

THE EFFECT OF CATION CONCENTRATION ON THE NITROGEN SPLITTING CONSTANT OF NITROXIDE FREE RADICALS

Hamza A. HUSSAIN

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

Received July 31, 1989

Accepted February 1, 1990

Nitroxide free radicals prepared from diethylamine, piperidine and pyrrolidine by oxidation with hydrogen peroxide were studied by ESR spectroscopy. The changes in the ^{14}N splitting constant (a_{N}) caused by the addition of KBr or tetraethylammonium bromide were measured in dependence on the concentration of the ions. For diethylamine nitroxide and piperidine nitroxide, the results are discussed in terms of two equilibria: the one, involving the anion, is associated with a gain or loss of hydrogen bonds to the nitroxide oxygen atom, the other is associated with the formation of solvent shared units involving the cation, which results in changes in the hydrogen bonding strength. The large increase in the a_{N} value in the case of pyrrolidine nitroxide is explained in terms of an interaction from one side of the positively charged N atom; the increase in a_{N} in the case of diethylamine and piperidine nitroxides is explained in terms of interactions with both sides of the positively charged N atom.

Nitroxide free radicals have been subject to chemical and physical investigation since 1914 (ref.¹). ESR spectroscopy is a powerful tool for studying not only free radicals of this kind themselves but also the associated solvation phenomena. Solvent effects have been investigated for the benzoquinone and related anions²⁻⁴. Neutral nitroxide radicals have been used recently as probes for the solvent behaviour⁵⁻⁷; they are also used extensively in biochemical systems⁸. Jolicoeur and Friedman⁵ examined aqueous solutions of 2,2,6,6-tetramethyl-4-piperidone-N-oxide and 2,2,6,6-tetramethylpiperidine-N-oxide, focussing their attention on line width measurements, and calculated the rotational correlation time and spin rotational correlation time values. The effect of salts on the ESR spectra of the nitroxide radical (2,2,6,6-tetramethylpiperidine) has also been studied⁹. It has been found that the effect is not caused by the increase in the ionic strength; instead, it is due to the solvation of the cation by hydrogen bonding, large cations decreasing this solvation and anions having a lower effect than cations. ESR spectroscopy has been also used for investigating the effect of the ionic strength¹⁰ and the dielectric constant¹¹ on the rate of the electron spin exchange of the peroxyamine disulfonate ion-radical (Framy's salt) in solution.

In this work we are concerned with the changes in the hyperfine splitting constant a_N of nitroxide free radicals derived from diethylamine (*I*), piperidine (*II*), and pyrrolidine (*III*), caused by the addition of KBr or tetraethylammonium bromide (TEABr) in aqueous solution. These nitroxide radicals can be prepared in high yields¹² in a very stable form.

EXPERIMENTAL

The nitrogen free radicals were prepared by adding several drops of 30% (v/v) hydrogen peroxide to diethylamine, piperidine and pyrrolidine, respectively. All chemicals were commercial grade and were used as received.

The ESR spectra were measured on a Varian EI09 spectrometer using an aqueous flat cell. The coupling constants are given relative to the peroxyamine disulfonate ion-radical ($a_N = 13.05$ G), which was prepared by the standard method¹³. The coupling constant values are accurate to ± 0.1 G.

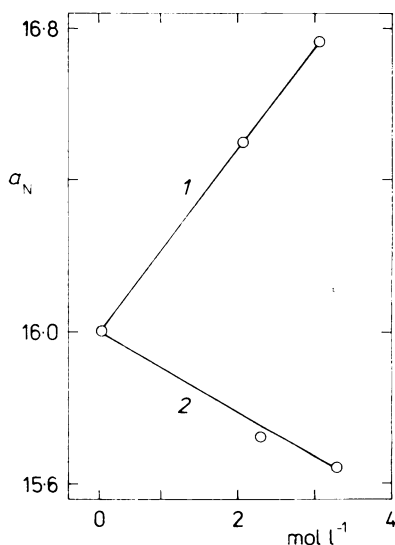


FIG. 1

Dependence of the hyperfine coupling constant a_N of diethylamine nitroxide in aqueous solution on the concentration of 1 KBr, 2 tetraethylammonium bromide

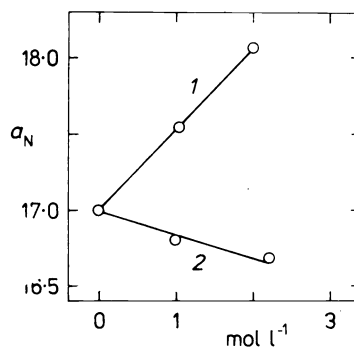


FIG. 2

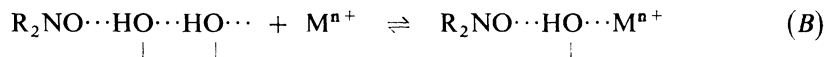
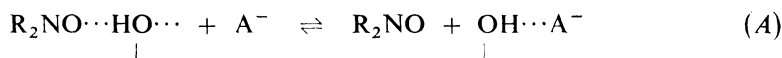
Dependence of the hyperfine coupling constant a_N of piperidine nitroxide in aqueous solution on the concentration of 1 KBr, 2 tetraethylammonium bromide

RESULTS AND DISCUSSION

The values of a_N for *I* and *II* are plotted in dependence on the concentrations of the electrolytes added in Figs 1 and 2.

A free radical can undergo π -electron spin density redistribution if the solvent environment is changed¹⁴, for instance, due to changes in the hydrogen bonding. The solvent effect on the coupling constant depends on the location of the nucleus in the radical and on the functional relationship between the spin density and the hyperfine coupling constant.

Jackson and coworkers¹⁵ studied the effect of addition of electrolytes on the a_N value of di-tert-butyl nitroxide in aqueous solution, and discussed the dependences in terms of the equilibria (A) and (B).



The first equilibrium is associated with a loss/gain of hydrogen bonds to the nitroxide oxygen atom; the second reaction is associated with the formation of solvent shared units involving the cation, which results in changes in the hydrogen bonding strength. The authors suggested that anions compete with the $\text{R}_2\text{NO}\cdot$ molecules for OH groups, thus causing a decrease in the a_N value, whereas cations act indirectly as a source of OH groups.

In our study we observed that for *I* and *II* the a_N values increased with increasing concentration of KBr and that the replacement of KBr by TEABr resulted in a decrease in a_N . This can be well understood in terms of equilibria (A) and (B). For *III*, the addition of KBr as well as TEABr induced a large increase in the a_N value, viz. from 16.6 G in water to 20.75 G in the presence of the salt in a concentration of 3 mol l⁻¹.

The difference between the behaviour of the acyclic and cyclic nitroxides can be explained as follows. The hydrogen bonding with the NO group gives rise to a partial positive charge of the nitrogen atom. In the acyclic nitroxides, the back side of the positively charged nitrogen atom is available for interaction with the solvent. In cyclic amines such as pyrrolidine, the back side of the nitrogen atom is sterically shielded by methylene groups, which prevents interaction of this side with the environment. As a result, the increase in the a_N value in such medium will be higher for cyclic amines than for acyclic amines. The ring size is, naturally, an important parameter with respect to the shielding of the back side of the nitrogen atom: the smaller the size, the more extensive the shielding and the larger the increase in the a_N value.

The author wishes to thank Prof. Basil H. Al-Sader for fruitful discussions and Mr Salih Al-Ali of the University of Basrah for running the ESR spectra.

REFERENCES

1. Wieland J., Offenbacker M.: *Chem. Ber.* **47**, 2111 (1914).
2. Stone E. W., Maki A. H.: *J. Chem. Phys.* **36**, 1944 (1962); *J. Am. Chem. Soc.* **87**, 454 (1965).
3. Gomgh T. E., Symons M. C. R.: *Trans. Faraday Soc.* **62**, 269 (1966).
4. Claxton T. A., Oakes J., Symons M. C. R.: *Trans. Faraday Soc.* **63**, 2115 (1967).
5. Jolicoeur C., Friedman H. L.: *Ber. Bunsenges. Phys. Chem.* **76**, 248 (1971).
6. Jolicoeur C., Friedman H. L.: *J. Solution Chem.* **3**, 15 (1974).
7. Lim Y. Y., Smith E. A., Symons M. C. R.: *J. Chem. Soc., Faraday Trans. 1*, **72**, 2876 (1976).
8. Stone T. J., Buchman T., Nordio P. L., McConnel H. M.: *Proc. Natl. Acad. Sci. U.S.A.* **54**, 1010 (1965).
9. Briere R., Ranat A., Ray P., Tchoubar B.: *J. Chim. Phys.* **63**, 1575 (1966).
10. Alibahai H., Hudson A., Hussain H. A.: *J. Chem. Soc.* **1969**, 678.
11. Hussain H. A., Kuder W. A. A.: *Collect. Czech. Chem. Commun.* **51**, 2433 (1986).
12. Hudson A., Hussain H. A.: *J. Chem. Soc., B* **1968**, 251.
13. Moser W., Howie R. A.: *J. Chem. Soc., A* **1968**, 3029.
14. Gendell J., Freed J. H., Fraenkel G. K.: *J. Chem. Phys.* **37**, 2832 (1962).
15. Jackson S. E., Smith E. A., Symons M. C. R.: *Faraday Discuss. Chem. Soc.* **1978**, 173.

Translation revised by P. Adámek.