

Trapping of Hydrogen Atoms Formed in the Photochemical Reaction Involving Hydrogen Peroxide, Methanol or Dimethyl Sulfoxide by Addition to α -Nitroso- β -hydroxy Compounds

Carl Lagercrantz

Department of Medical Physics, University of Göteborg, P.O. Box 33031, S-400 33 Göteborg, Sweden

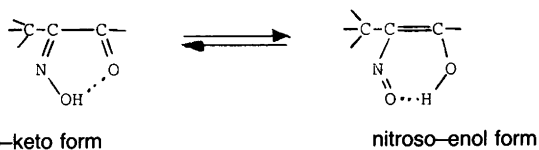
Lagercrantz, C., 1989. Trapping of Hydrogen Atoms Formed in the Photochemical Reaction Involving Hydrogen Peroxide, Methanol or Dimethyl Sulfoxide by Addition to α -Nitroso- β -hydroxy Compounds. – Acta Chem. Scand. 43: 509–510.

Irradiation of reaction mixtures containing methanol or dimethyl sulfoxide (DMSO), together with hydrogen peroxide with UV light gives rise to $\cdot\text{CH}_2\text{OH}$ (methanol) or $\cdot\text{CH}_3$ (DMSO) radicals that can be trapped in high yields by a variety of nitroso compounds, with the formation of stable nitroxide radicals.

A recent study of the radicals formed in the photochemical reaction involving methanol or DMSO and hydrogen peroxide has shown that hydrogen atoms are exclusively trapped by 1(2),3-dimethyl-4-nitrosopyrazole-5-ol. It has been suggested that this anomalous trapping reaction is connected in some way with a six-membered ring arrangement brought about by intramolecular hydrogen bonding involving the nitroso group in position 4 and the hydroxy group in position 5 on the pyrazole unit.¹

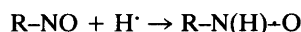
It has now been found that the trapping of hydrogen atoms in the photochemical reaction involving methanol or DMSO and hydrogen peroxide is not restricted to the use of 1(2),3-dimethyl-4-nitrosopyrazol-5-ol, but is also observed with other α -nitroso- β -hydroxy compounds. Thus, nitroxide radicals formed by the trapping of $\text{H}\cdot$ radicals were obtained with 1-nitroso-2-naphthol, isonitrosobarbituric acid, and a number of acyclic oximino dioxo compounds. A common property of these substances is a structure that allows the formation of the six-membered ring system mentioned above, either directly or after enolization of their keto forms.

Many of the spin-trapping reagents in this series were present mainly in the oximino-keto form. In order to establish a rapid equilibrium with conversion of some part of the



substance into the nitroso-enol form, a small amount of hydrogen chloride was added to the reaction mixtures.

The ESR spectra of the nitroxide radicals formed by trapping $\text{H}\cdot$ radicals exhibited six lines of equal intensity due to the interaction of the unpaired electron with one ^{14}N nucleus and one hydrogen atom.



Since the coupling constant a_{H} was only slightly smaller than a_{N} , i.e. $a_{\text{H}} = 11.7\text{--}12.0$ G and $a_{\text{N}} = 12.0\text{--}12.5$ G, the four central lines of the six-line spectra were incompletely resolved, or, in some cases, formed a superposition that gave rise to a four-line system with the intensities 1:2:2:1. Therefore, to identify the trapped radicals and evaluate the coupling constants it was sometimes convenient to perform the reaction in CH_3OD which led to the trapping of $\text{D}\cdot$ radicals, either directly or after exchange of protium for deuterium. The trapping of $\text{D}\cdot$ radicals gave rise to a spectrum with 3×3 lines of equal intensity, which was more easily interpreted than the spectra obtained by the trapping of $\text{H}\cdot$ (cf. Fig. 1).

The nitroxide radicals formed by the trapping of $\text{H}\cdot$ or $\text{D}\cdot$ radicals appeared after a few minutes of irradiation with UV light in the presence of small amounts of HCl and H_2O_2 . The radicals persisted for more than an hour, as long as the samples were irradiated. In some of the trapping reactions, additional unidentified radical species appeared at the beginning of the reaction. However, these species generally disappeared after some time during the irradiation.

A characteristic property of the substances in this series is the oxidation of their oximino-keto forms with ammonium hexanitratocerate(IV) to stable iminoxy radicals ($a_{\text{N}} = 25\text{--}32$ G).²

Nitroxide radicals formed by trapping $\text{H}\cdot$ or $\text{D}\cdot$ radicals in reaction mixtures of methanol or DMSO and small

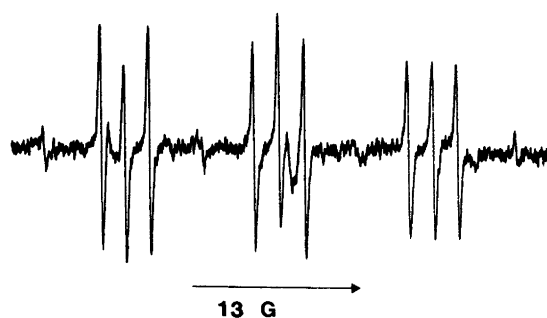


Fig. 1. The ESR spectrum of the nitroxide radicals formed by trapping of $D\cdot$ radicals. The reaction mixture contained 3-oximino-2,4-dioxopentane dissolved in CH_3OD to a concentration of 10 mM, together with 0.1 M HCl (10 μ l/0.5 ml) and H_2O_2 (10 μ l of 30% in H_2O in 0.5 ml). The sample was irradiated *in situ* in the ESR cavity with UV light. $a_N = 12.0$ G, $a_D = 1.82$ G.

amounts of HCl and H_2O_2 during irradiation of the samples with UV light have been obtained with the following substances.

I. *1(2),3-Dimethyl-4-nitrosopyrazole-5-ol*. The results obtained with this substance have been described in detail earlier.¹ The substance is very probably present in the oximino-keto and the nitroso-enol forms in nearly equal proportions at equilibrium.

II. *3-Oximino-2,4-dioxopentane, 2-oximino-1,3-dioxo-1-phenylbutane, 2-oximino-1,3-dioxo-1,3-diphenylpropane* and *ethyl 2-oximino-3-oxobutanoate*. These substances are mainly present in their oximino-keto forms. A very high yield of the nitroxide radicals formed in the trapping of $H\cdot$ or $D\cdot$ was obtained in the presence of catalytic amount of HCl after a few minutes of irradiation with UV light. In the absence of HCl, the radicals appeared but only after an irradiation time of 30–40 min. Fig. 1 shows the ESR spectrum of the nitroxide radicals obtained with 3-oximino-2,4-dioxopentane dissolved in CH_3OD .

III. *1-Nitroso-2-naphthol*. This substance is present mainly in the oximino-keto form, as indicated by the very high yield of iminoxy radicals obtained in the oxidation with ammonium hexanitratocerate(IV) ($a_N = 26.5$ G). In accordance with this finding, the yield of nitroxide radicals formed by the trapping of $H\cdot$ radicals was rather low.

IV. *5-Isonitrosobarbituric acid (violuric acid)*. This substance is also present mainly in the oximino-keto form, and the yield of nitroxide radicals formed by trapping of $H\cdot$ radicals was low.

V. *3-Oximino-2-oxobutane*. In the absence of catalytic amounts of HCl, nitroxide radicals formed in the trapping of $H\cdot$ radicals were observed after prolonged irradiation. In the presence of HCl 3-oximino-2-oxobutane reacted mainly as a conventional spin trap with the formation of nitroxide radicals by trapping $\cdot CH_2OH$ radicals formed by the abstraction of a hydrogen atom from the solvent methanol by $\cdot OH$ radicals generated by photolysis of the added H_2O_2 .

The present experiments have shown that the trapping of $H\cdot$ or $D\cdot$ radicals is a general reaction of α -nitroso- β -hydroxy compounds. It is suggested that the trapping of $H\cdot$ or $D\cdot$ radicals commences with the formation of a hydrogen-bonded complex between the α -nitroso- β -hydroxy compounds and hydrogen peroxide. The irradiation with UV light induces a homolytic cleavage of bound H_2O_2 that leads to the selective trapping of $H\cdot$ radicals, and the formation of nitroxide radicals. The alcohol of the reaction mixture is believed to be hydrogen bonded to the nitroxide radical forming a ring arrangement. The radical complex is considered to be stabilized by charge-transfer stimulated by the irradiation with UV light. The mechanism involved in the trapping of $H\cdot$ and $D\cdot$ radicals, and the formation of the radical complex have been studied in more detail by use of the nitroso-enol form of ethyl 2-oximino-3-oxobutanoate. The results of this study will be published in a forthcoming paper.³

Experimental

The dioxo-oximino substances (II) were prepared as described by Touster.⁴ Ammonium hexanitratocerate(IV), isonitrosobarbituric acid, 1-nitroso-2-naphthol and 3-oximino-2-oxobutane were obtained from Fluka AG and used as supplied; CH_3OD was from Merck.

The preparation of the radicals and the ESR measurements have been described earlier.¹

Acknowledgements. The author is indebted to Dr. R. E. Carter for valuable discussions. This work was supported by grants from *Adlerbertska Forskningsfonden*.

References

1. Lagercrantz, C. *Acta Chem. Scand.* 43 (1989) 78.
2. Lagercrantz, C. and Torssell, K. *Ark. Kemi* 29 (1968) 203.
3. Lagercrantz, C. *Acta Chem. Scand.* Submitted.
4. Touster, O. *Org. React. (N.Y.)* 7 (1953) 327.

Received February 1, 1989.