

Aminoxyl Radicals Formed in the Reaction Between 2-Oximinopropanoic Acid or 2-Oximinopropane and Short-Lived Radicals Studied by EPR Spectroscopy

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$R^1R^2C(R)\dot{N}(O)H$ radicals formed from 2-oximinopropanoic acid, or 2-oximinopropane by addition of R^* radicals and rearrangement, react as spin traps for a second R^* radical. The aminoxyl radicals $R^1R^2C(R)\dot{N}(O)R$ were very probably formed via an intermediate nitroso compound $R^1R^2C(R)N=O$. Similar results were obtained when *N-tert*-butylhydroxylamine was the parent substance.

It has previously been found that aminoxyl radicals, $R^1C(=O)-C(R)\dot{N}(O)H-C(=O)R^2$, are formed by the addition of R^* radicals to 1,3-dioxo-2-oximino compounds.^{1,2} The hydrogen atom of the aminoxyl group was found to be derived from the oximino group of the parent oxime by rearrangement and migration. In these experiments, the R^* radicals were formed from suitable donors by abstraction of a hydrogen atom by photochemically generated $^{\bullet}OH$ radicals (H_2O_2) or by the excited state of benzophenone. The coupling constant a_{HI} was only slightly smaller than a_N , i.e. $a_{HI} = 1.17-1.25$ mT and $a_N = 1.20-1.25$ 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 intensities 1:2:2:1. When the reaction was performed in a solvent/donor such as CH_3OD , the EPR spectrum exhibited 3×3 lines of equal intensity, indicating that the structure of the radicals was $R-\dot{N}(O)D$ in this case by exchange of protium for deuterium.

It has now been found that R^* radicals can be added to a number of other oxime compounds, such as 2-oximinopropanoic acid and 2-oximinopropane, with the formation of aminoxyl radicals $R^1R^2C(R)\dot{N}(O)H$ and $R^1R^2C(R)\dot{N}(O)D$, i.e. radicals of the same type as observed with 1,3-dioxo-2-oximino compounds.

Furthermore, it was found that a second R^* radical can be added to the $R^1R^2C(R)\dot{N}(O)H$ radicals with the formation of aminoxyl radicals of the type $R^1R^2C(R)\dot{N}(O)R$. This note describes the results obtained with 2-oximinopropanoic acid and 2-oximinopropane.

Results and discussion

The experiments were carried out with 2-oximinopropanoic acid, 2-oximinopropane and *N-tert*-butylhydroxylamine.

The coupling constants of the radicals are collected in Table 1.

Figs. 1(a)–(d) show the EPR spectra recorded for the radicals formed in a solution of 2-oximinopropanoic acid dissolved in methanol- d_4 together with a small amount of H_2O_2 , when irradiated with UV light *in situ* in the EPR cavity. The spectrum of Fig. 1(a) was observed after ca. 3 min of irradiation, and shows a superposition of a four-line system (1:2:2:1) and a 3×3 line system of equal intensity. Evidently, the radical species have the general structure $R^1\dot{N}(O)H$ and $R^1\dot{N}(O)D$. It was then observed that further irradiation of the sample brought about the appearance of an additional radical species [Fig. 1(b)]. The signal intensity of this new species increased with continued irradiation. Fig. 1(c) is the spectrum recorded after ca. 45 min of irradiation. An extensive change in the spectrum was observed when the UV light was extinguished. Fig. 1(d) shows the spectrum obtained in the dark after about an hour of irradiation. The spectra of the four-line and the 3×3 line systems have disappeared, leaving a high concentration of a 3×5 (1:2:3:2:1) system. It should be pointed out that the concentration of this species increased during the first few minutes in the dark after the UV light had been turned off. The spectrum of Fig. 1(d) was found to be stable for several hours. Evidently, the radical species of the 3×5 line system had the general structure $R^1\dot{N}(O)CD_2OD$.

Similar results were obtained with 2-oximinopropane dissolved in ethanol/ H_2O , or acetone, together with a small amount of H_2O_2 or benzoyl peroxide, when irradiated with UV light. The spectra exhibited the simultaneous presence of radicals of general structure $R\dot{N}(O)H$ and $R\dot{N}(O)CH(CH_3)OH$, or $R\dot{N}(O)CH_2C(=O)CH_3$.

It has previously been shown that aminoxyl radicals of the type $R^1\dot{N}(O)H$ are formed from oximes by the addition of photochemically generated R^* radicals to the C=N bond

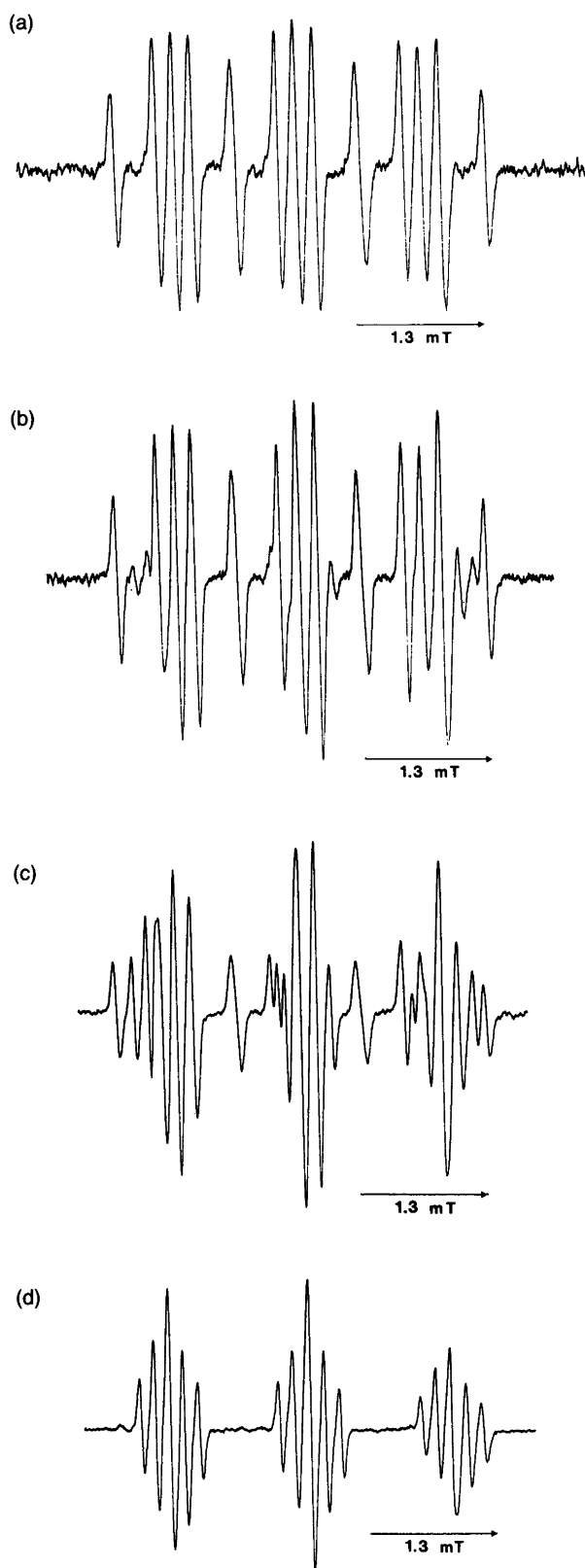


Fig. 1. EPR spectra of the radicals obtained in a solution of $\text{CH}_3\text{C}(=\text{NOH})\text{COOH}$ (50 mM) dissolved in methanol- d_4 together with a small amount of H_2O_2 , when irradiated with UV light: (a) after 3 min of irradiation; (b) after 10 min; (c) after 45 min; (d) in the dark after ca. 1 h of irradiation.

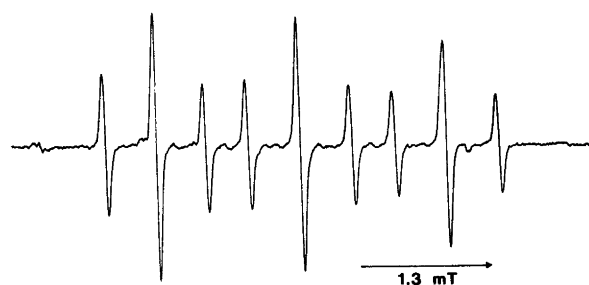


Fig. 2. The EPR spectrum obtained from a solution of *N-tert*-butylhydroxylamine · HCl 50 mM: dissolved in methanol together with a small amount of H_2O_2 . No irradiation with UV light.

noic acid, 2-oximinopropane and *N-tert*-butylhydroxylamine in some further donor/solvents in addition to those described above. In general, the coupling constants of the aminoxyl radicals are in agreement with those observed in earlier spin-trapping experiments performed with nitroso scavengers such as 2-methyl-2-nitrosopropane.⁴⁻⁶

Trapping of short-lived radicals of the type $\text{CH}_3\dot{\text{C}}\text{HOH}$ by use of nitroso compounds such as 2 (i.e. $\text{R}^1 \neq \text{R}^2 \neq \text{R}$) gives rise to aminoxyl radicals which contain two or more chiral centers. Therefore, these aminoxyl radicals exist as diastereomers, the coupling constants of which may differ slightly. However, no structures have been observed, so far, in the EPR spectra of this series which could be associated with pairs of diastereomers.

Conclusions. The experiments have shown that the oxime compounds 2-oximinopropanoic acid or 2-oximinopropane add photochemically generated R^\cdot radicals such as $\cdot\text{CH}_2\text{OH}$ or $\text{CH}_3\dot{\text{C}}\text{HOH}$ to form aminoxyl radicals, $\text{R}^1\text{R}^2\text{C}(\text{R})\dot{\text{N}}(\text{O})\text{H}$. The addition of the second R^\cdot radical to the primary aminoxyl radicals gave rise to $\text{R}^1\text{R}^2\text{C}(\text{R})\dot{\text{N}}(\text{O})\text{R}$, very probably via an intermediate nitroso compound $\text{R}^1\text{R}^2\text{C}(\text{R})\text{NO}$. The results obtained with *N-tert*-butylhydroxylamine indicated that the reaction did not involve the migration of a methyl group from the central carbon atom to the nitrogen atom. The intermediate nitroso compound is considered to be formed in a radical-driven Fenton reaction.

Experimental

2-Oximinopropanoic acid was prepared as described by Barry and Hartung.⁷ 2-Oximinopropane and *N-tert*-butylhydroxylamine · HCl were obtained from Fluka AG and methanol- d_4 from Merck.

The preparation of the radicals and the EPR measurements were as described earlier.^{1,2}

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