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Publisher *Taylor & Francis*

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Spectroscopy Letters

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597299>

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W. H. Wolodarsky^a; J. K. S. Wan^a

^a Department of Chemistry, Queen's University, Kingston, Ontario, Canada

To cite this Article Wolodarsky, W. H. and Wan, J. K. S. (1973) 'Electron Spin Resonance Study of the Solvent Effect on the Conformation of Some Iminoxy Radicals', *Spectroscopy Letters*, 6: 7, 429 — 433

To link to this Article: DOI: 10.1080/00387017308065480

URL: <http://dx.doi.org/10.1080/00387017308065480>

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ELECTRON SPIN RESONANCE STUDY OF THE SOLVENT EFFECT ON THE CONFORMATION OF SOME IMINOXY RADICALS

W.H. Wolodarsky and J.K.S. Wan
Department of Chemistry, Queen's University,
Kingston, Ontario, Canada

The reaction of nitrogen dioxide with carbonyl compounds having a methylene or vinyl group adjacent to the carbonyl leads to the formation of stable iminoxy radicals¹⁻³. Evidence^{1,2,4} has been presented that the precursor of these iminoxy radicals is probably the corresponding oxime formed by rearrangements of the intermediate nitroso compounds. There have also been reports on the e.s.r. detection of some cis-trans isomers of some iminoxy radicals in methanol or in neat liquid^{1,5}. We wish to report here a drastic solvent effect on the conformations of some iminoxy radicals formed by the reaction of NO₂ with trifluoroacetylacetone.

The reaction of nitrogen dioxide with trifluoroacetylacetone in carbon tetrachloride or purified chloroform was found to give iminoxy

radical $\text{CH}_3\text{COC}(\text{NO})\text{COCF}_3$, with only one conformation observed. The e.s.r. parameters of this syn isomer are listed in Table 1. The conformation is the syn isomer with respect to the CF_3 group. When a trace of ethanol was added to the

Table 1
E.s.r. parameters of $\text{CH}_3\text{COC}(\text{NO})\text{COCF}_3$ isomers
in various solvents at room temperature

Conformation	A_N	A_H	A_F	g-value
<u>Syn</u>	28.1 gauss	0.15	5.0	2.0039 ₅
<u>Anti</u>	29.9	0.65	---	2.0044 ₅

solvent, or when unpurified chloroform which contains 0.75% ethanol was used, both the syn and the anti forms of the same iminoxy radical were observed and their spectra are shown in Fig. 1. Fig. 1a is the experimental spectrum in chloroform solvent containing 1% ethanol; Fig. 1b is a computer-simulated spectrum using parameters of equimolar of both syn and anti isomers. This analysis reveals that the composition of the isomers in solvents with a trace of alcohol is almost equimolar at room temperature. Within the temperature range of 10-30°C, the results indicate that we are not dealing with a thermodynamic equilibrium mixture and that the presence of

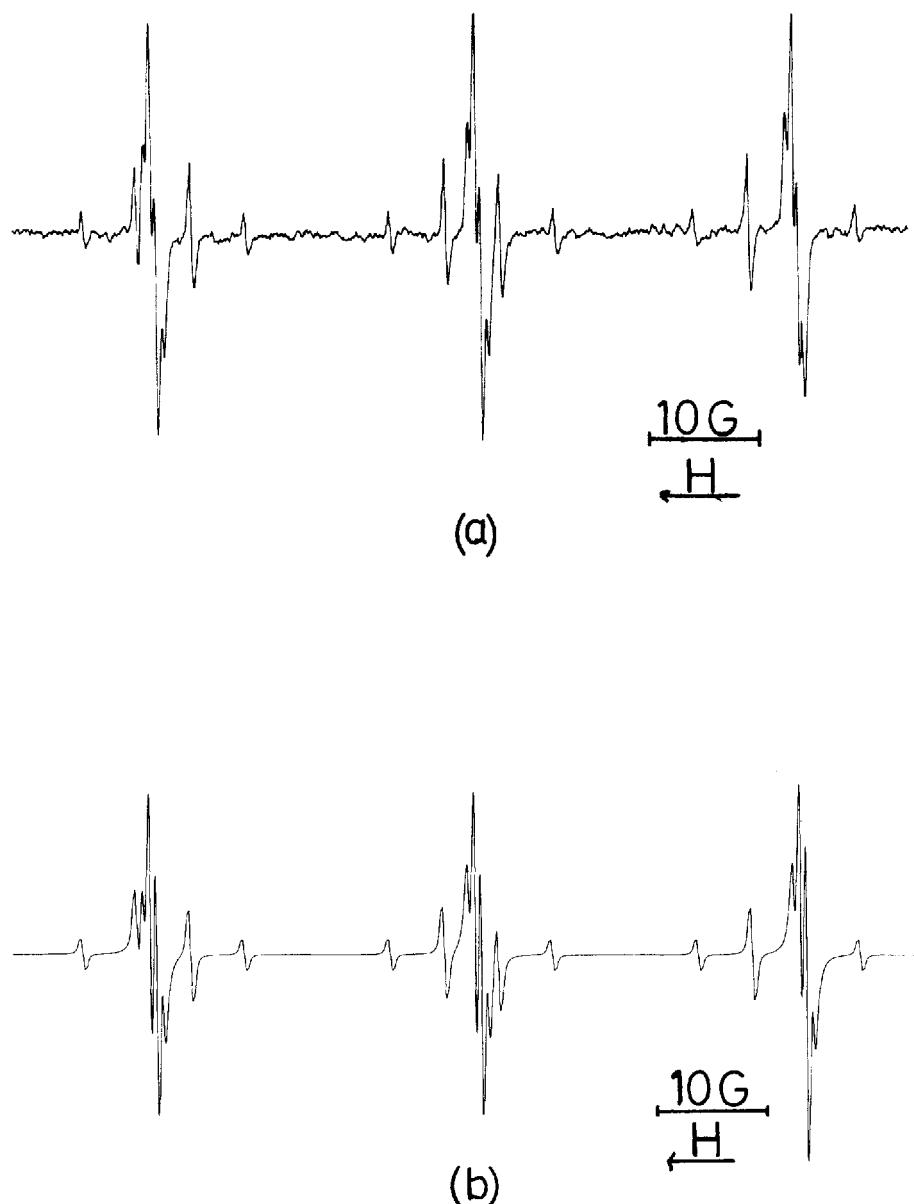


Fig. 1. E.s.r. spectra of $\text{CH}_3\text{COC(=NO)COCF}_3$ radicals in chloroform containing trace of ethanol.

alcohol is necessary in this temperature range to bring about the mixture. Experiments have not been extended to a wider temperature range, because the radicals at room temperature have lifetimes of about 3 to 5 hours and they will be greatly shortened at high temperatures. On the other hand, drastic lowering of the temperature will change the viscosity of the solvent and will broaden the e.s.r. lines, making it impossible to distinguish the isomers.

A plausible explanation for this drastic solvent effect on the radical conformation can be attributed to the presence of the intermediate oxime as a reaction product. In the carbon tetrachloride solvent, hydrogen-bonding is not available between the solvent and the oxime. Thus the oxime may have a preferred configuration via the $=\text{N}-\text{OH} \cdots \text{F}_3\text{C}-$ interaction. Baker and Shulgin⁶ have obtained some i.r. evidence of similar unexpected preferred position of the α -trifluoromethyl phenol via some strong intramolecular $\text{OH} \cdots \text{F}_3\text{C}-$ interactions.

When the oxime in the preferred position is oxidized to the iminoxy radical, only the syn isomer is observed. In the presence of alcohol, the oxime protons can be extensively hydrogen-bonded to the alcohol with both cis and trans forms of the oxime equally probable. Thus it leads to the formation of a almost equimolar mixture of the syn and anti forms of the resulting iminoxy radical.

This extreme sensitivity of iminoxy radical conformation to the environment may be of some interest to the potential use of stable iminoxy radicals as spin labels in biochemical systems.

ACKNOWLEDGMENT

This research is supported by the National Research Council of Canada.

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Received May 17, 1973

Accepted June 1, 1973