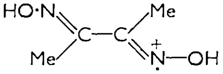
220. *Unstable Intermediates. Part XIX.* Electron-ejection and -trapping in Molecular Solids.*

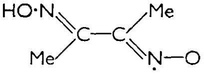
By M. C. R. Symons.

This is discussed in the light of electron-spin resonance results for solids exposed to high-energy radiation and it is concluded that there is at present little in favour of such processes.

Whilst it is generally agreed that the initial step in the radiolysis of most solids involves the ejection of electrons, only in a few cases is there good evidence for the trapping of such electrons. The well-known example of *F*-centres in " rare-gas " ionic crystals forms the basis of other postulates; but, although the evidence in favour of the currently accepted structure of *F*-centres, especially that derived from electron spin resonance studies is very strong,[1] no comparable evidence has been forthcoming for electrons similarly " trapped " in rigid polar media, such as the alcohols. In particular, although such trapped electrons have been posulated frequently, no electron spin resonance spectra have been assigned to them. It might be argued that the trapping sites vary so much that the resonance absorption is spread over a wide range of field, but, as discussed earlier,[2] it is hard to see why any such site should have a *g*-value very different from that of the free spin. However, even if resonance from the electrons cannot be detected, that from the resulting " holes " should be. Such " holes " are generally radical-ions but, again, well authenticated evidence for their permanent trapping comes largely from studies of irradiated alkali halides.[1] The best example for molecular solids is that of γ-irradiated crystalline dimethylglyoxime, studied by Miyagawa and Gordy,[3] who interpreted their results in terms of the radical-cation (I).



(I)



(II)

One purpose of this Paper is to give an alternative interpretation of these results [3] in terms of the neutral radical (II) which, it will be concluded, is a preferable representation.

Evidence in favour of the concept of trapped electrons is more prolific from spectral studies in the visible and ultraviolet region, but here it is less informative because of the greater difficulty of identifying bands. The situation has been summarised and extended

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* Part XVIII, preceding paper.

[1] Symons and Doyle, *Quart. Rev.*, 1960, **14**, 62.

[2] Symons, *J.*, 1959, 277.

[3] Miyagawa and Gordy, *J. Chem. Phys.*, 1959, **30**, 1590.

recently by Rao *et al.*,[4] who conclude that in rigid polar solvents such as tetrahydro-2-methylfuran " solvated " electrons are readily formed and trapped.

A typical example of the evidence [4] is that of γ-irradiated ethanol, which is characterised by a band in the 540 mμ region.[5,6] This can be ascribed to " solvated " electrons,[4,5] but the evidence in favour of this is not compelling.[6] A major difficulty of this theory is that polar molecules, which can certainly stabilise anions in fluid solution, can hardly do so to any extent in rigid glasses. Thus the usual models for " solvated " electrons [7] cannot be constructed and it is hard to understand why there should be a major difference between polar and non-polar solvents. It is significant that the 540 mμ band found with irradiated alcohols was previously found for alcohols after attack by hydroxyl radicals generated by photolysis of hydrogen peroxide,[6,8] in which circumstances electrons are not expected to be ejected. Also a similar band results when other primary and secondary alcohols are irradiated, but not when tertiary alcohols are used.

An important reaction which is not generally considered in this context is disproportionation. For example, when certain rigid glasses containing naphthalene were γ-irradiated the naphthalene anion was identified by its optical spectrum.[4] However, the spectrum of the corresponding cation is closely similar to that of the anion, and it seems probable that naphthalene acted as both a source and a sink of electrons. The resulting ions have their charges spread over such a large volume that solvent stabilisation is not required and thus the ions remain trapped.

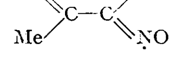
However, if such efficient trapping cannot occur, it seems probable that the electrons soon return to the source, especially if this is positively charged, and the resulting excited molecules decompose to give either diamagnetic fragments or the radicals that have been detected and characterised so thoroughly by electron spin resonance methods.

In view of these considerations, the results and conclusions of Miyagawa and Gordy are clearly important. They obtained no evidence for trapped electrons and, indeed, did not discuss the fate of the postulated ejected electrons. If they are trapped, it seems very probable that another dimethylglyoxime molecule would be the trap. The resulting radical-anion, however, would surely have given rise to a characteristic spectrum, which would differ markedly from that of the corresponding cation. This is supported by comparing the spectra of the comparable radicals NO_2^{2-} and NO_2.[9] No such spectrum was found.

Structure of the Radical Trapped in γ-Irradiated Dimethylglyoxime.—Results for this radical are given in Table 1, together with those for NO_2,[10] which is in many ways a comparable radical. The large isotropic hyperfine coupling to ^{14}N shows, as was stressed by

TABLE 1.

Principal values for ^{14}N Hyperfine and g-tensors for dimethylglyoxime radicals and nitrogen dioxide.

Radical	g_x	g_y	g_z	A_x (gauss)	A_y	A_z	A_{iso}
NO_2	2·0057	1·9910	2·0015	−5·27	−7·95	+13·22	+54·71
	2·0095	2·0063	2·0026	−6·67	−6·67	+13·33	+31·67

For NO_2 the z-direction is in the radical plane and bisects the ONO angle. This direction is similarly defined for the second radical. For both, x is perpendicular to the plane. (Values for A are as given in the literature although the second place is decimals is not significant.)

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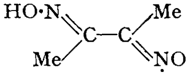
[4] Rao, Nash, Guarino, Ronayne, and Hamill, *J. Amer. Chem. Soc.*, 1961, **84**, 500.
[5] Alger, Anderson, and Webb, *J. Chem. Phys.*, 1959, **30**, 695.
[6] Symons and Townsend, *J.*, 1959, 263.
[7] Symons, *Quart. Rev.*, 1959, **13**, 99.
[8] Symons and Townsend, *J. Chem. Phys.*, 1956, **25**, 1299.
[9] Atkins and Symons, *J.*, 1962, 4794.
[10] Zeldes and Livingston, *J. Chem. Phys.*, 1961, **35**, 563.

Miyagawa and Gordy,[1] that the unpaired electron is in an orbital considerably localised on a single nitrogen atom, and having a large admixture of atomic 2*s*-character. Thus the discussion given for nitrogen dioxide[11] is probably applicable, and 2*s*- and $2p_z$-character can be calculated from the values of $|\psi(o)|^2$ and $\langle r^{-3}\rangle$ given by Smith *et al.*[12] Whatever may be the inaccuracies of this procedure, there can be no doubt that whilst the $2p_z$-characters for the dimethylglyoxime radical and nitrogen dioxide are comparable, the 2*s*-character for the latter is almost twice that of the former. This means that the C–N–O bond angle in the former radical is considerably greater than 134° which is the known O–N–O bond angle for the dioxide. The calculated values, given in Table 2, can be used to estimate this angle,[13] and the results for both radicals are tabulated. The value of 140° is much greater than the value of 120° suggested earlier,[3] and shows that there has been a large increase in the C–N–O angle on radical formation. This is in good accord with expectation for either structure (I) or (II).[14]

TABLE 2.

Values for 2*s*- and 2*p*-character on nitrogen derived from the tensors given in Table 1.

Radical	a^2_{2s}	$a^2_{2p_z}$	% on N	*p* : *s* ratio	RNR
NO_2	0·10	0·47	57	4·5	134°
	0·058	0·39	44·8	6·6	140°

Various reasons for preferring the present postulate that the radicals have structure (II) are: (i) As written, structure (I) is symmetrical, and it is probable that a rapid exchange of electrons between the two nitrogen atoms would make them equivalent. This difficulty does not arise for structure (II). (ii) Since there must be considerable unpaired electron density on oxygen (Table 2), the hydroxyl-proton should couple quite strongly, but no indication of further splitting was detected.[3] (iii) As stressed above, there was no evidence for trapped electrons or the expected radical-anions. (iv) The fact that the radical has changed its shape so markedly is better in accord with (II) than (I), since if structure (I) were correct, it would be quite possible that the powerful hydrogen-bond forces would hold the radical close to the configuration of the parent molecules.

Finally, it is noteworthy that, whilst the value for g_y for nitrogen dioxide is considerably smaller than that of the free-spin (2·0023), that for radical (II) is somewhat greater. This interesting reversal suggests that, in the latter radical, admixture of states involving excitation of π-electrons into the orbital of the unpaired electron is more important than states involving excitation of the unpaired electron into the vacant π^*-level, in contrast to nitrogen dioxide.

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DEPARTMENT OF CHEMISTRY, THE UNIVERSITY, LEICESTER. [*Received, September 12th,* 1962.]

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[11] Atkins, Keen, and Symons, *J.*, 1962, 2873.

[12] Smith, Sorokin, Gelles, and Lasher, *Phys. Rev.*, 1959, **115**, 1546.

[13] Coulson, Victor Henri Volume Commemoratif, Contribution à l'Étude de la Structure Moleculaire, Desoer, Liège, 1948, p. 15.

[14] Walsh, *J.*, 1953, 2266.