

ported between the metal plates of a conventional cell. The region between 65 and 135 cm^{-1} was scanned with a Perkin-Elmer Model 301 double-beam spectrometer.² Only one broad band was found and it was centered at $112 \pm 1 \text{ cm}^{-1}$.

No assignment of the four low-frequency fundamentals will be given here. However, one may note that the band is coincident with one of the three Raman lines of the liquid found in this region³ and hence arises from an E' mode. It is also likely that it corresponds to the single band of the gas found⁴ recently at 104 cm^{-1} , the frequency difference being associated with the phase difference.

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Intramolecular Hydrogen Bonding in ESR Spectra*

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IT is well known that naphthazarin (1,4-dihydroxy-5,8-naphthoquinone) and quinizarin (1,4-dihydroxy-9,10-anthraquinone) exhibit intramolecular hydrogen bonding.¹ We have performed electron spin resonance studies which show that the anion radicals of these compounds also contain hydrogen bonds and that the splitting constants have several interesting and unexpected characteristics.

The anion radical of naphthazarin was obtained by air oxidation of a weakly basic solution of 1,4,5,8-tetrahydroxynaphthalene in both water and ethanol. The formation of the radical depended quite critically

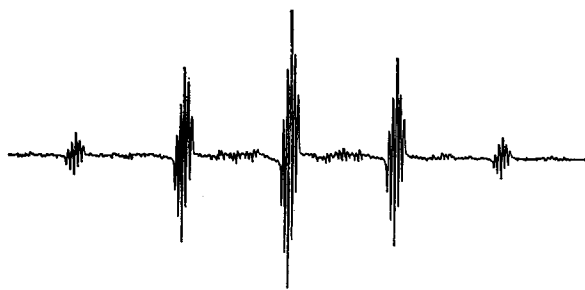


FIG. 1. Derivative of the ESR absorption spectrum of the anion radical formed by oxidation of naphthazarin in weakly basic D_2O solution. The lines of low intensity between the major components arise from an unknown by-product of the oxidation.

on the concentration of base, and it decayed with a half-life of less than $\frac{1}{2}$ h. The spectrum shows five sets of triplets with a separation of 2.36 G between sets and with approximate relative amplitudes of 1:4:6:4:1. The lines of the triplets are spaced 0.59 G apart, and have approximate relative amplitudes of 1:2:1. The spectrum thus arises from one set of four equivalent protons and another set of two equivalent protons. The linewidths in spectra produced under a variety of conditions were all extremely narrow, being only about 30 mG between points of extreme slope. The most reasonable structure for the radical is clearly that of the naphthazarin anion with two hydrogen bonds, one between each of the two pairs of neighboring oxygen atoms. This structure has been confirmed by carrying out the air oxidation of the tetrahydroxy compound in D_2O . As may be seen from Fig. 1, the major quintet splitting is retained in the spectrum, but the triplets are replaced by a second set of quintets with approximate relative amplitudes 1:2:3:2:1. The splitting constants are 2.34 and 0.079 G, respectively.²

The existence of four ring protons with equal splittings, and of two hydrogen-bonded protons with equal splittings, does not necessarily imply that the hydrogen atoms in the hydrogen bonds are located on the twofold symmetry axis passing midway between the nearest-neighbor oxygen atoms. Although such a structure would be consistent with the ESR spectra, the same equivalences would be observed if the protons in the hydrogen bonds were undergoing rapid transitions between two equilibrium positions on either side of the symmetry axis.³

If the environments of the protons and deuterons in the hydrogen bonds were the same, the ratio of the splitting constants would be determined only by the magnetic properties of the two nuclei, and the proton splitting constant would be⁴ 6.514 times the deuteron splitting constant. But the observed ratio here is 7.4, or 14% too high, indicating an unusually large isotope effect. The small difference of 0.02 G found for the ring-proton splittings in the protonated and deuterated spectra may thus be especially significant, but additional studies are necessary to verify that 0.02 G is within the limit of accuracy of the data. Although it is not possible at present to determine what characteristics of the hydrogen bond cause this large isotope effect, further investigations may be helpful in understanding the nature of hydrogen bonds.

A quite stable radical was also prepared by air oxidation of 1,4,9,10-tetrahydroxyanthracene in alkaline ethanolic solution. The spectrum had linewidths of 30 mG and was readily interpreted as resulting from the splittings of two different pairs of equivalent protons with splitting constants 2.10 and 0.92 G, and one group of four equivalent protons with a splitting of 0.53 G. The presence of splittings from only eight protons indicates again that the radical is present as the hydrogen-bonded anion radical of quinizarin. A comparison with

the results of Adams *et al.*⁵ on the trinegative anion radical of quinizarin containing no protons bonded to the oxygen atoms suggests that the four equivalent protons in the hydrogen-bonded radical ($a^H=0.53$ G) are in the same ring (at positions 5, 6, 7, and 8), and that the two-proton splitting of 2.10 G is attributable to the 2 and 3 positions. We thus tentatively assign the splitting of 0.92 G to the hydrogen-bonded protons. This value is almost twice that of the hydrogen-bonded protons in the naphthazarin radical. Since it is unlikely that the spin densities on the oxygen atoms would be larger in the quinizarin radical than in the naphthazarin radical, the considerably larger splitting in the quinizarin anion is undoubtedly caused by differences in the structure of the hydrogen bonds in the two compounds. Such differences are not unreasonable because in naphthazarin the adjacent pairs of oxygen atoms are equivalent while those in quinizarin are not. Preliminary attempts at obtaining the spectra of the hydrogen-bonded quinizarin radical in H_2O and D_2O have been unsuccessful because of the formation of a strong and stable spectrum of an unknown species.

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² The spectrum of the unprotonated naphthazarin trianion radical has not been observed, but that of the tetrahydroxy cation has been studied by J. R. Bolton and A. Carrington (private communication), who found that the ring-proton splitting was 2.34 G and the hydroxyl-proton splitting 1.43 G.

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Space Charge in Growing Oxide Films. II. Nonhomogeneous Field*

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DEVIATIONS from the equilibrium space charge distribution can occur for a growing oxide film. This was shown in I (reference 1) for a homogeneous field; the corresponding equation for appreciable space charge [Eq. (5)] was given. Numerical solutions to this equation, using the values of the parameters in I, have been obtained to illustrate departures from equilibrium for the potential $\phi(x)$ in addition to concentration $C(x)$, and also the effect of space charge magnitude $C(0)$ and film thickness L on these distributions.

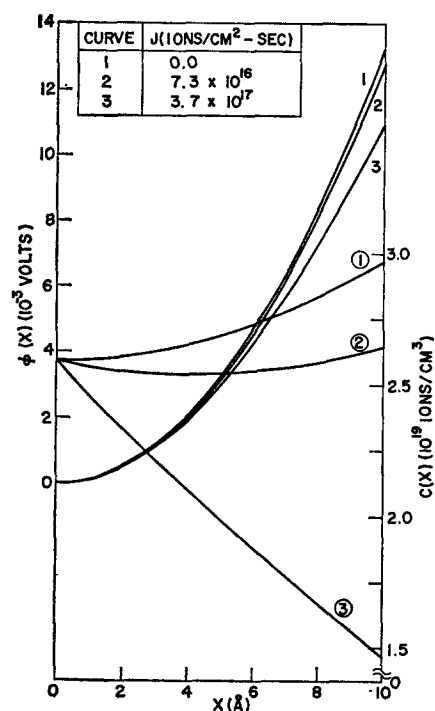


FIG. 1. Potential and space charge distributions for growth with zero surface charge [$\bar{D}C(0)/L=7.28 \times 10^{17}$ ions/cm²·sec].

Figure 1 shows the nonlinearity of $\phi(x)$ due to space charge and a significant dependence of $\phi(x)$ on growth rate for zero surface charge σ . Figure 2 shows the effects of $C(0)$ and L on $\phi(x)$ and $C(x)$ with fixed σ . For the 10-Å curves, the potential is nonlinear for the larger concentration since the space charge

$$Q = \int_0^L C(x) dx$$

is nonnegligible with respect to σ . The marked dependence of $C(x)/C(0)$ on $C(0)$ shows clearly the effect of space charge on distribution. Only a slight dependence of $\phi(x)$ on growth rate occurs because the surface charge predominates. For 100 Å, $C(x)$ differs markedly from the 10 Å curves, and the corresponding $\phi(x)$ is nearly linear. This shows that for a given ratio of σ/Q , the tendency towards double layer² formation increases with L . The field $E(x)$, however, is still nonzero through the film; this is due partially to non-neutrality of the system.

Growth rate and space charge effects thus can be appreciable for a nonnegligible Q with respect to σ for thin films. For neutrality, $Q=\sigma$, so the concept of a characteristic thickness for the space charge region,² outside of which transport occurs by simple diffusion under a uniform concentration gradient, is not rigorously applicable to thin growing films. The use of the argument that macroscopic charge cannot remain permanently in a region of finite conductivity to justify charge neutrality in the bulk of the oxide² is not valid