

## Detection of the Radical $\text{H}_2\dot{\text{C}}\text{O}^+$ by Electron Spin Resonance

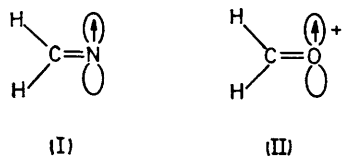
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**Summary** Exposure of solutions of formaldehyde in sulphuric acid to  $^{60}\text{Co}$   $\gamma$ -rays at 77 K gave a radical whose e.s.r. spectrum is in accord with the structure  $\text{H}_2\dot{\text{C}}\text{O}^+$ .

THE iminoxyl radical,  $\text{H}_2\dot{\text{C}}\text{N}$ , which is well characterised by e.s.r. spectroscopy,<sup>1</sup> and is a frequently detected intermediate,<sup>2</sup> has an electronic structure (I) in which the unpaired electron is strongly delocalised onto the two

hydrogen atoms [ $A(^1H) = 87.5$  G]. However, the iso-electronic radical  $H_2C\dot{O}^+$  (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  $^{60}Co$   $\gamma$ -rays at 77 K.

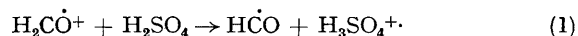


If these lines are taken as the  $M_I = \pm 1$  components of a triplet (the central region has intense components from  $HSO_4$  and  $\cdot SO_3H$  radicals which completely conceal the  $M_I = 0$  line) then the data given in the Table are obtained. These results are reasonable for  $H_2C\dot{O}^+$ . The positive shift in  $g_{||}$ , although not observed for  $H_2CN\dot{}$ , is nevertheless expected for structure (II).

	$A(^1H)/G^a$			$g$ values		
	$\parallel$	$\perp$	iso	$\parallel$	$\perp$	av.
$H_2CN\dot{}$	—	—	87.5	—	—	2.002
$H_2C\dot{O}^+$	93	89	90.3	2.025	2.000	2.017

<sup>a</sup>  $G = 10^{-4}$  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 ' $H_2C\dot{O}^+$ ' radical (equation 1).



This means that whereas  $HCN^-$  is a strong base,<sup>3</sup>  $H_2C\dot{O}^+$  is a strong acid even in concentrated sulphuric acid.

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<sup>1</sup> E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, 1962, **36**, 1938.

<sup>2</sup> M. C. R. Symons, *Tetrahedron*, 1973, **29**, 615.

<sup>3</sup> I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 185.