

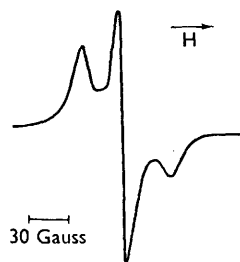
The Electron Spin Resonance Spectra of Aromatic Nitro-radical Anions adsorbed on Catalytic Aluminas

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ELECTRON SPIN RESONANCE spectra of polynitrobenzene anions in both fluid and rigid media, irrespective of whether the radicals are prepared by chemical or electrolytic procedures or by photolysis in alcoholic solution, can be analysed in terms of the interaction of the spin of the unpaired electron with the nuclear spins of two or more nearly equivalent nitrogen nuclei, although in some cases the second nitrogen splitting is masked by an alternating linewidth effect arising from modulation of the hyperfine couplings.¹ On the other hand, the spectra of the protonated form of the anions of mono- and poly-nitrobenzenes, either in fluid solution or in a glass, are characterised by a large hyperfine coupling to only one nitrogen nucleus.^{2,3}

We have now been able to generate a number of the radical anions by a different method⁴ in which electron transfer occurs at the surface of partially dehydrated catalytic aluminas when the parent compound is adsorbed from solution in benzene, cumene, or carbon tetrachloride. The spectra obtained in this way for the radical anions of nitrobenzene, the dinitrobenzenes and 1,3,5-trinitrobenzene are all strikingly similar; the Figure



FIGURE

The electron spin resonance spectrum (first derivative) of *m*-dinitrobenzene anion adsorbed on alumina at 20°C.

shows the spectrum for the adsorbed *m*-dinitrobenzene anion at room temperature. It resembles closely the spectrum reported for the corresponding protonated form in rigid media³ and exhibits an anisotropic coupling of the unpaired electron with only one nitrogen nucleus. By analogy with the solid-state spectrum the two outermost shoulders observed in the Figure are probably parallel hyperfine features giving a value of $A_{\parallel}^N = 32.3$ gauss. The spectrum is insufficiently well resolved to allow A_{\perp}^N to be measured directly, nor can this parameter be calculated from the spectrum in the absence of a value for A_{iso}^N for the anion-surface complex. Inspection of the spectrum shows however that the value of A_{\perp}^N cannot exceed 10.6 gauss because a splitting of greater magnitude could not be concealed in the central line. On this basis A_{iso}^N cannot exceed 17.8 gauss. Values of A_{\parallel}^N and estimated maximum values of A_{\perp}^N are given in the Table for a number of the adsorbed nitro-radical anions. Anisotropic parameters obtained from the solid state for the *m*-dinitrobenzene hydrogen-adduct³ are: $A_{\parallel}^N = 29.0$ gauss; $A_{\perp}^N = 7.6$ gauss; $A_{\text{iso}}^N = 14.8$ gauss.

The value of g_{\parallel} calculated from the outer parallel features using 1,1-diphenyl-2-picrylhydrazyl as reference ($g = 2.0036$) is 2.0027 for the adsorbed *m*-dinitrobenzene anion; g_{av} is 2.0044 (± 0.0003). If the isotropic g -value for the anion-surface complex does not differ greatly from g_{av} for the adsorbed species, g_{\perp} can be estimated from the present results; for the adsorbed *m*-dinitrobenzene anion the value is 2.0052. Values of g_{\parallel} , g_{\perp} , and g_{av} calculated in this manner from the spectra of the adsorbed radical-anions are given in the Table. Corresponding data for the hydrogen-adduct of *m*-dinitrobenzene in an organic glass³ are: $g_{\parallel} = 2.0016$; $g_{\perp} = 2.0061$; $g_{\text{av}} = 2.0046$.

In contrast with the relative instability of the

TABLE

Anisotropic parameters for nitro-radical anions adsorbed on alumina

	A_{\parallel}^N (gauss)	A_{\perp}^N	g_{\parallel}	g_{\perp}	g_{av}
Nitrobenzene radical anion	33.0	≤ 10.6	2.0023	2.0060	2.0048
<i>o</i> -Dinitrobenzene radical anion	32.6	≤ 9.1	2.0018	2.0057	2.0044
<i>m</i> -Dinitrobenzene radical anion	32.3	≤ 10.6	2.0027	2.0052	2.0044
<i>p</i> -Dinitrobenzene radical anion	29.8	≤ 8.9	2.0020	2.0056	2.0044
1,3,5-Trinitrobenzene radical anion	30.9	≤ 10.4	2.0025	2.0052	2.0043

nitro-anions and their corresponding hydrogen adducts in fluid solution, the adsorbed anions are remarkably stable, the radical-anion of 1,3,5-trinitrobenzene, for example, being observable for prolonged periods at 150°C. Change of solvent, or its complete removal, produced no detectable change in the spectra of the adsorbed anions.

The conclusion to be drawn from the present results is that the adsorbed anion-surface complex behaves essentially as an ion-pair in which the unpaired electron is almost wholly localised on one of the nitro-groups. This strong perturbation of the spin density in the adsorbed radical-anion may

result from powerful field gradients at the defect site in the alumina surface responsible for the adsorption process and for the electron-transfer resulting in radical formation. The fact that the mono-, di-, and 1,3,5-tri-nitrobenzene anions all give closely similar spectra when adsorbed on the alumina surface makes an alternative explanation of the present results based on alternating linewidths^{1c} less likely. The insensitivity of the spectra to change of solvent, or its absence, and to change in temperature accords with this view.

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