

# The Aminoxy Radicals Formed by Addition of Photochemically Generated Radicals to Ethyl 2-Oximino-3-oxobutanoate Studied by EPR Spectroscopy

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Aminoxy radicals  $\text{CH}_3\text{C}(=\text{O})-\text{C}(\text{R})\dot{\text{N}}(\text{O})\text{H}-\text{C}(=\text{O})-\text{OC}_2\text{H}_5$  are formed by the addition of R· radicals to ethyl 2-oximino-3-oxobutanoate. In addition to the interaction of the unpaired electron with one  $^{14}\text{N}$  nucleus and one hydrogen nucleus, the EPR spectra exhibited secondary splittings from magnetic nuclei of the added group R. The hydrogen atom of the nitroxide group is derived from the oximino group of the parent oxime by rearrangement and migration. The R· radicals are formed from suitable hydrogen donors by abstraction of a hydrogen atom by photochemically generated ·OH radicals ( $\text{H}_2\text{O}_2$ ), or by the excited state of benzophenone.

It has been found that aminoxy radicals are formed in the photochemical reaction involving some  $\alpha$ -oximino- $\beta$ -oxo compounds, when dissolved in methanol or dimethyl sulfoxide (DMSO) together with small amounts of hydrogen peroxide and HCl.<sup>1</sup> The EPR spectra of these radicals exhibited six lines of equal intensity due to the interaction of the unpaired electron with one  $^{14}\text{N}$  nucleus and one hydrogen nucleus, indicating that the radicals had the structure  $\text{R}'-\dot{\text{N}}(\text{O})\text{H}$ . The coupling constant  $a_{\text{H1}}$  was only slightly smaller than  $a_{\text{N}}$ , i.e.  $a_{\text{H1}} = 1.17\text{--}1.25$  mT and  $a_{\text{N}} = 1.20\text{--}1.25$  mT. Therefore, the four central lines of the six-line spectra were incompletely resolved, or in several cases formed a superposition that gave rise to a four-line system with the intensities 1:2:2:1. When the reaction was performed in  $\text{CH}_3\text{OD}$ , the EPR spectrum exhibited  $3 \times 3$  lines of equal intensity, indicating that the structure of the radical was  $\text{R}'-\dot{\text{N}}(\text{O})\text{D}$  in this case.

Such aminoxy radicals were first observed with 1(2),3-dimethyl-4-nitrosopyrazol-5-ol.<sup>2</sup> At that time, it was suggested that H· or D· radicals, generated by photochemical cleavage of  $\text{H}_2\text{O}_2$  of the reaction mixture, were trapped by the  $\alpha$ -nitroso- $\beta$ -hydroxy form of the test substances. When the reaction was performed in DMSO, the EPR spectra consisted of four main groups of lines (1:2:2:1), which were further split into a number of incompletely resolved lines. It was considered that the narrow hyperfine splittings obtained with DMSO originated from a non-zero spin density on the atoms of DMSO molecules bound to the aminoxy radicals in some kind of a donor–acceptor complex.<sup>2</sup>

It has been observed that aminoxy radicals of the same type are obtained in the photochemical reaction with ethyl 2-oximino-3-oxobutanoate dissolved in  $\text{H}_2\text{O}$  containing a small amount of an alcohol such as methanol, ethanol, 2-propanol or 1,2-ethanediol. The EPR spectra exhibited a

doublet splitting (secondary splittings) of the characteristic four-line (1:2:2:1) spectrum. Further splittings (tertiary splittings) were observed with ethanol.

A number of experiments has now been performed to elucidate the mechanism of formation of the aminoxy radicals, the origin of the hydrogen atom of  $\text{R}'-\dot{\text{N}}(\text{O})\text{H}$ , and the secondary and tertiary splittings.

## Results and discussion

The highest resolution of the secondary and tertiary splittings was observed when the reaction was performed in  $\text{H}_2\text{O}$  containing 1–5% of the alcohol. Ethyl 2-oximino-3-oxobutanoate is present mainly in the oximino-oxo form. To establish a rapid equilibrium, with conversion of some part of the substance to the nitroso-enol form, a small amount of hydrogen chloride or acetic acid was added to the reaction mixtures containing the oxime together with a

Table 1. Coupling constants of secondary ( $a_{\text{H2}}$ ) and tertiary ( $a_{\text{H3}}$ ) splittings observed for the EPR spectra of the aminoxy radicals formed from ethyl 2-oximino-3-oxobutanoate in the presence of some alcohols.<sup>a</sup>

	$a_{\text{H2}}$ /mT doublet	$a_{\text{H3}}$ /mT multiplet
$\text{CH}_3\text{OH}$ in $\text{H}_2\text{O}$	0.037	–
$\text{CD}_3\text{OD}$ in $\text{H}_2\text{O}$	–	–
$\text{CH}_3\text{CH}_2\text{OH}$ in $\text{H}_2\text{O}$	0.13	0.03 quartet 1:3:3:1
$\text{CD}_3\text{CD}_2\text{OD}$ in $\text{D}_2\text{O}$	–	–
$\text{CD}_3\text{CH}_2\text{OH}$ in $\text{H}_2\text{O}$	0.125	–
$\text{CH}_3(\text{CH}_2)_2\text{OH}$ in $\text{H}_2\text{O}$	0.095	Unresolved
$\text{HOCH}_2\text{CH}_2\text{OH}$ in $\text{H}_2\text{O}$	0.084	Unresolved

<sup>a</sup> $a_{\text{N}} = a_{\text{H1}} = 1.23$  mT.  $a_{\text{D1}} = 0.182$  mT.

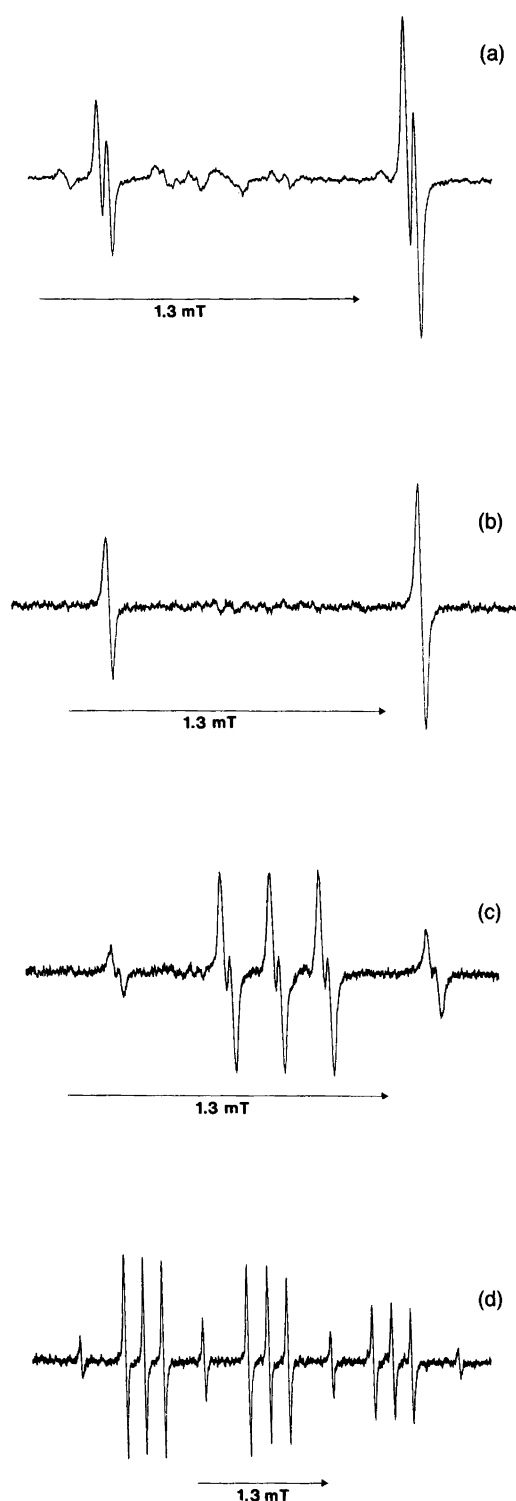


Fig. 1. (a) EPR spectrum of the aminoxy radicals formed from ethyl 2-oximino-3-oxobutanoate. The reaction mixture contained the oxime dissolved in  $\text{H}_2\text{O}$  to a concentration of 20 mmol, and  $\text{CH}_3\text{OH}$  to 3%, together with 0.1 M HCl (10  $\mu\text{l}$ /0.5 ml) and  $\text{H}_2\text{O}_2$  (10  $\mu\text{l}$  of 30% in  $\text{H}_2\text{O}$ /0.05 ml). The sample was irradiated *in situ* in the EPR cavity with UV light. The two low-field groups of a total of four groups of lines are shown. (b) The low-field part of the EPR spectrum obtained with  $\text{CD}_3\text{OD}$  in  $\text{H}_2\text{O}$ . (c) The same part of the spectrum observed with  $\text{CH}_3\text{OH}$  in  $\text{D}_2\text{O}$ . (d) Complete EPR spectrum obtained with  $\text{CH}_3\text{OD}$  in  $\text{D}_2\text{O}$ .

small amount of  $\text{H}_2\text{O}_2$ . The aminoxy radicals appeared after a few minutes of irradiation with UV light. The radicals persisted for more than an hour, as long as the samples were irradiated *in situ* in the EPR cavity, but disappeared when the light was turned off. The coupling constants of the secondary and tertiary splittings are collected in Table 1.

Fig. 1(a) shows part of the EPR spectrum of the aminoxy radicals obtained with ethyl 2-oximino-3-oxobutanoate dissolved in  $\text{H}_2\text{O}$  containing 3%  $\text{CH}_3\text{OH}$ . The two low-field groups of the four groups of lines (1:2:2:1) are shown. Each of the two lines is split into a narrow doublet. Since  $a_N \approx a_{\text{H1}} = 1.23$  mT, the high-field group of the two groups of lines is also resolved into a doublet.

Fig. 1(b) shows the same low-field part of the EPR spectrum obtained when the reaction was performed in  $\text{H}_2\text{O}$  containing 3%  $\text{CD}_3\text{OD}$ . The four-line system is preserved, but the doublet splitting of Fig. 1(a) is absent.

Fig. 1(c) shows the same part of the spectrum obtained when the reaction was performed in  $\text{D}_2\text{O}$  containing 3%  $\text{CH}_3\text{OH}$ . Two groups of lines are present, i.e. the group of lines corresponding to those of Figs. 1(a) and 1(b), indicating the presence of radicals of the type  $\text{R}'\text{-}\dot{\text{N}}(\text{O})\text{H}$ , and a triplet which constitutes the low-field part of a  $3 \times 3$  (1:1:1) system corresponding to  $\text{R}'\text{-}\dot{\text{N}}(\text{O})\text{D}$  radicals. The lines of both groups exhibit a narrow doublet splitting. However, the resolution of the doublet is lower than for the corresponding splitting in Fig. 1(a).

Fig. 1(d) shows the complete EPR spectrum of the aminoxy radicals formed in  $\text{D}_2\text{O}$  containing 3%  $\text{CH}_3\text{OD}$ . Both  $\text{R}'\text{-}\dot{\text{N}}(\text{O})\text{H}$  and  $\text{R}'\text{-}\dot{\text{N}}(\text{O})\text{D}$  radicals are present, but the doublet splittings present in the spectra of Figs. 1(a) and 1(c) are absent.

Fig. 2(a) shows the two low-field groups of a total of four of the EPR spectrum obtained with ethyl 2-oximino-3-oxobutanoate dissolved in  $\text{H}_2\text{O}$  containing about 3%  $\text{CH}_3\text{CH}_2\text{OH}$ . The two groups of lines are split into a doublet of about 0.1 mT which is further split into four narrow lines, very probably of relative intensity 1:3:3:1.

Fig. 2(b) shows the same part of the EPR spectrum obtained with the oxime dissolved in  $\text{D}_2\text{O}$  containing 3%  $\text{CH}_3\text{CH}_2\text{OH}$ . In addition to the two groups of lines present in Fig. 2(a), there is a multiplet of lines corresponding to the low-field deuterium triplet  $3 \times 3$  (1:1:1) that is further split into a number of narrow lines.

Fig. 2(c) shows the two low-field lines of the spectrum obtained with the oxime dissolved in  $\text{H}_2\text{O}$  containing 3% of  $\text{CD}_3\text{CD}_2\text{OD}$ . The secondary ( $a_{\text{H2}}$ ) and tertiary ( $a_{\text{H3}}$ ) splittings of Fig. 2(a) are absent.

Fig. 2(d) shows the same low-field part of the spectrum when the reaction was performed in  $\text{D}_2\text{O}$  with 3%  $\text{CD}_3\text{CD}_2\text{OD}$ . Two groups of lines are present: the low-field lines of the four-line system, and the two low-field triplet of a  $3 \times 3$  (1:1:1) system corresponding to radicals of the type  $\text{R}'\text{-}\dot{\text{N}}(\text{O})\text{D}$ . No secondary ( $a_{\text{H2}}$ ) or tertiary ( $a_{\text{H3}}$ ) splittings are present.

Fig. 2(e) shows the spectrum obtained when the reaction

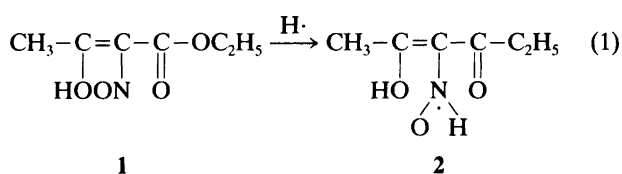
was performed in H<sub>2</sub>O with 5% CD<sub>3</sub>CH<sub>2</sub>OH. The doublet splitting  $a_{H_2}$  is present, but there are no tertiary splittings  $a_{H_3}$ .

The four-line spectrum was also observed without the addition of alcohols. However, the signal intensity was rather low in this case, and no doublet splitting could be detected.

The *g*-value of the aminooxyl radicals in this series was equal to 2.0062.

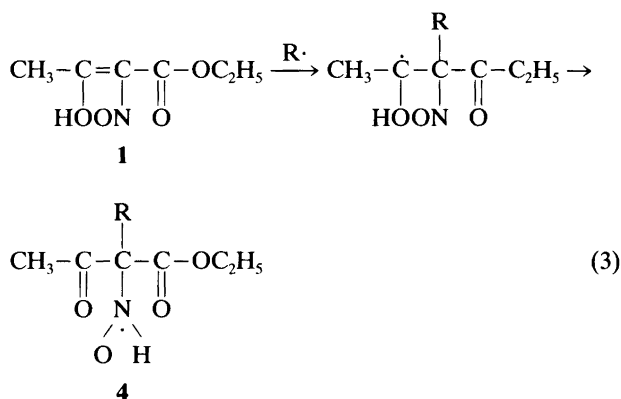
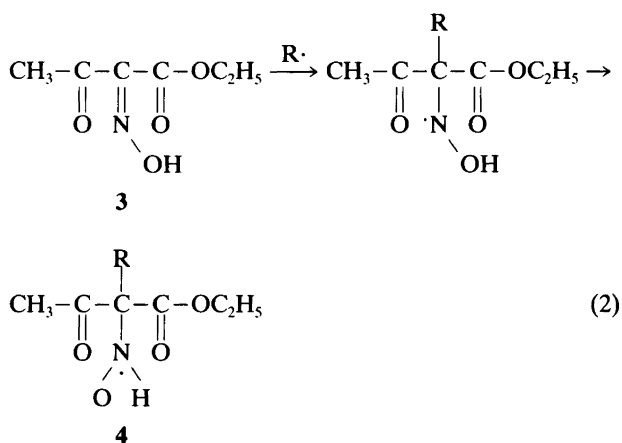
Preliminary experiments with a number of other dioxoimino compounds including the oxime of dibenzoylmethane [ $\varphi\text{O}-\text{C}(=\text{NOH})-\text{CO}\varphi$ ], gave rise to aminooxyl radicals exhibiting the characteristic four-line spectra with a secondary doublet splitting in the presence of alcohols.

On assuming that the aminooxyl radicals are formed by the addition of H· or D· radicals to the  $\alpha$ -nitroso- $\beta$ -enol form of the oxime, eqn. (1) is valid. Such a mechanism



might imply that the secondary ( $a_{H_2}$ ) and tertiary ( $a_{H_3}$ ) splittings originated from a transfer of unpaired spin density from the aminooxyl radical to the magnetic nuclei of the alcohols bound to the radical in some sort of a molecular complex.

However, such molecular complexes seem to be rather unlikely. A more realistic mechanism for the formation of the observed aminooxyl radicals, and of the origin of the secondary and tertiary splittings involves the addition of a radical R· to the double bond between the carbon and nitrogen atoms of the  $\alpha$ -oximino- $\beta$ -oxo form 3, or to the double bond between the carbon atoms of the  $\alpha$ -nitroso- $\beta$ -enol form 1 of the parent oxime. The addition of R· is followed by a rearrangement and migration of the hydrogen atom of the oximino group to form the nitroxide group, eqns. (2) and (3).



Aminooxyl radicals formed by the addition of hydroxy, amino or hydroxymethyl radicals to oximes of the type R<sup>1</sup>R<sup>2</sup>C=NOH (R<sup>1</sup>, R<sup>2</sup> = H, alkyl) have been described by Smith and Fox<sup>3</sup> (see also Aurich and Weiss<sup>4</sup>). In these experiments, ·OH radicals were formed in a flow system by the Fenton reaction.

Evidently, magnetic nuclei of the covalently bound group R in 4 are responsible for the observed secondary ( $a_{H_2}$ ) and tertiary ( $a_{H_3}$ ) splittings. Thus, the splittings observed with ethanol [Figs. 2(a)–2(e)] are consistent with the addition to 1 or 3 of the CH<sub>3</sub>CH–OH radical formed by the abstraction of a methylene hydrogen atom from ethanol by ·OH radicals generated in the photochemical cleavage of H<sub>2</sub>O<sub>2</sub>. The doublet splitting  $a_{H_2}$  originated from an interaction with the remaining hydrogen atom of the methylene group, and the quartet splittings from an interaction with the hydrogen atoms of the methyl group. In the same way, the secondary splittings observed with 1-propanol and 1,3-ethanediol (Table 1) originated from the addition of the radicals CH<sub>3</sub>CH<sub>2</sub>ĊH–OH or CH<sub>3</sub>ĊHCH<sub>2</sub>–OH, and HOCH<sub>2</sub>ĊH–OH to 1 or 3. No tertiary splittings could be resolved in these cases.

The expected secondary triplet (1:2:1) splitting due to the addition to 1 or 3 of the radical ·CH<sub>2</sub>OH formed from methanol could not be observed in the spectra of Figs. 1(a)–1(d). Evidently, the narrow doublet,  $a_{H_2} = 0.037$  mT, Fig. 1(a), originated from an interaction with a hydrogen atom. Since the doublet is replaced by a single line in a reaction mixture containing only 3% CD<sub>3</sub>OD in H<sub>2</sub>O, Fig. 1(b), it seems very probable that the doublet is due to an interaction with the hydrogen atom of the hydroxy group of methanol. If the doublet had been due to the hydrogen atom of an OH group added to 1 or 3, only a minor part of the hydrogen atoms of the OH group would have been exchanged. These apparent discrepancies are explained as follows. The radical ·CH<sub>2</sub>OH formed from methanol is added to 1 or 3. The hydrogen atoms attached to the carbon atoms of the CH<sub>2</sub>OH group are forced out of the plane of the nitroxide group due to the crowded steric arrangement with an oxo group on each side of the carbon atom carrying the CH<sub>2</sub>OH group. This situation prevents any large interaction of the unpaired electron with the two

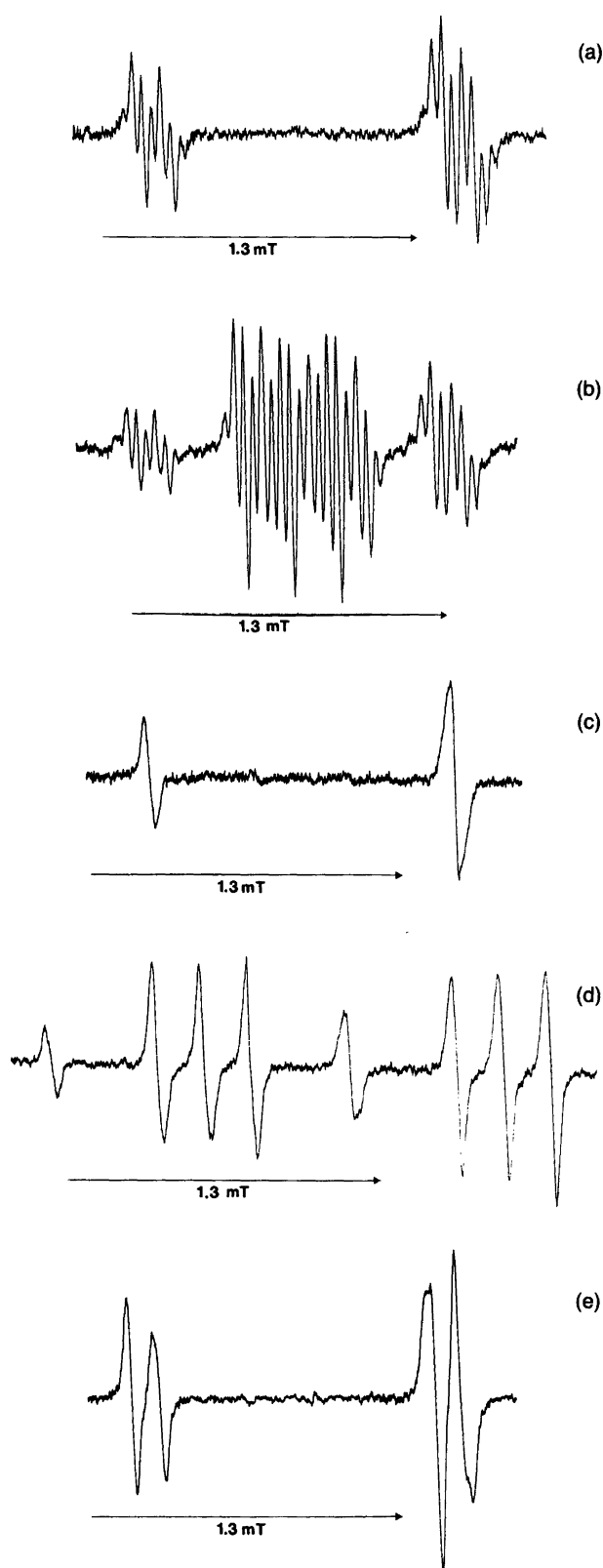


Fig. 2. (a) Low-field part of the EPR spectrum obtained with  $\text{CH}_3\text{CH}_2\text{OH}$  in  $\text{H}_2\text{O}$ . (b) Low-field part of the spectrum obtained with  $\text{CH}_3\text{CH}_2\text{OH}$  in  $\text{D}_2\text{O}$ . (c) Low-field part of the spectrum obtained with  $\text{CD}_3\text{CD}_2\text{OD}$  in  $\text{H}_2\text{O}$ . (d) The same low-field part of the EPR spectrum obtained with  $\text{CD}_3\text{CD}_2\text{OD}$  in  $\text{D}_2\text{O}$ . (e) The low-field part of the spectrum obtained with  $\text{CD}_3\text{CH}_2\text{OH}$  in  $\text{H}_2\text{O}$ .

(a) hydrogen atoms of the  $\text{CH}_2\text{OH}$  group, but allows an interaction with the hydrogen atom of the OH group that leads to the observed narrow doublet splitting. This interpretation is supported by the finding that the line width  $\Delta H_{pp}$  of the low-field line ( $M_1 = +1, +1/2$ ) is about 0.047 mT when the reaction was performed with  $\text{CH}_3\text{OD}$ , but only 0.020 mT with  $\text{CD}_3\text{OD}$  [Fig. 1(b)], clearly indicating some influence from the hydrogen atoms of an added group R derived from methanol.

(b) Alternatively, the oxidation of methanol to the corresponding aldehyde followed by the abstraction of a hydrogen atom would give rise to a radical  $\text{HC}=\text{O}$ , the addition of which to **1** or **3** might produce an EPR spectrum similar to that of Fig. 1(a). However, experiments with formaldehyde added to the reaction mixture in place of methanol did not produce a spectrum similar to that of Fig. 1(a). Therefore, this interpretation seems to be the less probable one.

(c) Since the hydrogen atom bound to the nitrogen atom of the nitroxide group ( $a_{\text{HI}}$ ) is easily exchanged for deuterium in aqueous solutions [Figs. 1(c), 1(d), Figs. 2(b), 2(d)], a direct demonstration of its origin from the parent oxime is difficult. Therefore, some experiments were performed with the oxime dissolved in non-aqueous media, the results of which indirectly confirmed the reaction mechanism given above [eqns. (2) and (3)].

(d) Fig. 3(a) shows the EPR spectrum of the aminoxy radicals observed when a solution of ethyl 2-oximino-3-oxobutanoate dissolved in dioxane together with a small amount of benzophenone was irradiated by UV light. The

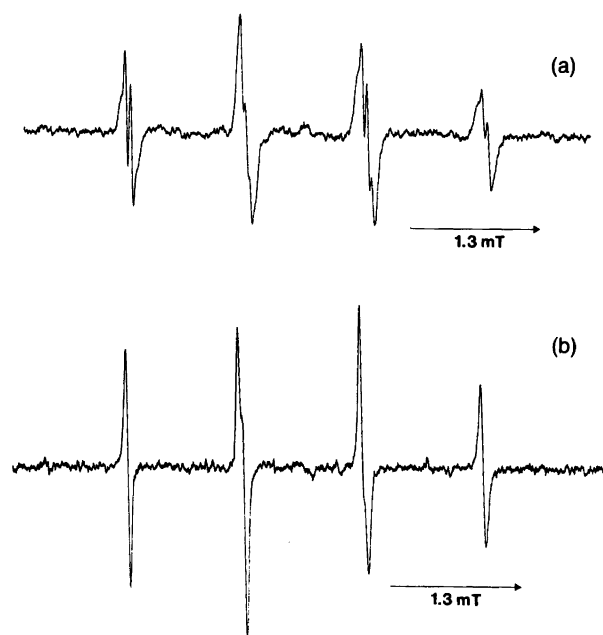
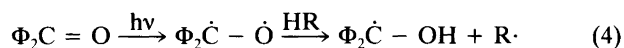


Fig. 3. (a) Complete EPR spectrum observed with the oxime dissolved in dioxane (20 mmol) together with benzophenone (10 mmol). (b) The spectrum obtained with dioxane- $d_8$  and benzophenone.

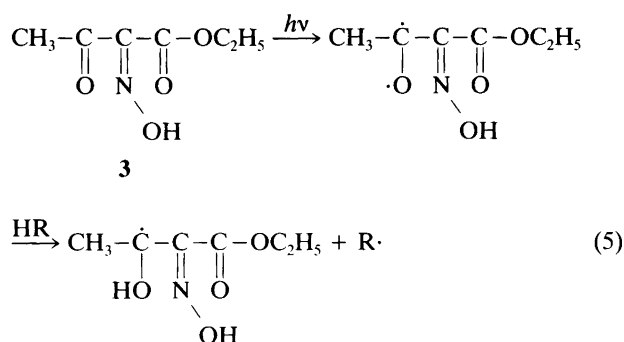
spectrum consisted of the four-line system (1:2:2:1),  $a_N \approx a_{H1} = 1.18$  mT. Each of the four lines is split into a doublet,  $a_{H2} = 0.053$  mT. The shape of the low-field line ( $M_I = +1, +1/2$ ) indicated the presence of further unresolved splittings. Fig. 3(b) shows the spectrum obtained in dioxane- $d_8$  solution. The four-line system is preserved, but the doublet splittings are now absent. Similar spectra were obtained with cyclohexane:  $a_N \approx a_{H1} = 1.22$  mT,  $a_{H2} = 0.102$  mT, and cyclohexane- $d_{12}$ :  $a_N \approx a_{H1} = 1.22$  mT, no doublet splittings.

Evidently, aminooxyl radicals **4** were formed according to eqns. (2) or (3). The  $R\cdot$  radical that is added to the double bond of **1** or **3** is generated by the abstraction of a hydrogen or deuterium atom from a  $-\text{CH}_2-$  or  $-\text{CD}_2-$  group of dioxane or cyclohexane by the triplet state of benzophenone, eqn. (4). In this equation, HR = dioxane or cyclo-



hexane, i.e.  $\text{R}\cdot = \text{C}_4\text{O}_2\text{H}_7\cdot$  or  $\text{C}_6\text{H}_{11}\cdot$ . Thus, the doublet splittings originated from an interaction with the remaining hydrogen atom of a methylene group, i.e.  $-\text{CH}-$ .

The formation of  $\text{R}\cdot$  radicals by hydrogen abstraction from suitable hydrogen donors mediated by an excited state of benzophenone has been demonstrated by the spin trapping technique.<sup>5,6</sup> In some spectra recorded here, aminooxyl radicals were present which had been formed in this way. Very probably the nitroso-enol form **1** constituted the spin trap in these reactions. The characteristic four-line spectrum could also be obtained without benzophenone but with a reduced yield of aminooxyl radicals. It is suggested that the formation of the radicals  $\text{R}\cdot$  from dioxane or cyclohexane is mediated by an excited state of the dioxo-oxime compounds, eqn. (5).



The results obtained with dioxane- $d_8$  and cyclohexane- $d_{12}$  support the reaction path given in eqns. (2) and (3) with a migration of the hydrogen atom of the oximino group to the nitroxide group, since no transfer of deuterium atoms from dioxane- $d_8$  or cyclohexane- $d_{12}$  to be bound directly to the nitrogen atom of the nitroxide group could be observed.

The four-line spectrum with secondary doublet splittings observed with the oxime of dibenzoylmethane (see above) indicated that the hydrogen atoms of the methyl and ethyl groups of ethyl 2-oximino-3-oxobutanoate were not involved in the interactions leading to the observed secondary and tertiary splittings. The single source of H-atoms is the oximino group in this case.

## Conclusions

The experiments have shown that aminooxyl radicals are formed by the addition of  $\text{R}\cdot$  radicals to ethyl 2-oximino-3-oxobutanoate, eqns. (2) or (3). Depending on the steric hindrance brought about by the two oxo groups in positions next to the carbon atom to which the radical  $\text{R}\cdot$  becomes attached, only relatively non-bulky radicals could be added or trapped. Thus, aminooxyl radicals were formed by the addition of carbon-centered  $\text{R}\cdot$  radicals of the type  $-\dot{\text{C}}\text{H}-$ , and very probably  $\cdot\text{CH}_2\text{OH}$ , produced by the abstraction of a hydrogen atom from suitable hydrogen donors by photochemically  $\cdot\text{O}$  generated  $\cdot\text{OH}$  radicals, or the excited state of benzophenone. The aminooxyl radicals were also formed by the addition of  $\cdot\text{OH}$  radicals. In this case, the EPR spectrum exhibited the characteristic four-line spectrum with no secondary splittings.

Evidently, the reaction constitutes a form of spin trapping. The instability of aminooxyl radicals of the type concerned, i.e.  $\text{R}'-\dot{\text{N}}(\text{O})\text{H}$ , and the steric hindrance of the addition of bulky  $\text{R}\cdot$  radicals, seem to limit its application to the trapping of some special radicals continuously formed in photochemical reactions.

In view of the conclusions drawn from the experiments described, it seems likely that the aminooxyl radicals obtained with 1(2),3-dimethyl-4-nitrosopyrazol-5-ol,<sup>2</sup> and a number of acyclic dioxo-oximino compounds,<sup>1</sup> are also formed by radical addition according to eqns. (2) or (3). Consequently, the very narrow splittings observed in the four-line spectra obtained with 1(2),3-dimethyl-4-nitrosopyrazol-5-ol dissolved in DMSO (see above)<sup>2</sup> are considered to originate from interaction with magnetic nuclei of a covalently bound group R derived from DMSO.

## Experimental

**Experiments.** Ethyl 2-oximino-3-oxobutanoate was prepared as described by Touster.<sup>7</sup> The deuteriated substances were obtained from Merck, Fluka AG, or Sigma Chemical Co.

**Preparation of radicals.** Ethyl 2-oximino-3-oxobutanoate was dissolved in  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$  to a concentration of between 10 and 20 mmol. The alcohol, i.e. methanol, ethanol or 1-propanol, was added to give a concentration of 2–10%. 10–20  $\mu\text{l}$  of 0.1 M HCl or acetic acid were added to 0.5 ml of the oxime solution, together with 20  $\mu\text{l}$  of 30%  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{O}$ . The experiments with dioxane or cyclohexane were performed with 20 to 30 mmol of the oxime, together with

about 10 mmol of benzophenone. The samples were irradiated with UV light from a mercury lamp (Osram HBO-200) *in situ* in the EPR cavity when contained in a flat cell.

*Electron spin resonance measurements.* The EPR spectra were recorded using a Varian E-9 spectrometer at 20°C with a microwave power of 0.2–0.5 mW and a 100 kHz modulation amplitude of 0.0025–0.02 mT. Hyperfine splitting constants were measured by comparison with the splittings of Fremy's radical ( $a_N = 1.30$  mT).

Estimation of the  $g$ -value of the nitroxide radicals in this series was made by using the superposition spectra obtained for a solution containing both aminooxyl radical and Fremy's radical. The  $g$ -value was calculated from the formula  $g = 0.7145 (\nu/H)$  where  $\nu$  is the microwave frequency and  $H$  (gauss) is the magnetic field, on the assumption that the  $g$ -value of Fremy's radical is equal to 2.0054.<sup>8</sup> The

microwave frequency was measured by the use of a cavity wavemeter.

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