An E.S.R. Study of Glyoxal Radical Cations

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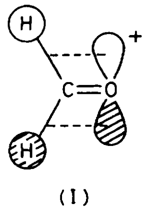
Radical cations of glyoxal, methylglyoxal, and dimethylglyoxal have been prepared, their e.s.r. spectra showing large α-proton couplings of *ca.* 83 G, (1 G = 10^{-4} T), which are somewhat greater than expected by comparison with the α-couplings of *ca.* 136 G in mono-aldehyde cations, assuming symmetrical delocalisation over both carbonyl groups in the glyoxal cations.

Evidence from e.s.r. spectroscopy for the radical cation $H_2CO^{\cdot+}$ in sulphuric acid was presented some time ago.[1] This cation has recently been very well-defined in inert-gas media,[2] this unsolvated species having the e.s.r. data presented in Table 1. Although the use of matrices such as $CFCl_3$ coupled with exposure to ionising radiation has been successful in the preparation of acetaldehyde and acetone cations,[3,4] formation of the parent cation, $H_2CO^{\cdot+}$, has not been reported in this or related media. Also, cations of the di-carbonyl derivatives of glyoxal $(HCO)_2^{\cdot+}$, methylglyoxal $[HC(O)–C(O)Me]^{\cdot+}$, and dimethylglyoxal $(MeCO)_2^{\cdot+}$ have not previously been studied by e.s.r. methods. We have succeeded in preparing these cations, using $CFCl_3$ as a solvent, and exposing the solutions to ^{60}Co γ-rays at 77 K.

The most important structural result for monocarbonyl cations is that the SOMO is formally the in-plane non-bonding 2*p* orbital on oxygen (I). However, there is extensive 'hyperconjugation' as evidenced by the large proton hyperfine coupling constants in the region of 130 G (Table 1).

The e.s.r. spectrum of the cation of glyoxal (see Figure 1) consists of a nearly isotropic triplet, showing that the spin density is delocalised over both carbonyl groups, the proton splitting being 84.2 G. This splitting is significantly larger than half the value found for the mono-carbonyl compounds (*ca.* 68 G). This enhancement is particularly noteworthy in view of the greater delocalisation of the positive charge in the glyoxal cation.

The *X*-band spectrum of the methylglyoxal cation consists of a doublet with a splitting of *ca.* 83 G and marked asymmetry. In order to facilitate extraction of the *g* and *A* tensor components, the spectrum was also studied at *Q*-band frequencies. The data are included in Table 1. It is noteworthy that the isotropic proton coupling is almost identical with that for the glyoxal cation, despite the change in symmetry.



(I)

Table 1. E.s.r. parameters for glyoxal radical cations.

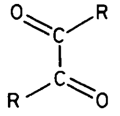
Radical	$A^H(G)^a$		g	
$(CHO)_2^{\cdot+}$	$A_{iso.}$	84.2	$g_{iso.}$	2.0029
$MeC(O)CHO^{\cdot+}$	A_x	81.0	g_x	2.0061
	A_y	82.0	g_y	2.0025
	A_z	86.25	g_z	1.9989
	$A_{iso.}$	83.1	$g_{aver.}$	2.0025
$(MeCO)_2^{\cdot+}$	Unresolved		$g_{aver.}$	2.0019
$H_2CO^{\cdot+}$ (Ne)[b]		132.7		2.0036

[a] 1 G = 10^{-4} T. [b] Ref. 2.

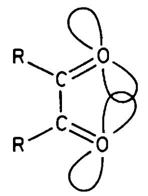
The spectrum of the dimethyl derivative shows no resolved hyperfine coupling, being a slightly asymmetric singlet, indicating partially resolved *g*-anisotropy. Increased librational motion of the smaller glyoxal cation probably accounts for its more isotropic spectrum. We note that the isotropic *g*-values appear to decrease with increasing methyl substitution, which is the reverse of the trend found in the cations of formaldehyde and acetone.[2,4]

The parent glyoxal molecules have all been shown to exist essentially in the *s-trans* conformation (II).[5–7] We might therefore expect that the cations would retain this geometry, unless the *s-cis* form (III) can be stabilised by a bonding interaction between the two oxygen atoms. Hopefully, calculations will be able to provide some insight into this problem and efforts are presently being made in this regard.[8]

In addition to features for the parent cations, the spectra from both glyoxal and methylglyoxal show wing features (α in Figure 1) which are separated by *ca.* 310 G. We are uncertain of the assignment of these features but suggest that they are



(II)



(III)

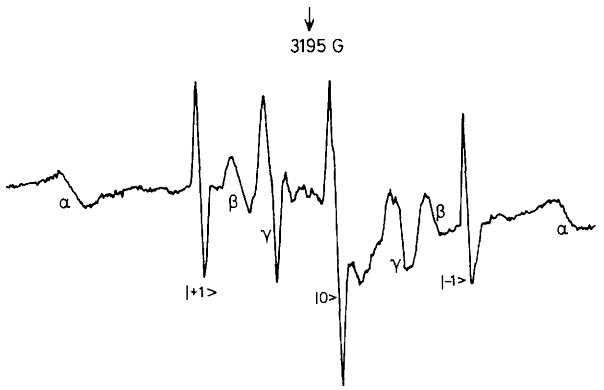


Figure 1. First derivative *X*-band e.s.r. spectrum for a dilute solution of glyoxal in $CFCl_3$ after exposure to ^{60}Co γ-rays at 77 K, showing the +1, 0, −1 features assigned to the parent cation. Other features marked α, β, and γ were less intense relative to those assigned to the parent cation on further dilution. Those marked β are assigned to $HCO^{\cdot}$ radicals: those marked α and γ are discussed in the text.

the $M_I = \pm1$ lines of a triplet of *ca.* 155 G, which can be assigned to acetal type cations. The g-values of *ca.* 2.006 are also in accord with such assignments.[9,10] The spectrum obtained from glyoxal also shows an asymmetric doublet (γ), similar to that assigned to methylglyoxal radical cations. Both sets of lines lost intensity at a greater rate than those assigned to the parent cations on dilution. These features will be discussed fully elsewhere.

It is of interest to compare these results with those for dicarbonyl anion-radicals. The SOMO for these anions is also delocalised, but is now a π^* orbital in contrast with the in-plane non-bonding orbitals of the cations.[11]

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