

present derivatives are under further study in these laboratories.

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Electron Spin Resonance Spectra of Different Solvates of *m*-Nitrophenol Negative Ion in a Mixed Solvent

Sir:

It is well known that e.s.r. spectra of many organic radicals and radical ions in solution are very sensitive to solvent composition.¹ Electron-nuclei spin-spin

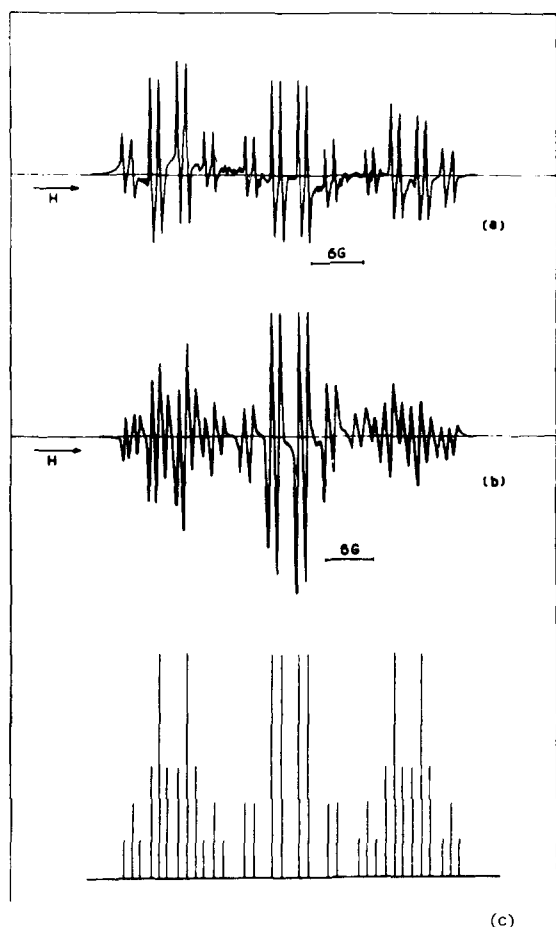
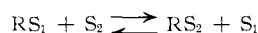


Fig. 1.—E.s.r. first derivative spectrum of *m*-nitrophenol ion in 50% water-DMF with electrolyte 0.1 *M* NEt_4ClO_4 : a, at room temperature; b, same at 0°; c, reconstruction of spectrum b based on superposition of the two spectra arising from two species in 1:1 ratio and differing only in a_N .

coupling constants undergo conspicuous variations with solvent and the behavior has been explained² through the formation of "solvates" or "complexes" in which the radical is linked to one or more solvent molecules as for example in the model reaction



where R is the radical and S_1 and S_2 are the two solvents.

The e.s.r. spectra obtained up to now in these cases always presented hyperfine patterns indicating coupling

constants corresponding to weighted averages of the values existing in the pure solvents.

During the course of an investigation of the e.s.r. spectra of *m*-nitrophenol negative ion produced by electrolysis in water-dimethylformamide (DMF) mixtures we have obtained spectra which are very clearly due to the superposition of two radical species which we logically identify with two different solvates.

Figure 1a shows the spectrum of *m*-nitrophenol anion in an approximately 50% mixture of water and DMF. The hyperfine pattern is due to a major triplet arising from the nitrogen coupling of 14.6 gauss; this splits into quartets (intensity 1:3:3:1) due to three almost equivalent protons and furthermore into doublets, the last splitting arising from the remaining proton with the smallest coupling constant.

The pattern remains practically the same in going from pure water to pure DMF, the only feature influenced being the main nitrogen splitting which decreases smoothly from 14.6 gauss in pure water to 12.3 gauss in pure DMF. The proton coupling constants are not influenced much by solvent composition at least up to almost unit DMF mole fraction where differences are noted among the three almost equivalent protons.

Figure 1b shows the spectrum obtained from the same solution of Fig. 1a at a lower temperature. The pattern of the central group is not affected but the two side groups now have a larger number of lines. The reconstruction of Fig. 1c shows how the pattern is easily explained on the basis of the superposition of two spectra of the type of Fig. 1a differing only in the major nitrogen splitting. Some of the lines of the side groups have a greater width because the overlapping is not so perfect as postulated in the reconstruction. We note also that in both spectra the high field group lines are wider than the corresponding low field ones as is currently observed in many cases.³

It is clear from this experiment that, in the case of sufficiently large differences among some coupling constants of the two alleged "solvates" RS_1 and RS_2 , it is possible to obtain conditions of sufficiently low rate of exchange among the two species such that the two spectra can be detected at the same time. Further details on this phenomenon and a comprehensive quantitative discussion will be published shortly.

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Novel C-4 Modified Tetracycline Derivatives

Sir:

The reaction of amphoteric tetracycline 1 with *N*-chlorosuccinimide to yield 11a-chlorotetracycline-6,12-hemiketal 2 has been reported.¹ A less than drastic change in chlorination conditions—treatment of tetracycline hydrochloride with *N*-chlorosuccinimide in water—leads to the isolation of a drastically different product, 4-oxo-4-dedimethylaminotetracycline 4,6-hem-

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(2) J. Gendell, J. H. Freed, and G. K. Fraenkel, *ibid.*, **37**, 2832 (1962).