Detection of the Radical $H_2C\dot{O}^+$ by Electron Spin Resonance

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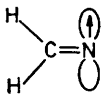
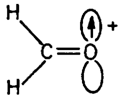
Summary Exposure of solutions of formaldehyde in sulphuric acid to ^{60}Co γ-rays at 77 K gave a radical whose e.s.r. spectrum is in accord with the structure $H_2C\dot{O}^+$.

THE iminoxyl radical, $H_2C\dot{N}$, which is well characterised by e.s.r. spectroscopy,[1] and is a frequently detected intermediate,[2] has an electronic structure (I) in which the unpaired electron is strongly delocalised onto the two hydrogen atoms [$A(^1H) = 87{\cdot}5$ G]. However, the isoelectronic radical $H_2\dot{C}O^+$ (II) has never been detected by e.s.r. spectroscopy. We find that a well defined, anisotropic, doublet is obtained after exposure of solutions of formaldehyde in H_2SO_4 (or D_2SO_4) to ^{60}Co γ-rays at 77 K.


(I)


(II)

If these lines are taken as the $M_I = \pm 1$ components of a triplet (the central region has intense components from $HS\dot{O}_4$ and $\cdot SO_3H$ radicals which completely conceal the $M_I = 0$ line) then the data given in the Table are obtained. These results are reasonable for $H_2\dot{C}O^+$. The positive shift in $g_{\parallel}$, although not observed for $H_2C\dot{N}$, is nevertheless expected for structure (II).

	$A(^1H)/G^a$			g values		
	$\parallel$	$\perp$	iso	$\parallel$	$\perp$	av.
$H_2C\dot{N}$	—	—	87·5	—	—	2·002
$H_2\dot{C}O^+$	93	89	90·3	2·025	2·000	2·017

[a] $G = 10^{-4}$ T.

This identification is supported by the observation that on annealing above 77 K these features were lost as an asymmetric doublet characteristic of $H\dot{C}O$ grew in with a final intensity equal to that for the '$H_2\dot{C}O^+$' radical (equation 1).

$$H_2\dot{C}O^+ + H_2SO_4 \rightarrow H\dot{C}O + H_3SO_4^{+\cdot} \qquad (1)$$

This means that whereas HCN^- is a strong base,[3] $H_2\dot{C}O^+$ is a strong acid even in concentrated sulphuric acid.

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[2] M. C. R. Symons, *Tetrahedron*, 1973, **29**, 615.

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