Effects of Temperature on the ESR Spectra of the Radical Anion of Dihydrophenazine in Trifluoroacetic, Trichloroacetic and Acetic Acids

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The radical anion of dihydrophenazine was prepared in high vacuum in trifluoroacetic, trichloroacetic and acetic acids. When the temperature was decreased, the triplet with the largest coupling constant in the ESR spectrum disappeared and the intensities of the lines due to the nitrogen nuclei diminished noticeably in all three solvents. The effects are caused by a proton exchange reaction with the solvent.

Under acidic conditions, two protons are transferred to the phenazine molecule and form coordinate bonds with the nitrogens.[1,2] Based on the UV and visible spectra, moreover, it has been proposed that the proton transfers are consecutive reactions and that a mono-protonated species is formed.[3]

The aim of this study was to investigate the protonations, the exchange reaction and the possible change in the conformation of the phenazine radical ion. The solvents, trifluoro-acetic, trichloroacetic, and acetic acids were chosen in order to determine the possible existence of couplings of the fluorine and chlorine nuclei. In the first two solvents radical cations of some aromatic hydrocarbons have been obtained and the solvents have acted as oxidants.[4–6]
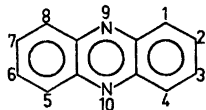
EXPERIMENTAL

The phenazine was from Fluka AG, the tri-fluoro- and trichloroacetic acids from Merck

AG, and acetic acid from Riedel-de Haën AG. All products were of analytical grade. The purity of phenazine was tested gas chromato-graphically.

The samples were prepared in high vacuum in an ampoule made of quartz glass.[4–6]

The ESR spectra were recorded with Varian model E-12 and E-9 spectrometers equipped with Varian variable temperature regulators. Varian 620/L Spectrosystem 100 computer facilities were used for the spectrum simulation.

The UV and visible spectra were recorded with a Beckman DK-2A spectrometer.

The theoretical spin densities were calculated on the Univac 1108 central computer of the Finnish Universities. Bond lengths taken from Pople and Beveridge [8] were used in the INDO calculations.[7]

We were unable to prepare the radical of phenazine with tribromoacetic acid. The same results were obtained with and without thallium (III) trifluoroacetate as oxidizing agent, and thus the solvent alone was used as the oxidant.

RESULTS AND DISCUSSION

The formation of coordinate bonds between two protons and the nitrogen atoms in phena-zine does not give rise to a radical unless the solvent can act as electron acceptor or donor. For instance, RH_2^{2+} and RH^+ do not give any ESR signal, but $RH_2^{\cdot+}$ and $R^{\cdot+}$ have an unpaired electron, the former being an anion radical with π-electron structure and the latter having the structure of a cation radical.

The formation of the dihydrophenazine radical anion (1) and the corresponding radical cation (2) may be written as follows:
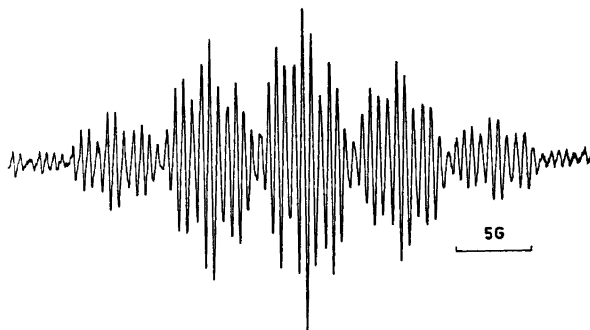
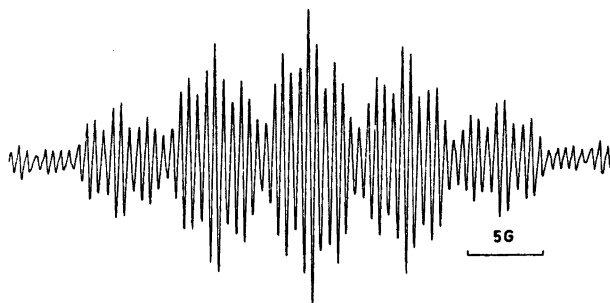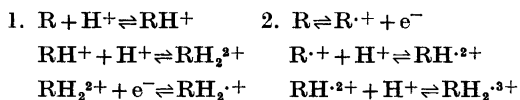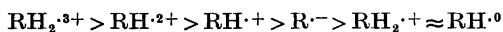*Fig 1.* The ESR spectrum of the radical anion of dihydrophenazine ($RH_2^{\cdot+}$) in trifluoroacetic acid at 338 K.

Fig. 2. The simulation of the ESR spectrum in Fig. 1 based on the coupling constants in Table 1 and line width of 0.12 G.

1. $R + H^+ \rightleftharpoons RH^+$ 2. $R \rightleftharpoons R^{\cdot+} + e^-$

   $RH^+ + H^+ \rightleftharpoons RH_2^{2+}$ $R^{\cdot+} + H^+ \rightleftharpoons RH^{\cdot 2+}$

   $RH_2^{2+} + e^- \rightleftharpoons RH_2^{\cdot+}$ $RH^{\cdot 2+} + H^+ \rightleftharpoons RH_2^{\cdot 3+}$

In strong acids like trifluoro- and trichloroacetic acids, radical cations are usually formed from aromatic hydrocarbons.[5,6]

The radicals $R^{\cdot-}$ and $RH^{\cdot 0}$ might appear as intermediates during the formation of the radical anion of dihydrophenazine, if the acceptance of the electron were the first stage of the reaction and the acceptance of two protons occurred only thereafter.

INDO calculations of the binding energy give the following order for the energies of the planar radicals:

$$RH_2^{\cdot 3+} > RH^{\cdot 2+} > RH^{\cdot+} > R^{\cdot-} > RH_2^{\cdot+} \approx RH^{\cdot 0}$$

The energy differences between the radicals are significant except for the last two radicals. According to the INDO calculations, reaction scheme 2 seems improbable. Fig. 1 shows the ESR spectrum of the radical anion of dihydrophenazine in trifluoroacetic acid at 338 K. Fig. 2 shows the simulation of the same spectrum, based on the coupling constants presented
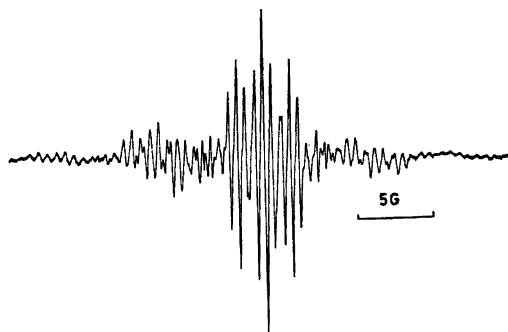

Fig. 3. The ESR spectrum of the radical anion of dihydrophenazine in trifluoroacetic acid at 253 K.

Table 1. Coupling constants (G) of the radical anion of dihydrophenazine. The temperatures are 338, 353 and 323 K, respectively.

Position	CF$_3$COOH	CCl$_3$COOH	CH$_3$COOH	Calculated (INDO)
1,4,5,8	0.53	0.56	0.62	-0.4
2,3,6,7	1.73	1.72	1.71	-0.8
9,10 (N)	6.20	6.12	6.10	7.6
9,10 (H)	6.75	6.70	6.67	-9.3

in Table 1, and Fig. 3 shows the ESR spectrum of the sample at 253 K. In this latter spectrum the innermost peak group has remained practically unchanged, while the outermost peaks have broadened. The higher temperature ESR spectrum of the dihydrophenazine radical anion in trifluoroacetic acid is obtained at room temperature and above. A similar ESR spectrum can be recorded above 353 K in trichloroacetic acid, and above room temperature in acetic acid. Since almost identical ESR spectra are obtained in all three solvents, couplings of the fluorine and chlorine nuclei are excluded.

The coupling constants presented in Table 1 do not differ significantly from those of the radical anion of dihydrophenazine prepared electrolytically in dimethylformamide.[2]

The broadening of the outermost lines might be due to conformational exchange. The protons in positions 9 and 10 of configuration A are both either axial or equatorial, whereas in configuration B, one is axial and the other equatorial.
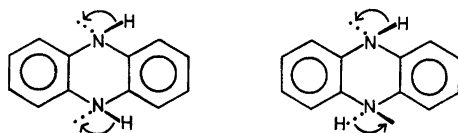
Configuration A   Configuration B

The values of the C$-$N bond in the INDO calculations were 0.137, 0.140 and 0.145 nm, the N$-$H bond was 0.101 nm and the angle CNH was either 109.47 or 120°.[8]

The INDO calculations assign the minimum energy to the planar molecule when the value 0.140 nm is used for the C$-$N bond. Further, according to the INDO calculations, the coupling constants in various conformations with A and B do not deviate significantly from the couplings of the planar molecule when the bond lengths 0.140 and 0.145 nm are used. On the other hand, when the bond length of 0.147 nm is used, all coupling constants in the various conformations are changing to such an extent that all lines in the ESR spectrum should broaden, not just the outermost lines. Thus, changes in the conformations, as exhibited by the INDO calculations, do not explain the broadening of the outermost lines in the ESR spectrum.

Fig. 4 shows how the lines of the protons in the phenyl rings split into small doublets (0.06 G). The doublet splitting occurs only at lower temperatures, where the coupling of the protons at positions 9 and 10 can no longer be observed and the lines due to the nitrogen nuclei have broadened.

The magnitude of the second order effect [9] is only about 0.014 G and the separation of the

Fig. 4. The ESR spectrum of the radical anion of dihydrophenazine in trifluoroacetic acid at 263 K. The lines of the central group are split into small doublets.

modulation side bonds is about 0.036 G for 100 kHz.[9]

Based on energy calculations alone the radical RH·[0] could appear, but the INDO calculations show that its presence would cause considerable changes in all coupling constants. A similar doublet has been observed for the radical cation of pentacene both in trifluoro- and trichloroacetic acids.[6]

The appearance of the doublet is obviously due to the formation of an ion pair between the acid dimer (HAA⁻) and the radical ion. Thus the remaining proton of the acid dimer is observed as a doublet in the ESR spectrum, and a proton exchange reaction between it and the protons at the 9,10 positions takes place. At higher temperatures the reaction is so fast that neither the line broadening nor the doublet can be observed.

Shortly after preparation the UV and visible spectra of the same sample in trifluoroacetic acid at room temperature shows peaks at λ(max) 385 and 260 nm and after a few hours also at 450 and 430 nm, which are consistent with literature values [2] and are due to the mono- and diprotonated forms of phenazine. At room temperature, however, the ESR spectrum shows only one radical; hence the monoprotonated form of phenazine is not a radical.

REFERENCES

1. Schieser, D. and Zvirblis, P. *J. Chem. Phys. 36* (1962) 2237.
2. Barton, B. and Fraenkel, G. *J. Chem. Phys. 41* (1964) 1455.
3. Bailey, D., Roe, D. and Hercules, D. *J. Am. Chem. Soc. 90* (1968) 6291.
4. Eloranta, J. and Sippula, A. *Finn. Chem. Lett.* (1975) 170.
5. Eloranta, J. and Ijäs, M. *Finn. Chem. Lett.* (1975) 174.
6. Eloranta, J. and Kolehmainen, S. *Finn. Chem. Lett.* (1976). *In press.*
7. Hase, H. and Schweig, A. *OCPE Program 261* (1973).
8. Pople, J. and Beveridge, D. *Approximate Molecular Orbital Theory*, McGraw-Hill, New York 1970.
9. Wertz, J. and Bolton, J. *Electron Spin Resonance*, McGraw-Hill, New York 1972, pp. 446, 454.
10. Elson, J. and Kochi, J. *J. Am. Chem. Soc. 95* (1973) 5061.