the second scavenger compete with each other. As shown in Fig. 3, plots of $1/\Delta G(N_2)$ vs. $[N_2O]/[S]$ give a straight line. The relative reactivity of S to N_2O is obtained from the slope of the straight line. Results obtained for several electron scavengers are summarized in Table 1,

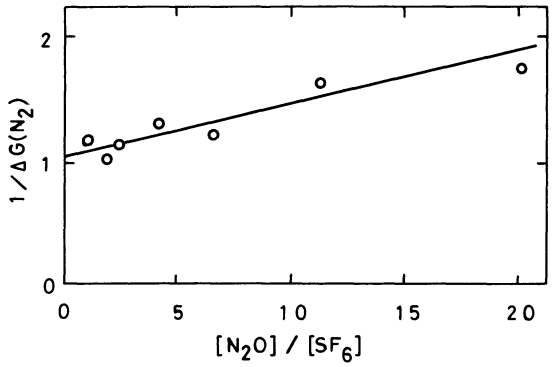

Fig. 3. Competition plots of $1/\Delta G(N_2)$ vs. $[N_2O]/[SF_6]$.

Table 1. Relative Rate Constants for Reactions of Electron with a Series of Electron Scavengers in Zeolite and Nonpolar Liquids

	k_4/k_3		
	MS	2,2-Dimethylpropane	Hexane
SF_6	85	86[a]	0.6[a]
C_2HCl_3	23	25.2[a]	1.3[a]
CCl_4	12.8	12.6[b]	0.7[a]
C_2H_5Br	0	0.1[b]	0.8[a]
CH_3Cl	0	0[c]	

a) Ref. 17. b) Ref. 16. c) Ref. 18.

together with values reported for electrons formed in irradiated nonpolar liquids. Accurate determination has failed for C_2H_5Br and CH_3Cl, because of their poor reactivity. A comparison of relative reactivities between MS and other systems indicates that the trend observed for MS is similar to that for 2,2-dimethylpropane. This suggests that the energy state of the elecron produced in MS is probaly very close to that of quasi-free electron generated in 2,2-dimethylpropane. The intercept of the straight line in Fig. 3 gives the initial yield of electrons witch react with N_2O or SF_6. Values from 0.85 to 1.1 were obtained by the experiments with SF_6, C_2HCl_3, and CCl_4. They are apparently inconsistent with the saturated $G(N_2)$, 2.8. As seen in Fig. 2, there remains a $G(N_2)$ which cannot effectively be depressed by the addition of SF_6. Similarly, a residual $G(N_2)$ was observed for the other scavengers. Since the size of the entrance to a supercavity of Molecular Sieve 13X allows the passage of a molecule below 0.8 nm in diameter, N_2O, SF_6, C_2HCl_3, and CCl_4 can enter the supercavity and hence the difference in molecular size does not explain the results. It will be explained on an assumption of two kinds of electrons, whose reactivities are different from each other. If it is assumed that the second electron, e_2^-, reacts with N_2O and SF_6 with a ratio of rate constants different from k_4/k_3, Eq. III is derived as follows:

$$e_2^- + N_2O \longrightarrow N_2 + O_{ad}^-, \quad (5)$$

$$e_2^- + SF_6 \longrightarrow \text{product(s)}, \quad (6)$$

$$G(N_2) = G_1\{k_3[N_2O]/(k_3[N_2O]+k_4[SF_6])\} + G_2\{k_5[N_2O]/(k_5[N_2O]+k_6[SF_6])\}, \quad (III)$$

where G_1 and G_2 denote the initial G-values of the first and the second electron, respectively. A computer simulation provides a curve shown in Fig. 2, by adopting $G_1=1.2$, $G_2=1.6$, $k_4/k_3=85$, and $k_6/k_5=6.7$. The curve appears to fit the experimental points fairly well. The first electron is considered to be quasi-free because its tendency in reactivity toward several electron scavengers is similar to that found in liquid 2,2-dimethylpropane by Allen et al.[16,17] The different reactivity of the second electron may be understood in terms of the different potential barriers at adsorption sites. Essentially the electrons generated in MS may be identical but the reactivity toward adsorbate is possibly affected by the potential barrier at adsorption site. The oxygen atoms of the SiO_2 network and Na^+ ions are considered as the possible candidates for the two kinds of adsorption sites where quasi-free electrons react with adsorbates. The reaction rate of the electron that reacts at the former site may be low due to its relatively high potential barrier, which is favorable for N_2O but not for the other scavengers. On the other hand, the potential barrier may be negligible at the latter site. However, further confirmation is indispensable for this speculation.

References

1) J. M. Cafrey, Jr. and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).
2) J. W. Sutherland and A. O. Allen, *J. Am. Chem. Soc.*, **83**, 1040 (1961).
3) J. G. Rabe, B. Rabe, and A. O. Allen, *J. Phys. Chem.*, **70**, 1098 (1966).
4) L. Abrams and A. O. Allen, *J. Phys. Chem.*, **73**, 2741 (1969).
5) G. R. Joppien and J. E. Willard, *J. Phys. Chem.*, **76**, 3158 (1972).
6) N. H. Sagert, J. A. Reid, and R. W. Robinson, *Can. J. Chem.*, **48**, 17 (1970).
7) J. W. Sutherland and R. Goodrich, *J. Am. Chem. Soc.*, **89**, 6779 (1967).
8) N. H. Sagert and R. W. Robinson, *Can. J. Chem.*, **46**, 207 (1968).
9) P-O. Kinell, T. Komatsu, A. Lund, T. Shiga, and A. Shimizu, *Acta Chem. Scand.*, **24**, 3265 (1970).
10) P. K. Wong, *J. Phys. Chem.*, **75**, 201 (1971).
11) K. Sogabe, A. Hasegawa, Y. Yamada, and M. Miura, *Bull. Chem. Soc. Jpn.*, **45**, 3362 (1972).
12) N. Kanzaki and I. Yasumori, *Bull. Chem. Soc. Jpn.*, **52**, 1923 (1979).
13) H. Ogura, Y. Tachika, Y. Suzuki, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai, *J. Nucl. Sci. Technol.*, **12**, 167 (1975).
14) H. Ogura, M. Hinata, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai, *J. Nucl. Sci. Technol.*, **15**, 433 (1978).
15) H. Ogura, C. Nakazato, M. Kondo, T. Sawai, and T. Sawai *J. Nucl. Sci. Technol.*, **16**, 57 (1979).
16) A. O. Allen and R. A. Holroyd, *J. Phys. Chem.*, **78**, 796 (1974).
17) A. O. Allen, T. E. Gangwer, and R. A. Holroyd, *J. Phys. Chem.*, **79**, 25 (1975).
18) K. Mori, K. Ito, and Y. Hatano, *J. Phys. Chem.*, **79**, 209 (1975).