# EFFECT OF DIELECTRIC CONSTANT ON THE RATE OF ELECTRON SPIN EXCHANGE OF FREMY'S SALT IN SOLUTION

Hamza A. HUSSAIN and Waleed A. A. KUDER

*Chemistry Department, College of Science, University of Baghdad, Jadiria, Baghdad, Iraq*

Received June 12th, 1985

The rate of electron spin exchange in aqueous solution of potassium nitrosodisulphonate $K_2(SO_3)_2NO$, has been investigated by ESR and found to depend on the dielectric constant of the medium. This observation lead to the calculation of the collision diameter 2 nm which corresponds to bimolecular collisions between species carrying two negative charges.

Because of its stability and ease of preparation, potassium nitrosodisulphonate (PND) (Fremy's salt) has been a subject of many investigations by ESR[1-4].

The exchange interactions between two unpaired spins normally takes the form $JS_1S_2$. Such coupling varies rapidly with distance and a reasonable model is obtained when it is assumed that spin exchange is effective only during collision. This intermolecular interaction is an efficient spin relaxation mechanism[5] that can lead to observable effects in ESR spectra.

PND has been the subject for such investigation[6-10].

According to the modified Bloch equations the exchange frequency in the slow exchange region can be calculated from expression (*1*)

$$\omega_e = 1/\tau = 0{\cdot}75\sqrt{3}\,\gamma_e(\Delta H - \Delta H_0)\,, \qquad (1)$$

where $\gamma_e$ is the gyromagnetic ratio of the electron and $\Delta H$ and $\Delta H_0$ are the peak-to--peak widths (in gauss) of the first derivative spectra in the presence and absence of exchange respectively[11].

Jones[9] fitted his data to an expression of form

$$\omega_e = bc^m\,, \qquad (2)$$

where $c$ is the molar concentration and $b$ and $m$ are adjustable parameters. The value of $b$ (which will be used as a rate constant $k$) was found to be approximately $10^9\ s^{-1}$, which is reasonable for a diffusion-controlled reaction. If exchange occurs during bimolecular collisions, the exchange frequency should be first order in radical concentration. However small but significant deviations of $m$ from unity were found.

Several papers[12-14] appeared in the literature dealing with the study of PND.

We now report our measurements of the rate of spin exchange as a function of the dielectric constant of the medium, as expected for bimolecular collisions between negatively charged species.

## EXPERIMENTAL

PND was prepared following Howie procedure[15] and was used immediately after preparation in order to minimize its decomposition. The ESR spectra were measuree with a Varian E-109 spectrometer at low levels of microwave power. The radical concentrations were determined using a Pye-Unicam SP 500 spectrophotometer. The molar extinction coefficient, $\varepsilon = 20{\cdot}8$ at 545 nm. The optical measurements were made during the recording of the ESR spectrum of each solution. The solutions were not degassed and thus contained atmospheric oxygen. We assumed that spin exchange with oxygen makes a constant contribution to the linewidth which can be included in $\Delta H_0$ together with other relaxation processes, such as rotational modulation of the $g$ and hyperfine tensors and spin rotational interaction. Mixture of ethanol and water was used

TABLE I
The values of $\Delta H_G$ for different concentration of PND in certain mixture

| $c$, mol $l^{-1}$ | $\Delta H_G$ |
|---|---|
| 0·046 | 2·7 |
| 0·030 | 1·5 |
| 0·007 | 0·6 |
| 0·002 | 0·31 |

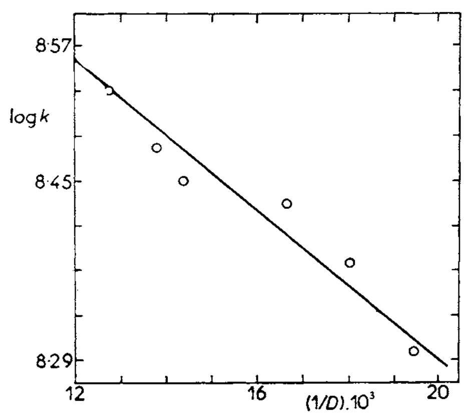


FIG. 1
Rate of spin exchange in solution of PND $vs$ $1/E_r$

to prepare solutions of different dielectric constant[16], for each mixture several values of $\Delta H$ measured at different concentration of PND (Table I) then for the same concentration of PND $\omega_e$ were calculated. In addition the dielectric constant for the prepared solutions were measured by Radelkis Universal dielectrometer Type OH-301. All measurements were made at 20°C.

## DISCUSSION

In our investigation we assumed that $m = 1$ in equation (*2*) and calculated the value of the rate constant $k$, for each solution.

It is well known that the dielectric constant has a great effect on the rate constant, and the dependence of the rate constant on the dielectric constant follows the expression

$$\ln k = \ln k'_0 - \frac{NZ_AZ_B\,e^2}{E_rRTr}\,, \qquad (3)$$

where $k'_0$ is the specific rate constant in a medium of infinite dielectric constant, $E_r$ is the dielectric constant of the mixture, $r$ is the collision diameter, $Z$, refers to the charge of the PND, $N$, e, and $R$, represent Avogadro number, the charge of the electron, and the molar gas constant respectively, and they have been used with their standard values.

This equation predicts a linear plot of log $k$ against $1/E_r$ with negative slope if the charges of the ions are of the same sign and a positive slope if the charges are of opposite sign.

Our experiments have demonstrated that the rate of electron spin exchange in aqueous–ethanol solutions of PND depends on the dielectric constant of the medium, the plot of log $k$ *vs* $1/E_r$ (Fig. 1) showed linear relationship with a slope from which the collision diameter, $r$, was calculated, it was found to be approximately equal to 2 nm. Our calculation of $r$ is reasonable taking into the consideration the charge of the radical ion.

### REFERENCES

1. Weissmann S. T., Tuttle T. R.: J. Phys. Chem. *61*, 28 (1957).
2. Windle J. J., Wiessmann A. K.: J. Chem. Phys. *39*, 1179 (1963).
3. Tchao Y. H., Herve J.: C. R. Acad. Sci. *248*, 2696 (1959).
4. Lloyd J. P., Pake G. E.: Phys. Rev. *94*, 579 (1954).
5. Pake G. E., Tuttle T. R.: Phys. Rev. Lett. *3*, 423 (1959).
6. Tchao A. H., Herve J.: C. R. Acad. Sci. *249*, 53 (1959).
7. Hausser K.: Arch. Sci. *13*, 239 (1960).
8. Hausser K.: Z. Elektrochem. *65*, 636 (1961).
9. Jones M. T.: J. Chem. Phys. *38*, 2892 (1963).
10. Alibahai H., Hudson A., Hussain H. A.: J. Chem. Soc. A, *1969*, 678.
11. Johnson C. S.: Mol. Phys. *12*, 25 (1967).

12. Baranov S. V.: Leningr. Univ., Fiz. Khim. *4*, 61 (1974).
13. Holmberg W. R., Wilwon B. J.: J. Chem. Phys. *61*, 921 (1974).
14. Lunicheva E. V., Etlis V. S., Perepletchikova: Khim. Prom., (Moscow), Ser. Metody Anal. Kontrolya Kach. Prod. *8*, 48 (1981).
15. Moser W., Howie R. A.: J. Chem. Soc. A, *1968*, 3029.
16. Frost A. A., Pearson R. G.: Kinetics and Mechanism, ch. *7*. Wiley, New York 1961.