

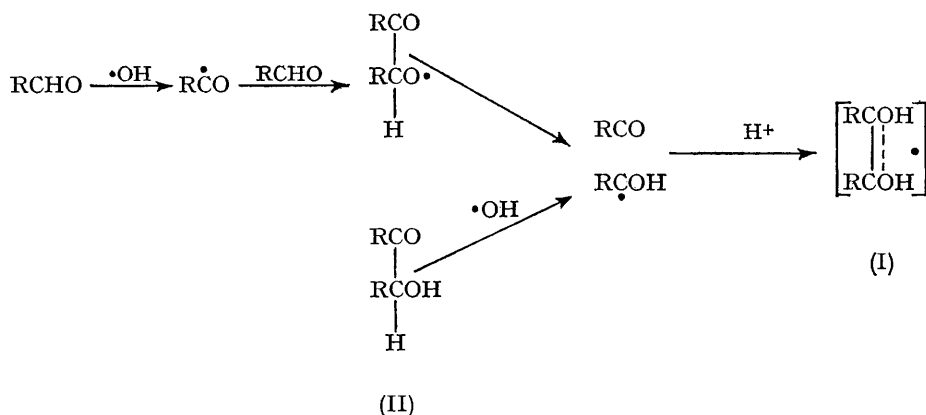
## Reactions of Acyl Radicals in Aqueous Solution Observed by e.s.r. Spectroscopy

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WHEN an acidified aqueous solution of titanous sulphate containing acetaldehyde was mixed rapidly with a solution of hydrogen peroxide and the reacting mixture passed into the cavity of an e.s.r. spectrometer (following the technique of Dixon and Norman<sup>1</sup>) a 7-line spectrum with the

parameters given in the Table (spectrum 1a) was obtained. It is suggested that this arises from the radical cation (I; R=Me) formed *via* the addition of an acetyl radical to the carbonyl bond of acetaldehyde:



*e.s.r. spectra from reaction between H<sub>2</sub>O<sub>2</sub> and Ti<sup>3+</sup> in the presence of various substrates in aqueous solution*

Spectrum	Description and origin	<i>g</i> value	$\alpha_{\text{H}}$ (oe)*	Assignment
1	a { Septet from acetaldehyde	2.0043	8.5 ± 0.2†	Radical (I); R = Me
	b { Septet A from acetoin	± 0.0003		
2	Septet B from acetoin	2.0042	9.8 ± 0.3	Radical (I) } <i>cis</i> - and <i>trans</i> -methyl groups?
		± 0.0003		
3	Quintet from propionaldehyde	2.0042	5.9 ± 0.2	Radical (I); R = Et
4	Quartet from acetaldehyde after previous mixing with peroxide	2.0024	22.8 ± 0.2	Methyl and/or acetyl (III)
		± 0.0002		
5	Doublet of quartets from acetaldehyde after previous mixing with peroxide	2.0030	$\alpha_{\text{H}}$ (CH <sub>2</sub> )	Methylcarbonyl (IV)
		± 0.0003	$\alpha_{\text{H}}$ (CH <sub>3</sub> )	
6	Triplet of quartets from propionaldehyde after previous mixing with peroxide	2.0023	$\alpha_{\text{H}}$ (CH <sub>2</sub> )	Ethyl
		± 0.0002	$\alpha_{\text{H}}$ (CH <sub>3</sub> )	
7	Triplet (?) from propionaldehyde with and without previous mixing with peroxide	2.0023	$\alpha_{\text{H}}$ (CH <sub>2</sub> )	Propionyl?
		± 0.0002	$\alpha_{\text{H}}$ (CH <sub>3</sub> )	

\* Line-widths of first-derivative spectra were all approximately 1 oe at a modulation amplitude of 1.3 oe.

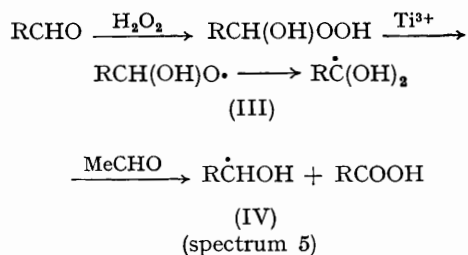
† Peak-peak heights in the ratios 1.9:6.8:16.2:20:17.6:8:1.9 compared with 1:6:15:20:15:6:1 for six equivalent protons.

The assignment is supported by the following facts: first, the same spectrum was obtained when the acetaldehyde in the titanous solution was replaced by acetoin (II; R = Me), but here the septet was accompanied by another, with somewhat larger splitting (spectrum 2). [This may perhaps have been due to a *cis-trans* isomer of (I), though it is not obvious why it should not also be obtained from acetaldehyde.] Secondly, when propionaldehyde replaced acetaldehyde a quintet (spectrum 3), as expected from (I; R = Et), was obtained. This occurred together with a triplet which is referred to below.

These spectra were observed with solutions at pH about 0.7 (after mixing). At pH 1–2 the septets from acetaldehyde and acetoin all showed an alternating line-width effect. This may be associated with ionization leading to incomplete equivalence<sup>2</sup> of the methyl groups in (I) which is the doubly protonated conjugate acid of the diacetyl ketyl anion.

When acetaldehyde (purified by fractionation in oxygen-free hydrogen) was premixed with the hydrogen peroxide rather than with the titanous solution, spectra (4 and 5) previously observed by Dixon, Norman, and Buley<sup>3,4</sup> were obtained in addition to the septet. Thus it appears that spectra 4 and 5 are consequent upon a reaction between the aldehyde and peroxide—presumably to form 1-hydroxyethyl hydroperoxide<sup>5</sup>—occurring before contact with the titanous solution. In confirmation of this, when the aldehyde was injected through a fine catheter into either the titanous or the hydrogen peroxide solution immediately before the mixing, the septet was obtained with only a trace of the other spectra. The reaction scheme suggested by Buley and Norman<sup>3</sup>

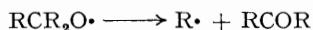
to account for spectra 4 and 5 must therefore be modified. A possible alternative is



However, the assignment<sup>3</sup> of spectrum 4 to (III; R = Me) must be accepted with reserve. The values of  $g$  and  $\alpha_{\text{H}}$  are indistinguishable from those of the methyl radical. Methyl radicals could arise from



The analogous reaction



(where R = Me) is very fast in aqueous solution.<sup>6</sup> The problem is partly, though not completely, resolved by the spectra from propionaldehyde described in Table I. After prior mixing with hydrogen peroxide it gave a well-defined spectrum (6) of the ethyl radical (Reaction A; R = Et). However, the triplet (7), which occurred when the propionaldehyde was premixed with the titanous solution, was also obtained. This triplet may be due to the propionyl radical or its hydrated form (III; R = Et). It is possible that acetyl radicals (hydrated or not) and methyl radicals have closely similar spectral parameters and that both are present in the acetaldehyde-peroxide system.

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<sup>2</sup> A. Carrington, *Mol. Phys.*, 1962, 5, 425.

<sup>3</sup> A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, 1964, 225.

<sup>4</sup> W. T. Dixon, R. O. C. Norman, and A. L. Buley, *J. Chem. Soc.*, 1964, 3627.

<sup>5</sup> C. N. Satterfield and L. C. Case, *Ind. Eng. Chem.*, 1954, 46, 998.

<sup>6</sup> M. F. R. Mulcahy, J. R. Steven, and J. C. Ward, *Austral. J. Chem.*, 1965 (in press).