

QUASI-FREE ELECTRON PRODUCED IN RADIOLYSIS OF ZEOLITE

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Relative reaction rates were determined for the reaction of electron produced in radiolysis of zeolite with several electron scavengers by a competition method using N_2O as a reference compound. A trend in the relative reactivities was very close to that reported for liquid 2,2-dimethylpropane.

A compound adsorbed on the surface of a solid is radiolyzed through a reaction with an electron or a positive hole produced in bulk of the solid.^{1,2)} We have been studying a radiation chemical decomposition of methanol adsorbed on zeolite and found that formation of molecular hydrogen decreased in the presence of N_2O . The result suggests that a precursor of the molecular hydrogen is an electron generated in bulk of zeolite. Energy state of the electron produced in a solid insulator is of special interest, because it reflects a property of the conduction band. In nonpolar liquid such as 2,2-dimethylpropane or tetramethylsilane, quasi-free electron has been established to produce in radiolysis³⁻⁶⁾ and its reactivity toward some good electron scavengers has been extensively discussed in terms of V_0 , namely the energy of the bottom of the conduction band relative to vacuum.^{7,8)}

In the present study, the determination of the relative reaction rate was attempted for the reactions of the electron produced in gamma-radiolysis of zeolite with several electron scavengers which were used for nonpolar liquids to elucidate the energy state of the excess electron. Concomitantly, an effect of adsorption on the reactivity of the electron scavengers was investigated.

Zeolite (molecular sieve 13 X) was obtained from Nippon Kuromatokogyo K. K. The specific surface area is $1030 \text{ m}^2 \text{ g}^{-1}$. N_2O , SF_6 , and CH_3Cl were purchased from Takachiho Kagakukogyo K. K. CCl_4 and C_2HCl_3 were of spectrograde from Merck.

C_2H_5Br was obtained from B. D. H. About 12 g of molecular sieve 13 X was degassed in quartz vessel at 600 °C for 24 h under the pressure below 10^{-3} Pa and divided

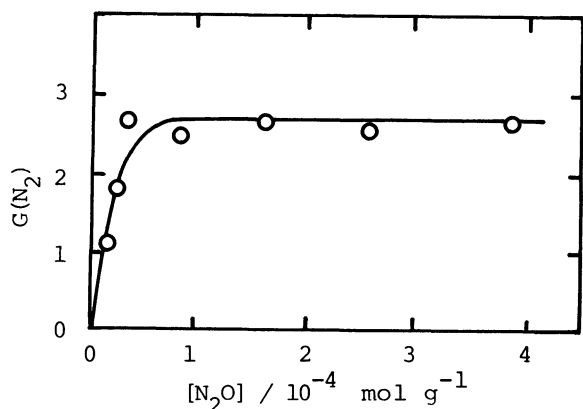


Fig. 1. $G(N_2)$ vs. $[N_2O]$.

to six ampules attached to the vessel by ca. 2 g each. Scavenger was introduced into the ampules through breakable seals. All procedures were carried out 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 N_2 formed from N_2O was determined by gas chromatography. As shown in Fig. 1, $G(N_2)$ increases with increasing amount of N_2O introduced into an ampule. Then, it reaches a plateau at about 5×10^{-5} mol of N_2O per g of molecular sieve 13 X. In experiments of competition with the second scavenger, 4×10^{-4} mol g^{-1} of N_2O was used. Formation of molecular nitrogen decreased with increasing amount of the second scavenger. 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 1 and 2.



where S denotes an electron scavenger added to the system as a competitor of N_2O .

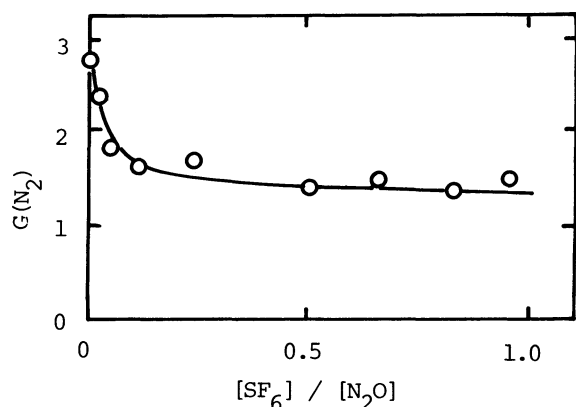


Fig. 2. Decrease in $G(N_2)$ in the presence of the second scavenger.

increases with increasing amount of N_2O

The competition kinetics is expressed by Eq. 3.

$$\frac{1}{\Delta G(N_2)} = \frac{1}{G(e^-)} \left\{ 1 + \frac{k_1 [N_2O]}{k_2 [S]} \right\}, \quad (3)$$

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 a primary yield of the electron. Fig. 3 shows the plots of $1/\Delta G(N_2)$ vs. $[N_2O]/[S]$ for SF_6 as the second scavenger. Relative reactivity of SF_6 is obtained from the slope of a

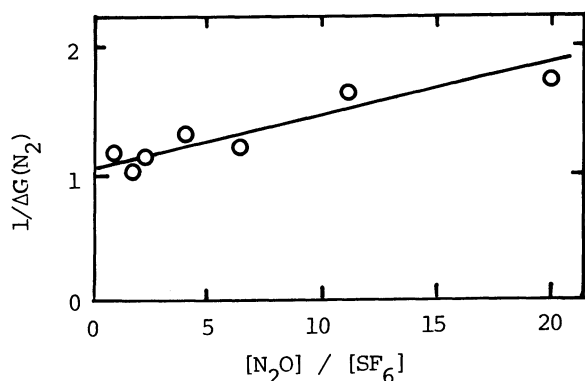


Fig. 3. Competition plots of N_2O-SF_6 system.

lar sieve 13 X and other systems indicates that a trend observed for the molecular sieve is very similar to that for 2,2-dimethylpropane. This suggests that the energy state of the electron produced in molecular sieve 13 X may be very close to that of quasi-free electron generated in 2,2-dimethylpropane, for which the values from -0.35 to -0.43 eV were reported as V_0 .¹¹⁻¹³⁾

straight line in Fig. 3. Similarly the relative reactivity was estimated for other scavengers. The results are summarized in Table 1, together with the values reported for quasi-free electrons formed in nonpolar liquids and for solvated electron in methanol. The accurate determination has failed for C_2H_5Br and CH_3Cl , because of their low reactivity. Comparison of the relative reactivities between molecu-

Table 1. Relative rate constants for the reactions of some electron scavengers with electrons produced in various systems

Scavenger	k_s/k_{N_2O}			
	13 X	2,2-Dimethylpropane	n-Hexane	Solvated electron in methanol
SF_6	85	86 ^{a)}	0.6 ^{a)}	3.2 ^{b)}
C_2HCl_3	23	25.2 ^{a)}	1.3 ^{a)}	
CCl_4	12.8	12.6 ^{c)}	0.7 ^{a)}	4.0 ^{d)}
C_2H_5Br	~0	0.1 ^{c)}	0.8 ^{a)}	
CH_3Cl	~0	0 ^{e)}		

a) Ref. 6. b) Ref. 9. c) Ref. 3. d) Ref. 10. e) Ref. 5.

On the other hand, the initial yield of the electron, $G(e^-)$, can be estimated from the intercept of the straight line in Fig. 3. The values from 0.85 to 1.1 were obtained as $G(e^-)$ from the experiments of SF_6 , C_2HCl_3 , and CCl_4 . They are in good agreement with those reported for the electron produced in 2,2-dimethylpropane as G-value for free ions, 0.86 to 1.1.¹⁴⁻¹⁷⁾ Since the diameter of an entrance to a supercavity of molecular sieve 13 X is noticed to be ca. 0.8 nm,

molecular size of the scavengers used in the present study is small enough to enter the supercavity. If the argument on the correlation between V_0 and the reaction rate of excess electron in nonpolar liquid can be applied to the present system, which consists of solid adsorbent and adsorbed molecules, it is concluded that the electron formed in molecular sieve 13 X by gamma-irradiation is quasi-free and the energy of the electron is nearly -0.43 eV relative to vacuum. If there is no significant change of the energy state at adsorption site compared with bulk, the energy is taken as that for the bottom of the conduction band. Furthermore, the results imply that the scavenger molecules adsorbed on molecular sieve 13 X are not notably affected by adsorption.

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