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Electron Spin Resonance Study on Spin Exchange and Electron Transfer of Pyrazine Anion

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Abstract

The rate of Heisenberg spin exchange and electron transfer was studied by means of electron spin resonance for pyrazine anion formed by sodium reduction in dimethoxyethane and tetrahydrofuran. Pyrazine anion is known to form a contact ionpair with Na^+ , where the counteranion changes its location between the sites associated with lone-pair electrons of two nitrogen atoms in the pyrazine ring. The results indicated that the spin exchange is not affected by the intramolecular exchange of the cation location, whereas the electron transfer shows a comparatively large rate constant ($\sim 10^8 \text{ M}^{-1} \text{ sec}^{-1}$) and a large activation energy (5.3 kcal/mol) in tetrahydrofuran. Conclusions are that the spin exchange is a diffusion-controlled process and that the electron transfer is facilitated by the exchange of the cation location.

Introduction

Ion pairs are very often formed between an aromatic anion and an alkali metal cation, when aromatic compounds are reduced by alkali metals. The effect of ion-pairing on chemical reactions involving the anion has been studied for Heisenberg spin exchange and electron transfer by means of electron spin resonance method. The reaction rate has been found to be little dependent for the spin exchange but largely dependent for the electron transfer on the state of ion pairs^{1)~8)}.

In the present investigation, we studied the spin exchange and the electron transfer for pyrazine anion. Pyrazine has two nitrogen atoms in its ring, so that it has two sites of the cation close to the nitrogen atoms to form the ion pair. It has been disclosed that the metal cation exchanges its location between the two sites rapidly enough to average the proton and nitrogen hyperfine coupling constants, when pyrazine is reduced by K or $\text{Na}^9,10)$. The primary concern is in studying the effect of the intramolecular exchange of the cation location on the intermolecular processes such as the spin exchange and the electron transfer.

Experimental

Sample Preparation. Pyrazine of analytical grade was dried with CaH_2 ,

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purified by sublimation and kept in a desiccator. Dimethoxyethane (DME) and tetrahydrofuran (THF) of analytical grade were distilled, dried with CaH_2 and treated with Na-K alloy in *vacuo*. Hexamethylphosphorictriamide (HMPA) of analytical grade was used after distillation under reduced pressure.

Solutions of pyrazine anion were prepared in a glass apparatus as shown in Fig. 1. Solvent was transferred by vacuum distillation into the vessel V, where a measured amount of pyrazine was placed beforehand. The solution of pyrazine was degassed by freezing-pumping-thawing technique and sealed at the striction S_1 under the vacuum of about 10^{-5} torr. It was then introduced into the alkali metal-mirrored reaction vessel through the break seal B, so that pyrazine was reduced to form its anion. Pyrazine or HMPA was added, if necessary, into the solution of pyrazine anion from an additional vessel through a break seal after removing the reaction vessel from the glass apparatus by sealing at the striction S_2 . The concentration of the pyrazine anion was determined from its optical absorption at 365 nm and the reported molar extinction coefficient, $(1.2 \pm 0.3) \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (11).

ESR Measurements. Electron spin resonance (ESR) spectra of the anion were recorded with a conventional X-band spectrometer (JEOL, Model JES-NE-2X) in a temperature range of 233 and 293 K.

Analysis of Data

Spin Exchange. The Heisenberg spin exchange is a second order process with respect of the concentration of the pyrazine anion. The rate of exchange increases with the concentration, so that the width of hyperfine lines becomes broadened because of the decrease in spin-spin relaxation time of the anion. The second order rate constant, k_{HE} , has been related to the increase of the line with, δH_{HE} :

$$k_{HE} = \frac{\sqrt{3}}{2} f_M \cdot \gamma_e \cdot \frac{\delta H_{HE}}{[\text{Py}^-]} \quad (1)$$

In the above equation, f_M is the spectral index number and depends on the probability of changing magnetic quantum number of nuclei, M , on an electron spin exchange. It is approximately unity in this investigation⁽¹²⁾. γ_e is the absolute value of electronic gyromagnetic ratio. $[\text{Py}^-]$ is the concentration of pyrazine anion. Thus the rate constant is determined from the observed linewidth at

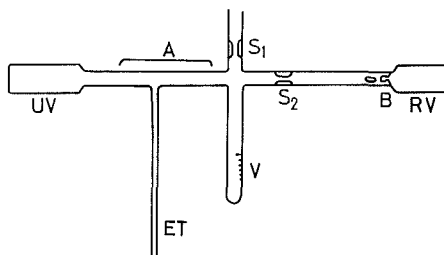


Fig. 1. Glass apparatus for preparing pyrazine anion. S_1 and S_2 ; strictions, B; break seal, V; vessel, RV; reaction vessel, ET; ESR sample tube, UV; cell for optical absorption measurement, A; location where additional vessels are connected, if necessary, through break seals.

several anion concentrations.

Electron Transfer. When neutral pyrazine is added to the solution of pyrazine anion, the lifetime of a particular anion is limited by the electron transfer reaction, $\text{Py}^- + \text{Py} \rightarrow \text{Py} + \text{Py}^-$. According to the uncertainty principle, the width of the hyperfine lines becomes larger. The second order rate constant for the electron transfer reaction is expressed by the relationship,

$$k_{TE} = 2.83 \times 10^6 \frac{3\pi\delta H_{ET}}{[\text{Py}]}, \quad (2)$$

where δH_{ET} is the increment of the linewidth by the addition of neutral pyrazine and $[\text{Py}]$ is the concentration of the added pyrazine¹¹. The rate constant is determined from the dependence of hyperfine linewidth on the concentration of added pyrazine.

Results

Figure 2 shows the ESR spectra of pyrazine anions. When pyrazine is reduced by K, the spectrum of anion indicates the hyperfine constant of 7.2 G due to two equivalent nitrogen nuclei and that of 2.5 G due to four equivalent protons. An additional splitting due to sodium nucleus by 0.7 G is observed, when the anion is formed by Na. These spectra agree with those reported by Atherton et al.^{9),10)} and indicate a rapid exchange of the cation location. Even

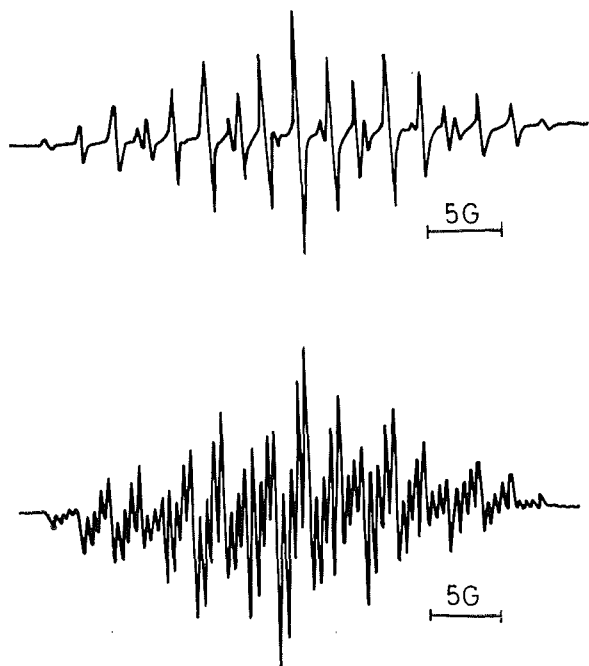


Fig. 2. ESR spectra of pyrazine anion in tetrahydrofuran formed by (A) potassium reduction and (B) sodium reduction recorded at room temperature.

for Na^+ as a counteranion, the first three hyperfine lines from the ends are not overlapping with others. Therefore, the line width was examined for these hyperfine lines.

The observed dependence of the hyperfine linewidth on the concentration of the anion is shown for the reduction with Na in DME in Fig. 3. The width was found to be linearly dependent on the concentration. Extrapolation to zero concentration was taken as $\delta_{HE}=0$. The slope of lines in Fig. 3 gives the second

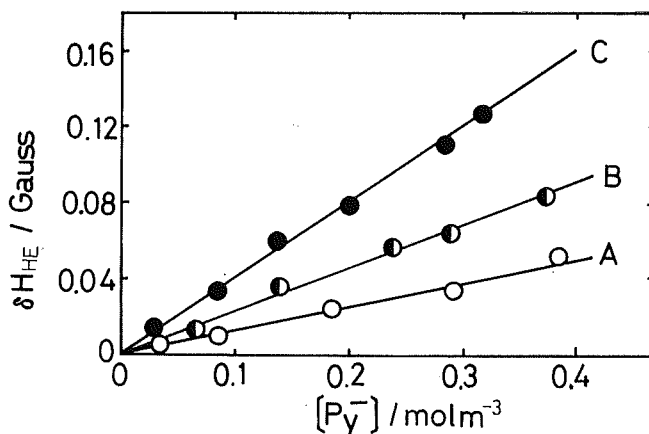


Fig. 3. Increase in the width of ESR hyperfine lines of pyrazine anion ion-pairing with Na^+ in dimethoxyethane with the concentration of the anion, observed at (A) 237, (B) 265 and (C) 289 K.

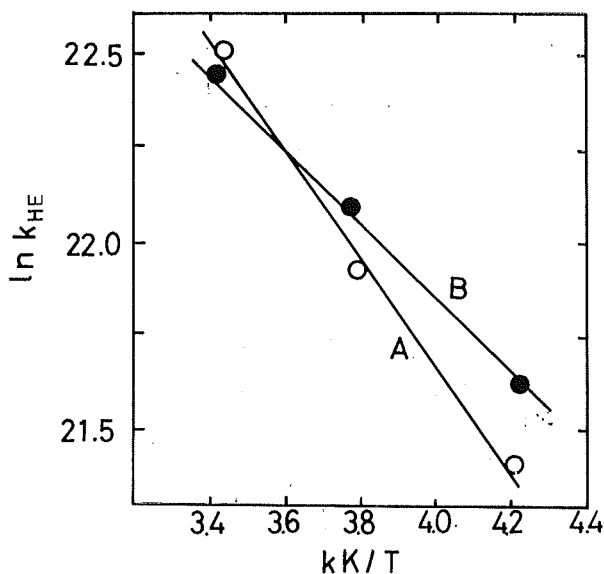


Fig. 4. Arrhenius plot of the rate constant of spin exchange of pyrazine anion ion-pairing with Na^+ in (A) dimethoxyethane and (B) tetrahydrofuran.

order rate constant for the spin exchange reaction. Similar results were obtained for THF as solvent. The rate constants were plotted as a function of reciprocal temperature in Fig. 4. This Arrhenius plots give the activation energy of 3.0 and 2.3 kcal/mol for DME and THF, respectively.

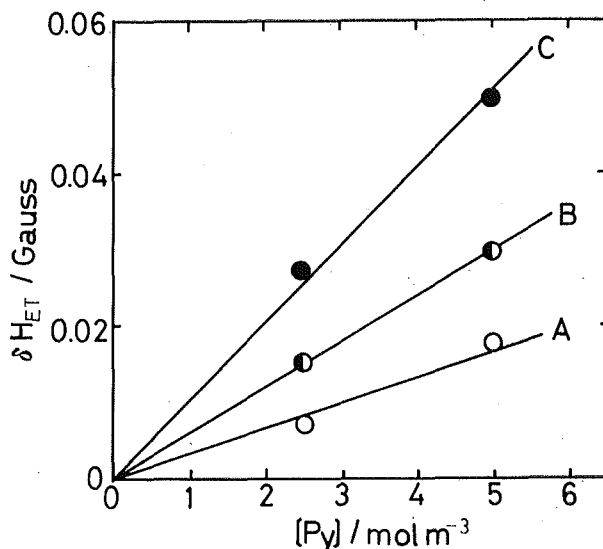


Fig. 5. Increment of the width of ESR hyperfine lines of pyrazine anion ion-pairing with Na^+ in tetrahydrofuran containing 4 vol. % hexamethylphosphorotriamide by the addition of neutral pyrazine observed at (A) 253, (B) 273 and (C) 293 K.

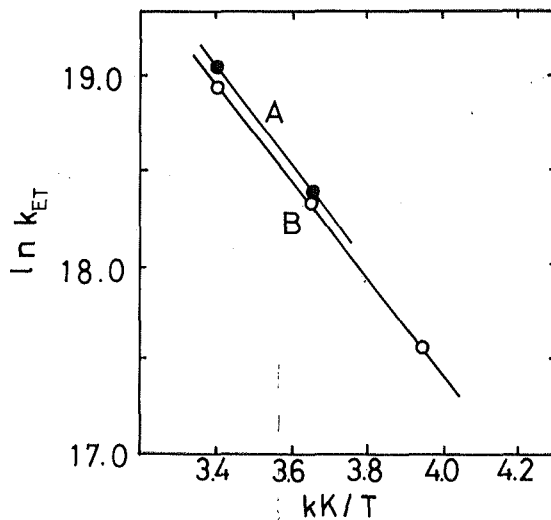


Fig. 6. Arrhenius plot of the rate constant of electron transfer of pyrazine anion ion-pairing with Na^+ in (A) tetrahydrofuran and (B) tetrahydrofuran containing hexamethylphosphorotriamide.

Figure 5 shows the increment of the linewidth caused by the addition of neutral pyrazine, typically in the solvent of THF with HMPA (4% in volume) mixed in. From the slope of observed linear relationship, the second order rate constant was determined for the electron transfer reaction and plotted as a function of reciprocal temperature in Fig. 6, which gives an activation energy of 5.2 kcal/mol. The rate constant and the activation energy were determined also for pure THF as solvent, but no significant difference was found between the absence or presence of HMPA.

Pyrazine anion forms very probably the contact ion pair with Na^+ in THF on the analogy of the reported behavior of aromatic anions¹⁰. HMPA is a good solvent to solvate selectively the counterion of the aromatic anions, so that its addition causes a change in the ion pair state. However, no effect of the HMPA addition was observed for the pyrazine anion in THF.

Discussion

Spin Exchange. The spin exchange process is known to be almost independent of the state of ion pairs and proceeds with a diffusion-controlled rate. According to the diffusion model developed by Brown^{12,13}, the lifetime of a reactant, τ , is expressed by

$$1/\tau = 4\pi \cdot d \cdot D \cdot C \quad (3)$$

for bimolecular reactions, where d refers to the reaction distance, C to the concentration of the reactant, and D to the diffusion constant given by the well known Stokes-Einstein relationship, $D = kT/6\pi a\eta$, from the radius of the reactant molecule, a , and the viscosity of solvent, η .

If one takes twice the radius as the reaction distance, k_{HE} is calculated from the reported η values¹⁴ after the equation (3). The calculated rate constants as well as the activation energy are shown in Table 1, where the observed results

TABLE 1 Rate constant and activation energy of spin exchange of pyrazine anion

Solvent	Temperature (K)	Observed		Calculated	
		k_{HE} ($\text{M}^{-1} \text{sec}^{-1}$)	E_A (kcal/mol)	k_{HE} ($\text{M}^{-1} \text{sec}^{-1}$)	E_A (kcal/mol)
THF	289	5.8×10^9	2.3	6.6×10^9	2.3
	265	4.4		4.5	
	237	2.2		2.7	
DME	289	6.0	3.0	6.6	2.5
	265	3.3		4.4	
	237	2.0		2.5	
THF-DME	289	4.0		—	
THF-HMPA	293	3.8		—	

are also cited for comparison. The observed results are in good agreement with the calculated ones. This leads to a conclusion that the spin exchange is a diffusion-controlled process also for pyrazine anion.

The observed activation energy in DME seems a little too large as compared with the calculated one. The reason is not known for this difference. The observed frequency factor is in the order of magnitude of 10^{11} sec^{-1} in both THF and DME.

Electron Transfer. It was found that pyrazine anion forms an ion pair with Li^+ , where the cation associates statically with the non-bonding electrons in one of two nitrogen atoms. In contrast, Na^+ ion changes dynamically its location between the two nitrogen atoms in the ion pair as follows¹⁰⁾;

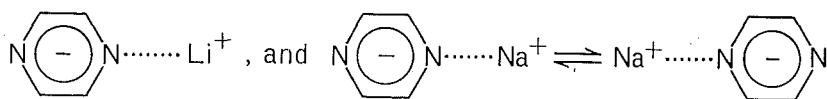


Figure 7 shows the observed dependence of sodium hyperfine coupling constant on temperature as well as the reported coupling of lithium in the ion pair¹⁵⁾. The dependence is much affected by the dynamic exchange of cation location, and is reverse for the the two cations.

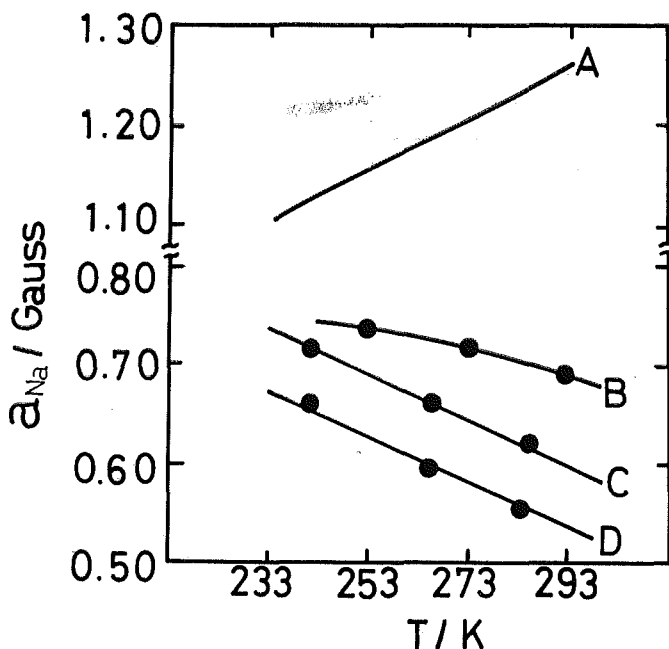
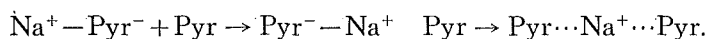


Fig. 7. Temperature dependence of hyperfine splitting due to counteraction in ESR spectra of pyrazine anion (A) ion-pairing with Li^+ in tetrahydrofuran¹⁴⁾, (B) with Na^+ in tetrahydrofuran containing hexamethylphosphoric triamide, (C) with Na^+ in tetrahydrofuran and D with Na^+ in dimethoxyethane.

Pyrazine anion was shown to form a contact ion pair with Na^+ by the appearance of the hyperfine splitting due to the cation. The observed rate constant of electron transfer reaction is in the order of magnitude of $10^8 \text{ M}^{-1} \text{ sec}^{-1}$. This value lies at the upper limit of the rate constant observed for aromatic anions forming a contact ion pair ($5 \times 10^6 - 1 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$)⁴⁾, and is similar to that observed for tetracyanoethylene anion, $(0.9-1.9) \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ ¹³⁾. The observed activation energy seems to be larger than that for aromatic anions in a contact ion pair state (4-6 kcal/mol).

The transition state of the electron transfer reaction is believed to have a symmetric configuration with two anions (partially charged) and a cation, namely, a sandwich structure. Hirota *et al.* considered that the activation energy of the reaction was mainly determined by the energy needed for the rearrangement of solvent molecules around the reactants⁴⁾. Ogasawara *et al.* suggested in the case of tetracyanoethylene that it depends on the energy required for the displacement of the countercation against the Coulombic interaction in the ion pair¹³⁾. According to these arguments, the formation of the transition state might be divided into two steps:



The first step is the rearrangement of the reactant molecules, which requires the displacement of the cation to the midst of the two pyrazine molecules and also the rearrangement of the solvent molecules. This step seems to be facilitated if the cation undergoes the dynamic exchange of its location. The second step seems to occur with a larger activation energy in heterocyclic anions than in aromatic anions because of a stronger Coulombic interaction in ion pairs involving the former anions caused by their lone-pair electrons. The above consideration gives a qualitative interpretation for the observed large rate constant as well as the large activation energy. As a matter of fact, the electron transfer reaction of pyrazine anion is different from that of durosemiquinone anion³⁾ and 2, 2'-bipyridine anion¹⁰⁾, which form astatic contact ion pair and give a small rate constant and a large activation energy.

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