# Electronic Conduction in Solid Nitrobenzene Containing Nitrobenzene Anion Radical and Tetrabutylammonium Perchlorate

Kosaku SUGA,* Hirofumi TAKEMURA, and Masamichi FUJIHIRA
Department of Biomolecular Engineering, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227
(Received March 30, 1989)

The electric conductivities of frozen nitrobenzene containing various amount of tetrabutylammonium perchlorate and nitrobenzene anion radical were measured. The conductivity increased markedly with the concentration of the nitrobenzene anion radical. The mechanism of the electric conduction of the nitrobenzene is discussed and it is concluded that at low concentration of anion radical the increase of the electric conductivity is due to electronic conduction by a hopping mechanism. The rate constant of electron transfer (hopping) between any nearest neighbored sites is about $10^5\ s^{-1}$ at $-15\ °C$, which is smaller by 2 orders than that in hypothetical liquid nitrobenzene at the same temperature.

The ionic conductivity and the diffusion coefficient of an ionic species in a solution are expected to increase by its fast electron exchange reaction with other species in the solution as suggested by Levich, Dahms, and Ruff and Friedrich.[1-3] In our previous paper,[4] we reported that the contribution of the fast electron exchange reaction of the anthracene anion radical with anthracene to its ionic conductivity was successfully detected in a dimethylformamide solution. However, we could not detect such a contribution to the diffusion coefficient of the nitrobenzene anion radical ($NB^-$) which was undergoing a fast electron exchange reaction with nitrobenzene (NB) as a solvent.[5] In the latter experiment, it was difficult to detect the smaller contribution of the electron exchange reaction to the total conductivity, since the solution contained large amounts of tetraalkylammonium salts as supporting electrolytes.

In this paper, we report the electric conductivity of solid nitrobenzene containing its anion radical and tetrabutylammonium perchlorate (TBAP), and discuss the contribution of the electron exchange reaction between nitrobenzene and its anion radical to the conductivity of the solid, because in such a solid the contribution of the ion migration may be neglected. Furthermore, we discuss the difference between the rate constants of the electron exchange reactions in solution and in the solid state.

## Experimental

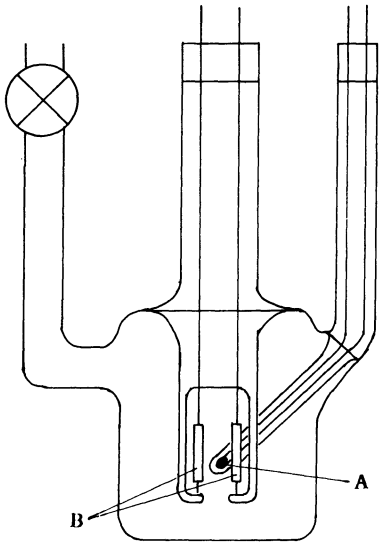
**Reagents.** Commercially obtained nitrobenzene was dried with calcium chloride and distilled under reduced pressure in a nitrogen atmosphere. It was then passed through a column packed with activated alumina. Tetrabutylammonium perchlorate was prepared and purified as described in the previous paper.[6]

**Preparation of Sample Solutions.** Sample solutions of nitrobenzene containing various amounts of its anion radical and TBAP were prepared by electrolysis in an air-tight glass cell filled with nitrogen as described in the previous paper.[5] The concentration of $NB^-$ in the solution was determined by the electric change consumed during the electrolysis.

**Measurements of Electric Conductivity.** Figure 1 shows the conductivity cell used for measurements in this experiment. Electrodes were made of two platinum disks of 1 cm diameter, which were fixed 3 mm apart from each other with face to face. The temperatures of the samples in the vicinity of the electrodes were measured with a thermister thermometer inserted into the cell as shown in Fig. 1. The sample solution prepared by the electrolysis was transferred to the conductivity cell under nitrogen atmosphere and the cell was cooled in a Dewar-type thermostat filled with liquid air–ethanol refrigerant. The conductivity or resistivity of the cell containing the sample solid was measured with a Mita-Musen Model 12K impedance bridge. The cell constant was determined by measuring the conductivity of a standard KCl solution.

## Results and Discussion

Figure 2 shows the temperature dependence of the conductivities ($\sigma$) of solid NB containing 0.1 M




A:Thermister thermometer

B:Platinum disk electrode

Fig. 1. The conductivity cell used in this experiment.

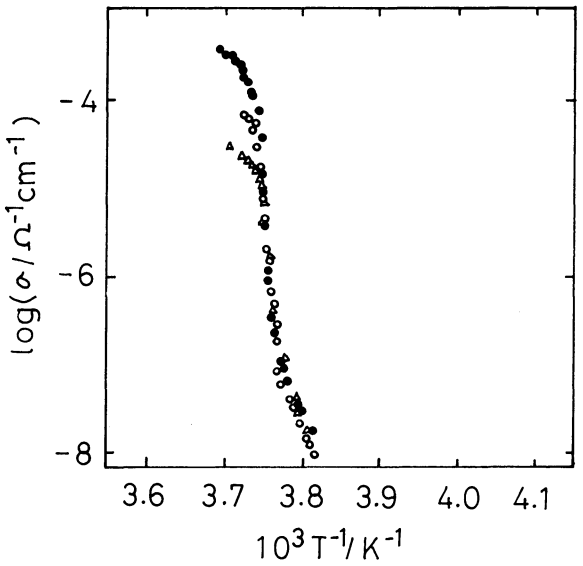



Fig. 2. Temperature dependence of the electric conductivity of NB containing (●) 0.63 M, (○) 0.27 M, (△) 0.10 M TBAP in the absence of $NB^-$.

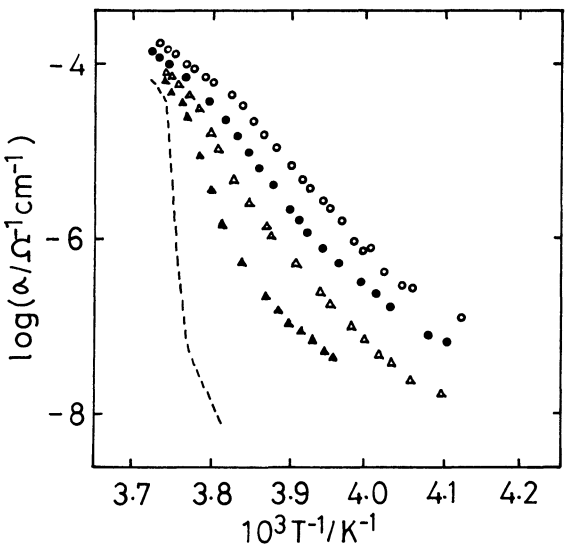



Fig. 3. Temperature dependence of the electric conductivity of NB containing 0.27 M TBAP and (○) 130 mM, (●) 87 mM, (△) 65 mM, and (▲) 43 mM $NB^-$. Dashed line shows the conductivity at $[NB^-]=0$.

(1 M=1 mol $dm^{-3}$), 0.27 M and 0.63 M TBAP in the absence of $NB^-$. In the temperature range used for this experiment, $\sigma$ decreases rapidly with lowering temperature. Below −6.5 °C the conductivity does not depend on the concentration of TBAP.

Figure 3 shows the temperature dependence of the conductivity of NB cotaining 0.27 M TBAP and various amounts of $NB^-$. The conductivity increased remarkably with the concentration of $NB^-$ especially at low temperatures. The apparent activation energies for these conductivities determined from the linear part of the curves in this figure are about 170 kJ $mol^{-1}$. Solid NB samples containing other concentrations of TBAP and various amounts of $NB^-$ showed behavior similar to Fig. 3.

Since the migration of ions is difficult in the solid state, the electric conduction of solid NB containing $NB^-$ may be mainly determined by electronic conduction. In fact, the conductivity of solid NB in the absence of $NB^-$ is much smaller than samples containing $NB^-$, especially at low temperature.

Electronic conduction in solids is generally classified to two categories, i.e. band conduction and hopping conduction. If the present case is the former, conduction electrons in solid NB are supplied by $NB^-$ and they may be trapped by the electric potential induced by positively charged tetrabutylammonium cations ($TBA^+$). In other words, the electrons are trapped in the donor levels which are the highest occupied molecular orbitals of $NB^-$ residing in the vicinity of $TBA^+$. In such a case, the activation energy of $\sigma$ is mainly determined by the excitation energy of the donor electron to the conduction level. The observed large activation energy of about 170 kJ $mol^{-1}$, however, can not be explained by a band conduction model, because the excitation energy estimated from the Coulomb interaction energy between $NB^-$ and $TBA^+$ is not large enough.

If the present case is the latter, the conductivity is represented by the following equation according to Bagley.[7]

$$\sigma = ne^2\delta^2 k_1/k_B T \quad (1)$$

where $n$, $\delta$, $k_1$, and $k_B$ denote the number of hopping electrons in unit volume, the jumping distance of hopping electron between two sites, the first-order rate constant of electron hopping and the Boltzmann constant, respectively. Other nomenclature has the usual meaning. This equation has a close relation with the following equation derived by Ruff and Friedrich[3] for the ionic conductivity of ionic species A which is undergoing fast electron exchange with other species B.

$$\lambda_A = \lambda_A^0 + \pi F^2 \delta^2 k_2 c_B/4RT \quad (2)$$

where $\lambda_A$, $\lambda_A^0$, $\delta$, $k_2$, and $c_B$ represent the ionic conductivity of A in the presence and absence of B, the electron jumping distance, the second-order rate constant of electron exchange between A and B, and the concentration of B, respectively. The second term of Eq. 2 represents the contribution of the electron exchange to the ionic conductivity of A. The conductivity $\sigma$ is related to the ionic conductivity $\lambda$ by the following equation.

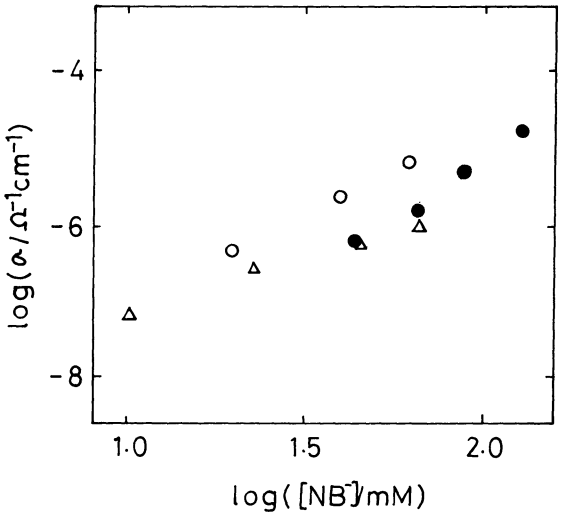



Fig. 4. The electric conductivity, $\sigma$ vs. the concentration of $NB^-$ plots for NB containing (○) 0.1 M, (●) 0.27 M, and (△) 0.63 M TBAP at −15 °C.

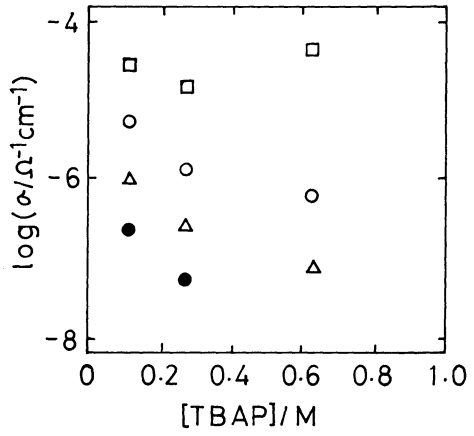



Fig. 5. The electric conductivity, $\sigma$ vs. the concentration of TBAP plots for NB containing 65 mM $NB^-$ at (□) −10 °C, (○) −15 °C, (△) −20 °C, and (●) −25 °C.

$$\sigma = \sum_i \lambda_i c_i \quad (3)$$

where the summation is taken for all ionic species, i.e. $NB^-$, $TBA^+$, and $ClO_4^-$ in this case. Since migration of the ionic species can be neglected in this experiment, we consider only the second term of Eq. 2. In this case, $NB^-$ and NB correspond to A and B, respectively. The following equation, therefore, is derived from Eq. 3.

$$\sigma = \pi F^2 \delta^2 k_2 c_A c_B / 4RT = \pi [NB^-] F^2 \delta^2 k_2 [NB] / 4RT. \quad (4)$$

Considering that $N_A e = F$, $n/N_A = [NB^-]$, $k_2[NB] = k_1$, and $R = N_A k_B$ ($N_A$: Avogadro's number, $F$: Faraday's constant), we can obtain Eq. 1 except for the factor $\pi/4$. The difference of this factor is due to the neglect of the electron hopping or jumping directions other than in the direction parallel to the electric field in the derivation of Eq. 1 by Bagley. Coincidence between the Eqs. 1 and 4 shows that hopping conductivity denoted by Eq. 1 is equivalent to the contribution of electron exchange to the ionic conductivity denoted by Eq. 2.

In the case of the hopping conduction, the electron hopping process is the activation process and needs a certain value of activation energy. Such an activation energy is included in the equation which represents the rate constant of electron hopping or electron exchange as follows;

$$\begin{aligned} k_1 &= k_2[NB] = \nu[NB]\exp(-\Delta G^*/RT) \\ &= \nu[NB]\exp(\Delta S^*/R)\exp(-\Delta H^*/RT), \end{aligned} \quad (5)$$

where $\nu$, $\Delta G^*$, $\Delta S^*$, and $\Delta H^*$ denote the frequency of electron hopping with zero activation free energy, activation free energy, activation entropy, and activation enthalpy for electron hopping, respectively. Therefore, the fact that the observed conductivity of solid nitrobenzene has a large activation energy does not contradict this hopping mechanism.

If the hopping mechanism can be applied to the solid nitrobenzene in this experiment, Eqs. 1 and 4 show that the conductivity of solid nitrobenzene must be proportional to the number in unit volume or the concentration of $NB^-$.

Figure 4 shows the plots of $\log(\sigma/\Omega^{-1}\,cm^{-1})$ vs. $\log([NB^-]/mM)$ for NB containing various concentrations of TBAP at −15 °C. It is apparent that the conductivity increases with the concentration of $NB^-$, although the value of $\sigma$ at constant $[NB^-]$ and temperature is dependent on the concentration of TBAP as shown in Fig. 5. In these plots, there is fairly good linearity between $\log(\sigma/\Omega^{-1}\,cm^{-1})$ and $\log([NB^-]/mM)$ when the concentration of TBAP is constant. The slope of the plots is about 1 at low concentration of $NB^-$, while it increases to about 3 at high concentration of $NB^-$. Although the reason for this is not obvious at the present stage, the conductivity is almost proportional to $[NB^-]$ at low concentration of $NB^-$. In this concentration range, the rate constant of electron hopping therefore can be determined, if appropriate jumping distance is assumed. If the jumping distance $\delta$ is assumed to be 10 Å, the rate constant $k_1 = k_2[NB]$ is estimated to be about $10^5\ s^{-1}$ at −15 °C. The corresponding rate constant in solution is estimated to be about $10^7\ s^{-1}$ at the same temperature by an extrapolation.[5] Such a large difference between the values of $k_1$ in the solid and in solution can be attributed to the freezing of the molecular motion (orientational and vibrational) in solid NB needed for the formation of activation states of an electron transfer reaction.[8] In particular, near the freezing point of NB at which the measurements were

performed in this experiment, the sudden freezing of molecular motion with the decrease of the temperature may occur.

In the quantum mechanical treatment of electron transfer reactions,[8c] the first-order rate constant for electron transfer at fixed distance is given by the following equation,

$$k_1 = (2\pi/\hbar)H_{AB}^2(FC) \quad (6)$$

where $H_{AB}$ is the matrix element describing the electronic coupling between the electronic states of reactants and products, and the quantity (FC) is the 'Franck-Condon' factor, which is a sum of products of overlap integrals of the vibrational and solvational wave functions of the reactants with those of the products, suitably weighted by Boltzmann factors for the vibrational and solvational energy levels of reactants. With freezing of the sample solution, the orientational vibration of $NB^-$ and NB molecules may be frozen easily and the frequencies of these vibrations may increase remarkably. Consequently, the separation of these vibrational levels increases considerably, the contribution of these vibrations to the value of (FC) can be expected to decrease greatly.

Therefore, the larger activation energy observed in solid NB compared with that observed in solution (about 35 kJ $mol^{-1}$)[5] can also be attributed to the apparent decrease in the value of (FC) as a result of such sudden freezing of molecular motion with the decrease of the temperature.

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