

Electron Spin Resonance Data for Mono- and Di-anions of *m*-Dinitrobenzene: Radiation-induced Addition of Two Electrons at 77 K

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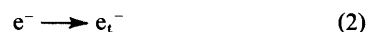
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Exposure of dilute solutions of *m*-dinitrobenzene or *s*-trinitrobenzene in methyltetrahydrofuran to ^{60}Co γ -rays at 77 K gave two species detectable by e.s.r. spectroscopy. One, favoured at low doses, had features characteristic of monoanions with the unpaired electrons primarily localised on one nitro-group. Similar anions were formed from the nitro-derivatives in methanol (CD_3OD). At high γ -ray doses a second species grew in at the expense of the monoanions. These had half-field ($\Delta M_s \pm 2$) transitions characteristic of triplet states, and well defined features in the parallel regions of the anisotropic $\Delta M_s \pm 1$ transitions. These parallel features, which exhibited no resolved hyperfine coupling to ^{14}N were used to estimate average effective separations between the two unpaired electrons, giving values in the region of 5–6 Å. The $\Delta M_s \pm 1$ perpendicular features were poorly defined but gave clear evidence of ^{14}N hyperfine coupling. The (^{14}N) parallel features were better resolved in the $\Delta M_s \pm 2$ transitions, which showed five shoulders indicating two equivalent nitrogen nuclei with about half the coupling of the monoanions. These results are all in accord with the postulate that the species involved are dianions in triplet states. Each unpaired electron must be strongly localised on one nitro-group which cannot be twisted far from the limit of coplanarity. Absence of ^{14}N coupling on the $\Delta M_s \pm 1$ parallel features can then be understood since the ^{14}N parallel axes are perpendicular to the principal axis for the zero-field coupling. The alternative explanation for these results, that solvent radicals are trapped close to the radical anions is considered, but ruled out on the grounds that the $\Delta M_s \pm 2$ features should then be triplets rather than quintets, and because there would be no barrier to chemical reactions between such radicals and the nitrobenzene anions.

It is well established that radiolysis of dilute solutions of substrates in solvents such as methanol or methyltetrahydrofuran (MeTHF) is an excellent method for adding electrons to give radical-anions of the substrates.¹ We established some time ago that nitrobenzenes can be converted into their anions using this procedure.² We showed that the spectra were usually similar to those obtained by freezing solutions of the anions prepared chemically, and that the data could be used to give approximate spin densities on nitrogen.

Recently, Konishi *et al.*³ have shown that for *m*-dinitrobenzene (*m*-DNB) and *s*-trinitrobenzene (*s*-TNB) in MeTHF solution, a triplet-state species can be formed by radiolysis at 77 K. No such species could be obtained from nitrobenzene, or from the *o*- and *p*-dinitro-derivatives. Only the outermost (parallel) features of the $\Delta M_s \pm 1$ transition were resolved, but for both the *m*-dinitro- and *s*-trinitro-derivatives, two pairs of parallel features were detected. This was taken to mean that two different sets of radical-pairs were formed.³ These workers failed to detect e.s.r. features for the monoanions, but established their presence by visible spectroscopy. The anion e.s.r. features would have been completely concealed beneath the intense features for MeTHF radicals. One significant aspect of their results was that the initial rate of formation of the triplet species was much less than that of the radical-anions as gauged by optical spectroscopy.

These results were interpreted in terms of pair-trapping. The possibility that dianions were being formed was briefly considered but dismissed. The phenomenon of pair-trapping of radicals in solids, first observed by e.s.r. spectroscopy in potassium persulphate crystals,⁴ is now well established.⁵ However, it has never previously been postulated for MeTHF systems. In order to explain the specificity of *m*-DNB and *s*-TNB, structure (I) was proposed. This, it was suggested, is such a stable configuration that radical-radical reactions do not occur: for the other nitro-derivatives it was supposed to be efficient. The slow initial growth of the pair-species was explained in terms of the mechanism of reactions (1)–(5).

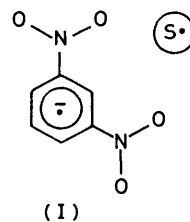


It was supposed that hole migration occurred [reaction (4)] until the cations and anions were close together, the cation then being stabilised by reaction (5), where $\cdot(\text{MeTHF})^+$ is the parent radical-cation, and $\text{MeTHF}\cdot$ is the neutral radical formed by proton transfer.

It occurred to us that these results were better explained in terms of the formation of dianions in their triplet states. We have therefore repeated and extended this work in the hope of differentiating between the two alternative interpretations.

Experimental

The nitrobenzenes were of the best grades available and were used as supplied. Solutions (between 10^{-4} and 10^{-3}M) were degassed *in vacuo* by freeze-thaw procedures, and were frozen as small glassy beads in liquid nitrogen prior to exposure to



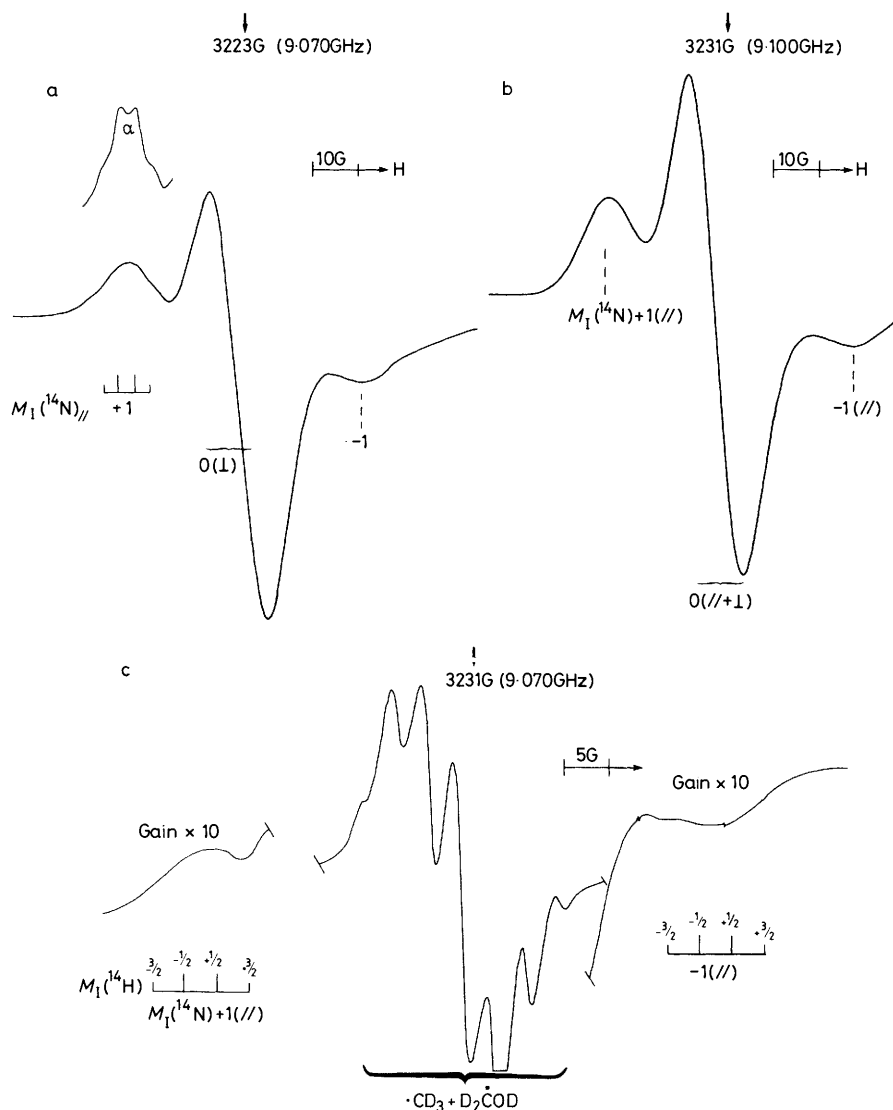


Figure 1. First derivative X-band e.s.r. spectra for dilute solutions of *m*-DNB and *s*-TNB in CD_3OD or MeTHF after low exposure to ^{60}Co γ -rays at 77 K followed by annealing to reduce the concentration of solvent radicals: a, *m*-DNB in MeTHF at 77 K showing features assigned to (*m*-DNB) $^-$ anions. Feature α is the $M_1 + 1$ parallel line measured during the annealing process, showing proton hyperfine lines from three nearly equivalent protons. b, *s*-TNB in MeTHF at 77 K showing features assigned to (*s*-TNB) $^-$ anions. c, *s*-TNB in CD_3OD at 77 K showing features assigned to (*s*-TNB) $^-$: central features are for $\cdot\text{CD}_3 + \text{D}_2\dot{\text{C}}\text{OD}$ radicals

^{60}Co γ -rays at 77 K in a Vickrad source. Doses varied from 0.1 to 6 Mrad.

E.s.r. spectra were measured with a Varian E-109 X-band spectrometer calibrated with a Hewlett-Packard 5246L frequency counter and a Bruker B-H12E field probe, which were standardised with a sample of diphenylpicrylhydrazyl. Samples were annealed until the central e.s.r. features due to MeTHF radicals were lost or reduced, and then recooled to 77 K for measurement.

Results and Discussion

Monoanions.—The e.s.r. spectra for the monoanions (Figure 1 and Table 1) establish that for both *m*-DNB and *s*-TNB the excess electrons are confined to only one nitro-group. Thus broad triplets were obtained, characteristic of mononitro-derivatives, each of the outer (parallel) components being split into quartets from three nearly equivalent protons. The perpendicular coupling is small, and is lost in the width of the

intense central component. This is typical of solid-state e.s.r. spectra for aromatic nitro-anions. This is, perhaps, surprising since the LUMO for both these molecules is normally symmetric so that two or three equivalent nitrogen nuclei would have been expected. However, we have previously shown that relatively minor perturbations from cations or even protic solvent molecules are sufficient to move the anions of *m*-DNB from the symmetric to the antisymmetric state.⁶⁻⁸ The situation envisaged is shown schematically in Figure 2. These are two equivalent asymmetric orbitals, each centred on one of the two nitro-groups. We suggest that in the present examples, the perturbations introduced by the added electron sets in preferably around one nitro-group. This is expected for methanolic solutions since hydrogen-bonding develops readily at 77 K when anions are formed from neutral molecules,⁹ and marked linewidth alternation is exhibited by fluid solutions.^{7,8} It is less clear that the asymmetric structure should be favoured in MeTHF solution and we have looked carefully for a switch to the thermodynamically favoured symmetric structure on

Table 1. E.s.r. parameters for mono- and di-anions of *m*-dinitrobenzene and *s*-trinitrobenzene at 77 K

Anion	Solvent	Hyperfine coupling constants (G) ^a			Zero-field splitting (G) ^a	
		¹⁴ N	¹⁴ N _⊥	¹ H	D	D _⊥
<i>(m</i> -DNB) ⁻ ^b	MeTHF	27 (1N)	0 ± 3	ca. 3.5 (3 H)		
	CD ₃ OD	30 (1N)	0 ± 3	ca. 3.5 (3 H)		
<i>(m</i> -DNB) ²⁻	MeTHF	13 (2N) ^d	0 ± 3	<i>e</i>	363	ca. 182
	MeTHF ^c	<i>e</i>	<i>e</i>	<i>e</i>	350 + 295 ^g	<i>e</i>
<i>(m</i> -DNB) ²⁻	CD ₃ OD	15 (2N) ^d	0 ± 3	<i>e</i>	240	ca. 120
<i>(s</i> -TNB) ⁻	MeTHF	27 (1N)	0 ± 3	ca. 3.5		
	CD ₃ OD	29 (1N) ^f	0 ± 3	ca. 3.5		
<i>(s</i> -TNB) ²⁻	MeTHF	13 (2N) ^d	0 ± 3	<i>e</i>	463	ca. 232
	MeTHF ^c	<i>e</i>	<i>e</i>	<i>e</i>	458 + 273 ^g	<i>e</i>
	CD ₃ OD	15 (2N) ^d	0 ± 3	<i>e</i>	284	ca. 142

^a G 10⁻⁴ T. ^b DNB = dinitrobenzene, TNB = trinitrobenzene. ^c Ref. 3. ^d Based mainly on ΔM_s 2 transition. $A(^{14}\text{N}) = 0$ on D_{||} features
^e Not resolved. ^f Possible 2N species, see text. ^g Assigned to separate species in ref. 3.

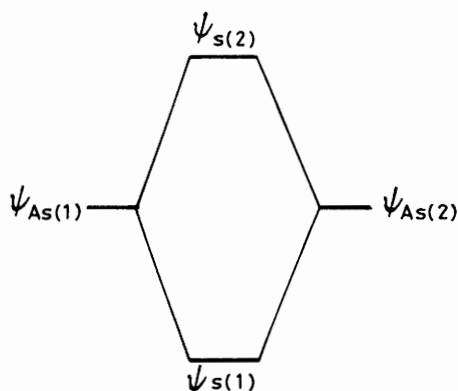


Figure 2. Combination of the ground state SOMO ($\psi_{s(1)}$) for (*m*-DNB)⁻ and the low-lying excited state ($\psi_{s(2)}$) to give two equivalent asymmetric levels ($\psi_{M(1)}$ and $\psi_{M(2)}$) which are selected in the present study on the addition of either one or two electrons

annealing, to no avail. The spectra leave no doubt that, for both compounds, the first formed structure is one having an asymmetric wavefunction for the HOMO (Figure 1).

The Triplet Species.—As stressed by Konishi *et al.*³ the e.s.r. spectra for these species leave no doubt that they are triplets. The issue is purely one of identification: are they radical-pairs³ or are they dianions?

Our results are not identical with those already published (Table 1). In particular, we failed to detect the inner shoulders separated by 295 G reported for *m*-DNB in MeTHF.³ We do not understand this difference. We have been able to get further details of the $\Delta M_s \pm 1$ transitions, and, as indicated in Figure 3, have obtained some hint that the 'perpendicular' features include ¹⁴N hyperfine coupling. This idea also accommodates the inner features found for *s*-TNB by Konishi *et al.*³ However, clear evidence for ¹⁴N hyperfine coupling is shown by the $\Delta M_s \pm 2$ transitions (Figure 4). This was not resolved in the previous study.³ The zero-field splitting is not present in these half-field transitions, so the spectra are dominated by the ¹⁴N features. As with the monoanions, only the parallel features are resolved, but in these spectra there are five shoulders, indicating two equivalent nitrogen nuclei. The splitting is about half those for the monoanions, indicating fast exchange, as expected for the doubly charged anions.

This constitutes the strongest evidence in favour of the concept that the triplet-state species are doubly charged anions. The radical-pair model (I) would exhibit coupling to

Table 2. Mean separation (*r*) between the unpaired electrons for the dianions estimated from the zero-field splitting parameters

Dianion-solvent	(<i>m</i> -DNB) ²⁻ -MeTHF	(<i>m</i> -DNB) ²⁻ -CD ₃ OD	(<i>s</i> -TNB) ²⁻ -MeTHF	(<i>s</i> -TNB) ²⁻ -CD ₃ OD
<i>r</i> /Å	5.3	6.1	4.9	5.8

only one coupled ¹⁴N nucleus, as for the mono-charged anion. In slow exchange the hyperfine coupling should be the same, whilst in fast exchange half the normal value should be obtained. The fact that five rather than three features are seen strongly supports our spectral interpretation.

Structure.—Here we consider what is to be expected if a second electron is added to the monoanions. Since the first electron is strongly confined to a single nitro-group, this should also be true of a second electron. Hence a triplet state giving a species with two equivalent nitrogen atoms is to be expected for both substrates. The effect of charge repulsion should be to localise the electrons even more on the two nitro-groups. This is required by the relatively small values of the zero-field parameters. These have been used to derive mean values for the separation between the two unpaired electrons (Table 2). These values require that the two electrons be strongly confined to the nitro-groups since they were both delocalised into the benzene rings the coupling would be much larger. The separation between the two nitrogen atoms is ca. 5 Å, but there is considerable delocalisation onto oxygen, so that, for confined electrons, values between 5 and 6 Å are reasonable. It is not clear why the zero-field splitting for these species in methanol (CD₃OD) is less than those for MeTHF solutions. Probably solvation at oxygen increases the extent of localisation. Even though localisation must be extensive for the species in MeTHF, a small increase can have a disproportionate effect on the zero-field splitting because of the large contribution from electrons delocalised into the benzene rings. That such a shift of spin-density onto NO₂ is induced by solvation is clearly evidenced by the enhanced value of $A_{||}$ (¹⁴N) for the monoanions on going from MeTHF to methanol solutions (Table 1). A measure of the spin-densities on nitrogen for these forms of the monoanions can be obtained from the hyperfine tensor components. Taking reasonable values for A_{iso} from liquid-phase data,⁶⁻⁸ and using the usual procedures,⁵ we get values of ca. 58 and 61% for solutions in aprotic MeTHF and alcohol solvents, respectively.

The degree of localisation must be at least as great for the dianions. The measured values for $A_{||}$ will only be principal

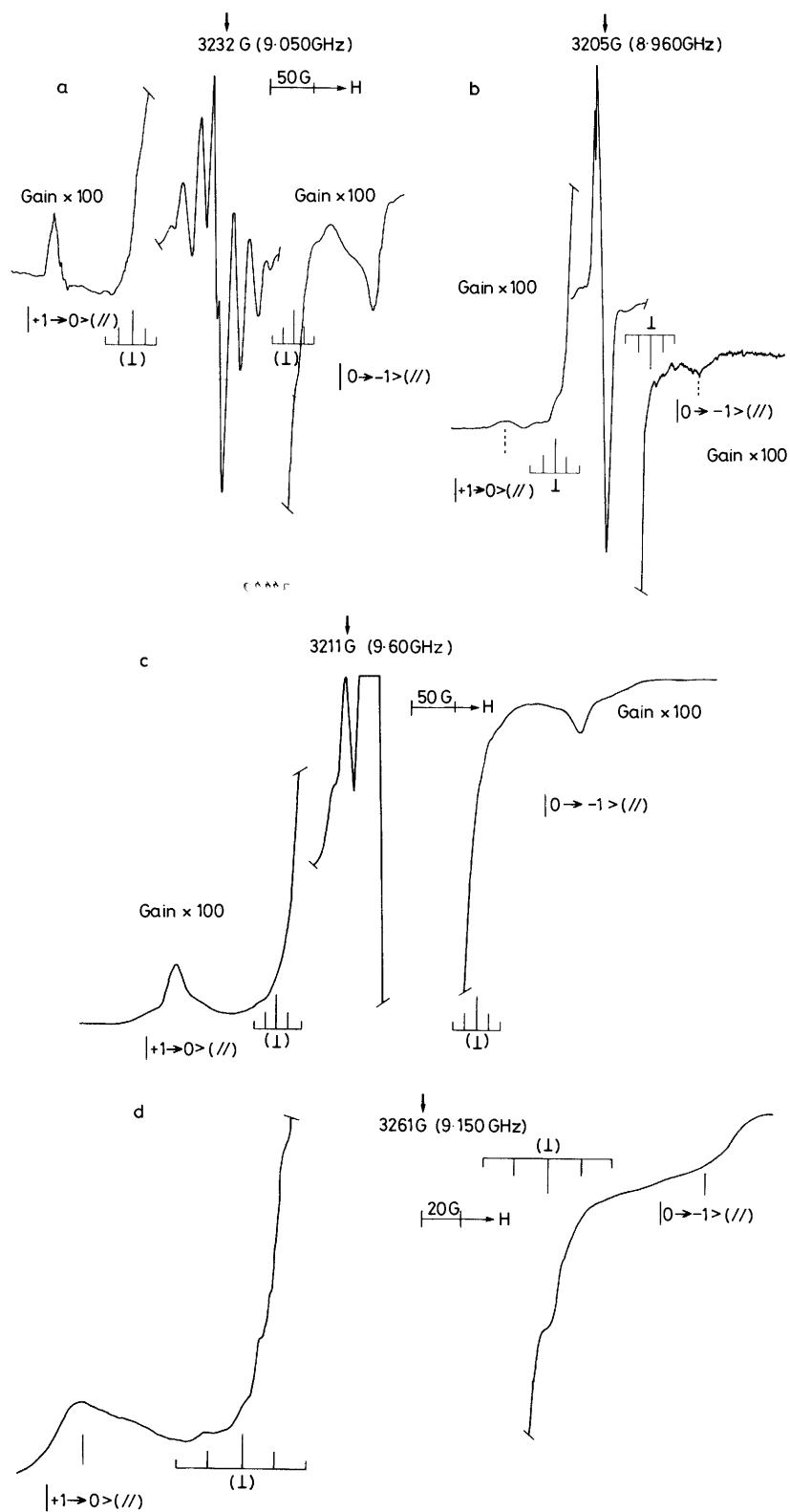


Figure 3. First derivative X-band e.s.r. spectra for dilute solutions of *m*-DNB and *s*-TNB in MeTHF or CD₃OD after prolonged exposure to ⁶⁰Co γ-rays at 77 K, showing outer features assigned to (*m*-DNB)²⁺ or (*s*-TNB)²⁻ anions: only the outer (parallel) features are well defined. a, *m*-DNB in MeTHF; b, *m*-DNB in CD₃OD; c, *s*-TNB in MeTHF; d, *s*-TNB in CD₃OD

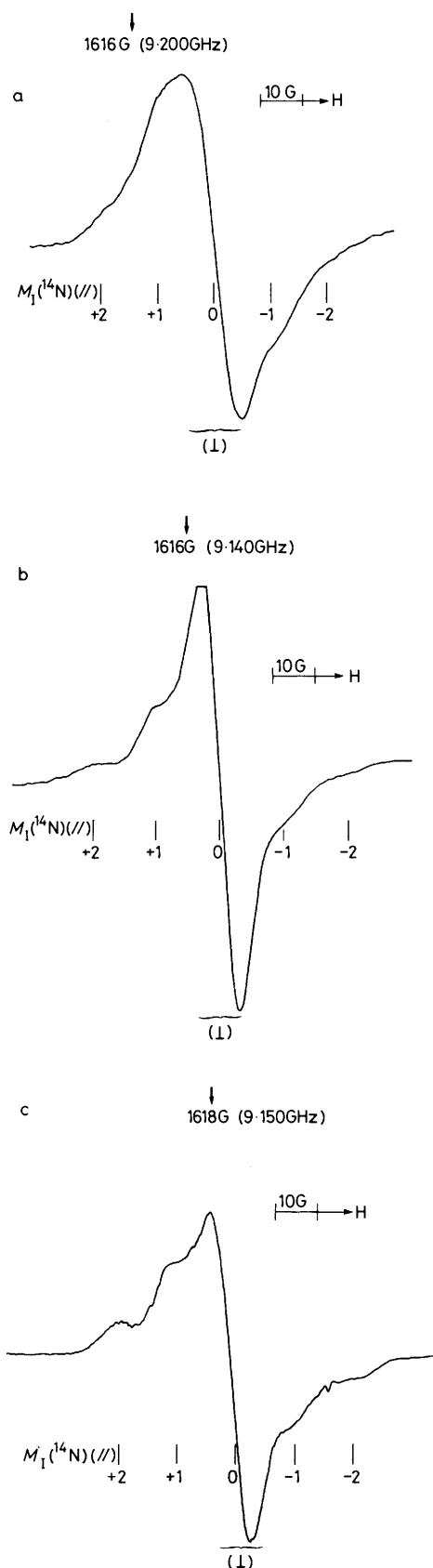


Figure 4. First derivative X-band e.s.r. spectra for dilute solutions of *m*-DNB and *s*-TNB in MeTHF or CD₃OD after prolonged exposure to ⁶⁰Co γ-rays at 77 K, showing half-field transitions ($\Delta M_s \pm 2$) assigned to (*m*-DNB)²⁻ or (*s*-TNB)²⁻. a, *m*-DNB in MeTHF; b, *m*-DNB in CD₃OD; c, *s*-TNB in CD₃OD

values (A_{zz}) if the nitro-groups are coplanar. This is unlikely to be exactly true, so that they represent lower limits for A_{zz} . The extent of localisation can also be gauged, in principle, from the proton hyperfine coupling. If it remains the same as for the monoanions, we expect $A(^1\text{H})$ ca. 3.5 G, but if localisation on the NO₂ groups is increased, this value should fall. The narrowest features are the parallel lines for the $\Delta M_s \pm 1$ transition. No proton splitting can be detected for these lines, so we can place an upper limit of ca. 3 G on the coupling constants. Unfortunately, no firm conclusions can be placed on this result. Nevertheless, we conclude that the dianion model is in reasonable accord with all the results.

The objection that *m*-DNB should not give a triplet species on the addition of two extra electrons is not valid. Since addition of one electron gives the asymmetric structure found, for example, in fluid aqueous solutions,⁸ then the second electron must, by symmetry, occupy the alternative orbital and hence a triplet state is to be expected. It is particularly significant that nitrobenzene and *o*- or *p*-dinitrobenzene do not give these species since they have no low-lying states that can mix in this way. Thus their dianions should not be triplet species.

The Radical-pair Model.—The strongest argument against this model is that it predicts a triplet for the ¹⁴N hyperfine structure in the $\Delta M_s \pm 2$ transition, whereas a quintet is observed. However, we consider this concept to be innately improbable from a mechanistic viewpoint. First, it is unlikely that positive charge migration is efficient [process (4)]. There is no evidence that substrates with low ionization potentials give radical-cations in this medium: indeed, its great efficacy as a medium for specifically forming electron-addition products¹ is evidence against hole migration. If it were efficient, then we require the coincidence that reaction to give the neutral MeTHF radicals should occur only when the separation between cations and anions is in the 5–6 Å region. At that separation charge transfer from the anion to the cation would be extremely efficient, so that pair-trapping would be a rare event. Even if such pairs could be formed, there would seem to be no barrier to reaction between the highly reactive MeTHF radicals and the reactive radical-anions. Ring or oxygen addition would, in our view, be expected even at 77 K.

Aspects of Mechanism.—If our conclusions are correct these results have important implications for radiation chemistry. Our results suggest that the ease of electron capture by the monoanions is comparable with that for addition to the neutral molecules. At high doses we have been able to reach a point at which the intensity of the monoanion features appeared to fall. It is difficult to quantify these changes and only qualitative trends could be relied on. This was attempted by Konishi *et al.*³ but it seems to us most probable that their optical data relate to the total concentration of mono- and di-anions rather than to just the concentration of monoanions. If this is correct, their Figure 5 compares the total increase in the mono- and di-anion concentration together with that of the dianions alone. These trends are in qualitative agreement with expectation and confirm that second electrons add with remarkable efficacy. These conclusions may have some significance with respect to the problems of radiation damage in electron microscopy.⁹

Acknowledgement

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