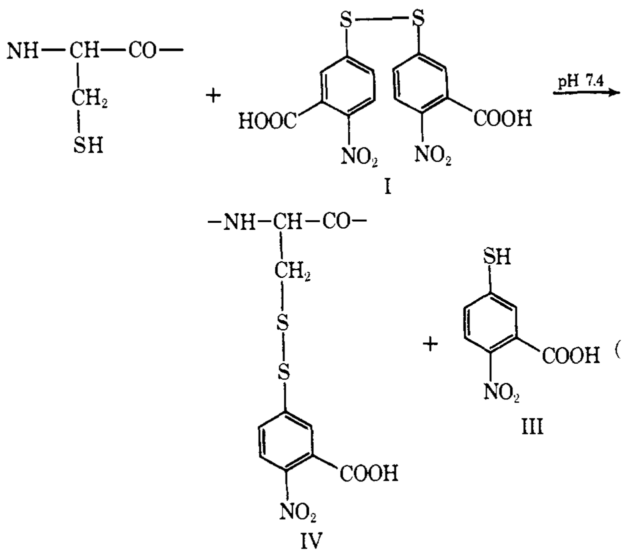
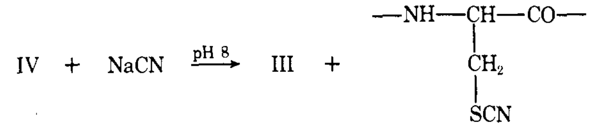


(3)



(4)

cleavage of peptide chains at the modified sites: (1) by cyclization to *N*-acyl-2-iminothiazolidine-4-carboxamide derivatives, followed by splitting of the *N*-acyl bond, as in the cyanide cleavage of cystine peptides;[5,6] and (2) *via* elimination of thiocyanate to form dehydroalanine residues.[14] Studies in both directions are now in progress. Again, S-cyanylation with ^{14}C-NTCB is advantageous for studying the cleavage reactions, in following either the appearance of radioactive 2-iminothiazolidine peptide derivatives or the eliminated radioactive thiocyanate.

Acknowledgment. We wish to thank Professor A. Nassner for helpful discussions. The work was supported by Grant No. AM-5098 from the U. S. Public Health Service.

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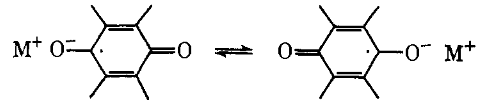
Detection of the Free Durosemiquinone Anion by Electron Nuclear Double Resonance Induced Electron Spin Resonance[1]

Sir:

In recent years there has been considerable interest in the structure and stability of the ion pair formed by the reaction of an alkali metal with duroquinone in ether solutions. The esr spectrum of the paramagnetic compound obtained can often be explained in terms of a rapidly equilibrating tight ion pair of the form



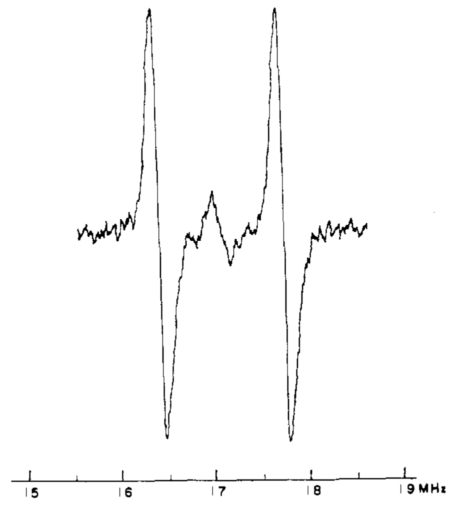


Figure 1. The high-frequency half of the endor spectrum of durosemiquinone at −78°.

the exact nature of the spectrum depending on the metal ion, the solvent, and their effects on the intramolecular ion-exchange rate. It has been suggested[2] and disputed[3] that for the anion formed from sodium or potassium in 1,2-dimethoxyethane (DME) solution, an additional solvent-separated ion pair or free ion must also be present to explain the entire temperature dependence of the esr spectrum.

While the low-temperature endor spectrum of the radical prepared with potassium in DME at low temperature shows the two pairs of lines corresponding to the two inequivalent sets of six protons observed in the esr spectrum of the radical under these conditions, careful investigation of the spectrum has shown an additional much weaker pair of lines with a coupling constant intermediate to those of the strong lines.[4a,b] The high-frequency half of a typical such endor spectrum is shown in Figure 1. Because the *g* value of the radical species responsible for the weak lines is not necessarily the same as that for the strong ones, the amplitude of the low-frequency magnetic field modulation has been adjusted to extend over the entire esr spectrum rather than just over the most intense line, as is normally done in endor experiments. This results in a substantial (>4) loss in the signal-to-noise ratio for the strong lines, but, we believe, more reliable intensity ratios.

To elucidate the structure of the radical responsible for the weak endor line, we have performed an endor-induced esr experiment.[5] The experiment is done by irradiating the sample at the frequency of the first-derivative maximum of an endor line and then sweeping the dc magnetic field through the esr resonance condition while monitoring the endor signal intensity. The resulting spectrum appears similar to that of the esr spectrum of the radical whose endor is being irradiated but exists only because of this rf irradiation. Figure 2 shows the endor-induced esr spectrum obtained at

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Research Foundation of the State University of New York for support of this research.

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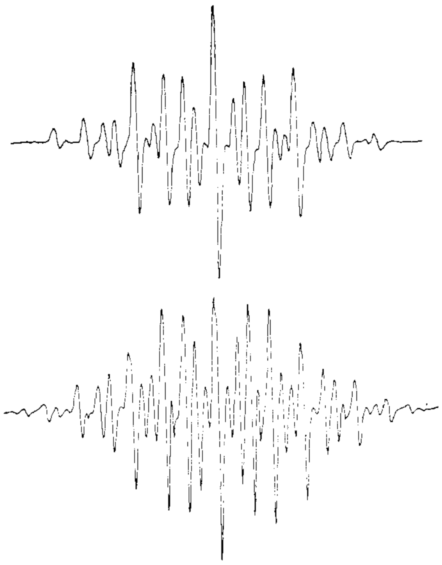

Figure 2. (Upper) The endor-induced esr spectrum of durosemiquinone from irradiation at 16.5 MHz. (Lower) The esr spectrum of durosemiquinone at −78°.

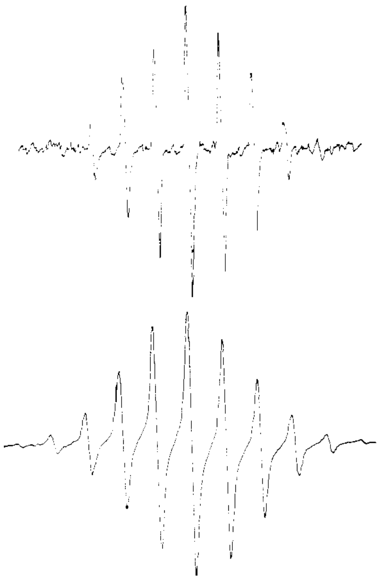

Figure 3. (Upper) The endor-induced esr spectrum of durosemiquinone from irradiation at 17.1 MHz. (Lower) The esr spectrum of durosemiquinone at +80°.

−78° by irradiating the lower frequency strong endor line at 16.5 MHz and the normal esr spectrum obtained at that temperature. Figure 3 shows the spectrum obtained under identical conditions except that the rf irradiation frequency was 17.1 MHz, that of the weak endor line. This spectrum is strikingly similar to the normal esr spectrum of the free ion or rapidly equilibrating ion pair obtained at high temperature, as can be seen from the esr spectrum taken at +80° also shown in Figure 3. Thus we believe there is a substantial amount of free ion present even at −78°. If the relative endor enhancements for the two radicals are the same, then the ratio of ion pair to free ion at −78° is about ten for a solution 10^{-3} *M* in durosemiquinone.

Another possible origin of the weak endor line is that it arises from a sodium durosemiquinone ion pair, the sodium impurity being introduced through the use of Pyrex apparatus.[6] We have prepared the radical with sodium–potassium alloy and the esr spectrum is identical with that in Figure 2, indicating that the ion-exchange equilibrium strongly favors potassium, making small amounts of sodium undetectable by esr or endor. Also, since no alkali metal splittings are observed in Figure 3, we believe our spectrum is that of the free ion. Preliminary measurements indicate that ΔH for the ion-pair dissociation reaction is negative, contrary to the previous suggestion;[2] however, the suggestion by these authors of the presence of the free durosemiquinone radical is confirmed.

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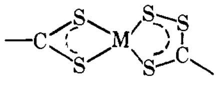
Structural Characterization of Tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) Bromide. A Ni–S_6 Complex with Unusual Chemical Properties

Sir:

Studies of nickel(II) dithiolates by ourselves[1,2] and others[3–5] have led to the conclusion that oxidation produces compounds which may be formulated as ligand-oxidized species. This is especially true[3] with complexes of the dithioaromatic acids[2] where oxidation has been shown to produce[6] a planar nickel(II) complex in which one of the ligands contains S_2 incorporated into a chelate ring (I). While the "extra" ligand sulfur atoms are best added by oxidation with sulfur or polysulfides, bromine or iodine oxidation of the anionic 1,1-dithiolato complexes[7] also produces sulfur-rich species, presumably by destructive oxidation of some of the ligand. Thus we were skeptical of the formulation suggested by Brinkhoff, *et al.*,[8] for the product obtained by the bromine oxidation of bis(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(II), $Ni(Bu_2dtc)_2$, in CCl_4. These authors[8] described the material as tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide, $Ni(Bu_2dtc)_3Br$, from their measurement of the physical and chemical properties of the material. Recently Nigo, *et al.*,[9] claimed the product of bromine oxidation of $Ni(Et_2dtc)_2$ (Et = ethyl) in $CHCl_3$ to be $Ni(Et_2dtc)_2Br_2$. Neither group apparently succeeded in producing crystallized material with a reproducible melting point.



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