Submitted to J. of Physical Chem.
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September 1969

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The Mechanism for the ESR Broadening of Nitrosyl Disulfonate Anion by other Paramagnetic Species in Solution

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A paramagnetic ion such as nitrosyl disulfonate anion (NDS^{2-}) has sufficiently sharp electron spin resonance (esr) absorptions that broadening by paramagnetic species in aqueous solution can readily be measured. Pearson and Buch[1] (PB) have investigated the broadening of NDS^{2-} both by paramagnetic cations and by anions. They found that $Ni(H_2O)_6^{2+}$ was typical of a class of cations which give a linear increase in line width, ΔH, with concentration of added cation.

For the case of $Ni(H_2O)_6^{2+}$, PB assumed that ΔH was a direct measure of the rate of formation of an $Ni(H_2O)_6^{2+}$ - NDS^{2-} complex. Since PB made measurements at only one temperature, we have checked their assumption by making measurements over a range of temperatures.

At 25°C our $Ni(H_2O)_6^{2+}$ results[2] are close to PB, but with a temperature variation, shown in Fig. 1, corresponding to an activation energy of 4.95 kcal/mole. If one assumes a simple one step ion-pair model with an electron spin relaxation time which is shorter than the lifetime of the complex, Equation (7) from PB predicts that

$$\Delta H(G) = \frac{k_2[Ni^{2+}]}{1.52 \times 10^7 \text{ sec}^{-1}} \qquad (1)$$

where k_2 is the second-order rate constant for the formation of the ion-pair. As PB pointed out the 25°C value for k_2 calculated from Equation (1) is only a factor of two smaller than that predicted by the theory of diffusion controlled reactions.[3] The activation energy predicted by this theory for k_2 is only 3.5 kcal/mole. This small value is due to the fact that the temperature coefficient of the dielectric constant of water counterbalances the activation energy for viscosity in the theoretical equation[4] for k_2.

For $Ni(H_2O)_6^{2+}$ there is one obvious reason for the failure of Equation (1). If the electron spin relaxation time of the complex T_{2B} is not smaller than its lifetime τ_B, then ΔH is decreased over the value given by Equation (1) by the factor $\tau_B/(\tau_B + T_{2B})$. A factor of two decrease in ΔH would occur when $T_{2B} = \tau_B$, and the theoretical value of k_2 would allow us to at least make this assumption. It is even possible

that T_{2B} is two or three times τ_B, for the theoretical evaluation of k_2 is not certain. When $T_{2B} \gg \tau_B$, ΔH depends upon $k_2 \tau_B / T_{2B}$. From our knowledge[5,6] of these constants it is quite probable that they have an activation energy of 5.0 kcal/mole.

If we assume that NDS^{2-} and $Ni(H_2O)_6^{2+}$ interact via dipole-dipole interaction, the very short electronic relaxation time[5] for $Ni(H_2O)_6^{2+}$ makes it quite probable that $T_{2B} \geq \tau_B$. This would not seem to be possible for the other cations such as $Cr(H_2O)_6^{3+}$, $Gd(H_2O)_6^{3+}$ and $Cu(H_2O)_6^{2+}$ which PB found gave almost exactly the same broadening as did $Ni(H_2O)_6^{2+}$. If these ions also have activation energies much greater than 3.5 kcal/mole, then we must have a second explanation. It is also quite possible that at least two ion-pair states are responsible for the rate of relaxation of NDS^{2-}. If the final relaxing outer sphere complex was proceded by another non-relaxing outer sphere complex, then the simple diffusion controlled theory would have to be modified. Such a two step process would most probably have a higher activation energy.

Also shown in Fig. 1 are some results for dissolved O_2. Because we did not have a true solubility equilibrium it is difficult to get very accurate broadenings. The two lines for O_2 correspond to 5.6 and 4.4 kcal/mole and our best estimate of the molar broadening is 700 GM^{-1} at 25°C. This is to be compared to 1080 GM^{-1} for $Ni(H_2O)_6^{2+}$ at 25°C. For O_2 Equation (1) gives an effective bimolecular rate constant of 1.0×10^{10} M^{-1} sec^{-1}.

For a neutral species like O_2 one can compose a diffusion controlled mechanism, and with σ_{ab} = 3A we calculate[3] that $k_{ab} = 1 \times 10^{10}\ M^{-1}\ sec^{-1}$ at 25°C. With a dependence upon T/η it should have an activation energy of 5.0 kcal/mole. The electronic relaxation time for O_2 should be at least as short as for $Ni(H_2O)_6^{2+}$, but the life-time for any complex should be much smaller for O_2. Since neither NDS^{2-} or O_2 are strongly hydrated it is not unreasonable that they can rapidly diffuse close enough together so that NDS^{2-} is relaxed on every collision. One would expect that O_2 would have a much smaller specific broadening effect upon the esr absorption of a strongly hydrated cation. Our results[7] for $Mn(H_2O)_6^{2+}$ indicate that this is indeed the case.

We have also extended the PB results for the broadening of NDS^{2-} by paramagnetic anions. The presence of small amounts of paramagnetic impurity cations can be very important, in this case, for the molar broadenings can be very small[8]. There is little or no activation energy to such broadenings. These are long distance interactions and it is not a diffusion controlled process. A theoretical consideration of anion-anion interactions[9] shows that they largely depend upon the electronic relaxation times of the broadening anion. Anion-anion broadening should be a good method for measuring very short electronic relaxation times.

Acknowledgement. This work was performed under the auspices of the U. S. Atomic Energy Commission.

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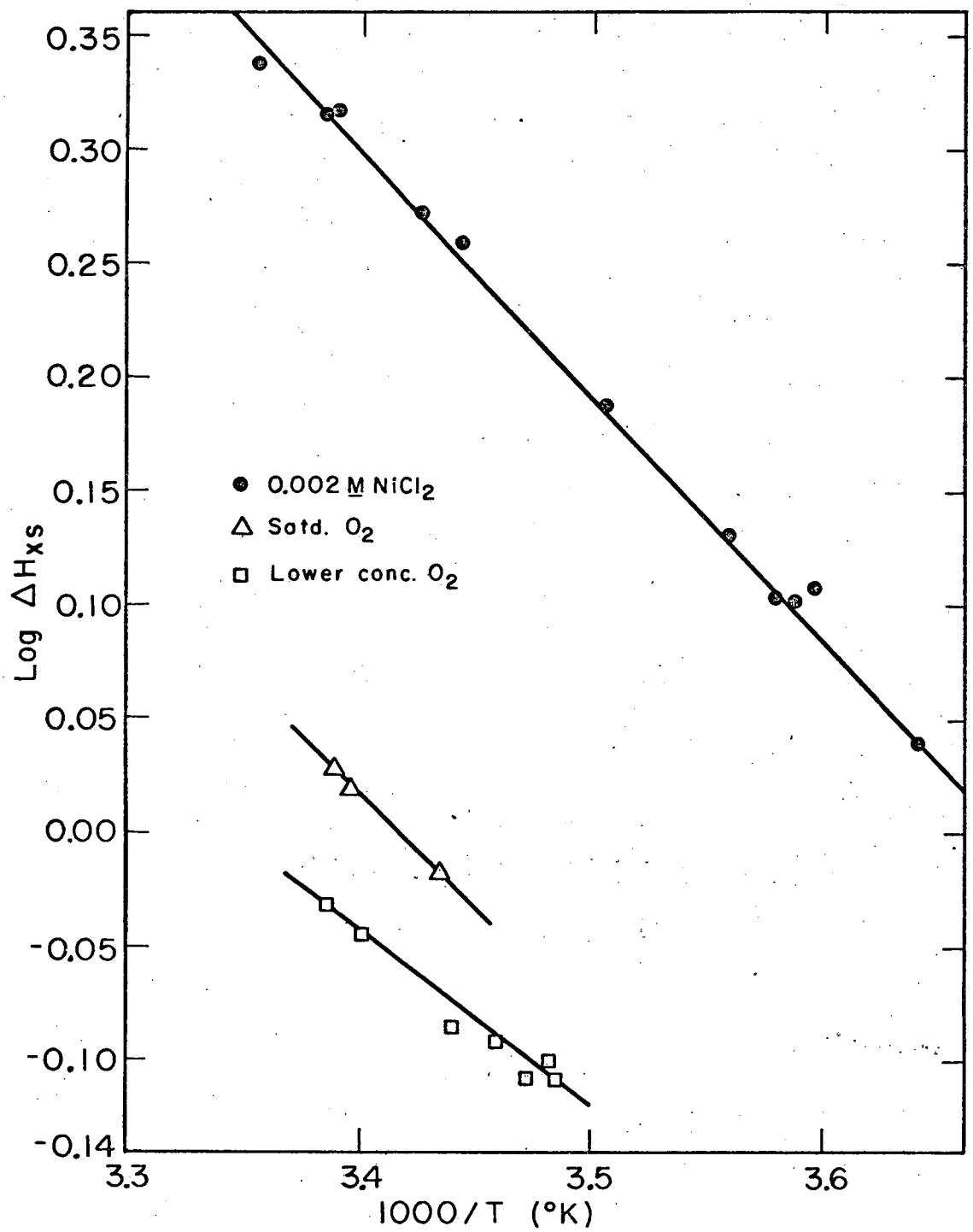

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Figure 1. A Plot of the ESR Line Width Increase for Nitrosyl Disulfonate Anion by $Ni(H_2O)_6^{2+}$ and Dissolved O_2. The O_2 data were taken with sealed tubes. The 25°C results for O_2 are in agreement with those of M. T. Jones, J. Chem. Phys., 38, 2892 (1963) and K. Hausser, Z. Electrochem., 65, 636 (1961).

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