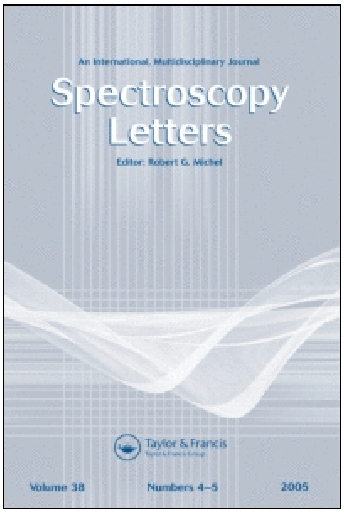

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Electron Spin Resonance Study of the Solvent Effect on the Conformation of Some Iminoxy Radicals

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

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The reaction of nitrogen dioxide with carbonyl compounds having a methylene or vinyl group adjacent to the corbonyl leads to the formation of stable iminoxy radicals[1-3]. 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 NO_2 with trifluoroacetylacetone.

The reaction of nitrogen dioxide with trifluoroacetylacetone in carbon tetrachlroide or purified chloroform was found to give iminoxy radical $CH_3COC(=\dot{N}O)COCF_3$, 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 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

Table 1

E.s.r. parameters of $CH_3COC(=\dot{N}O)COCF_3$ isomers in various solvents at room temperature

Conformation	A_N	A_H	A_F	g-value
Syn	28.1 gauss	0.15	5.0	2.0039_5
Anti	29.9	0.65	---	2.0044_5

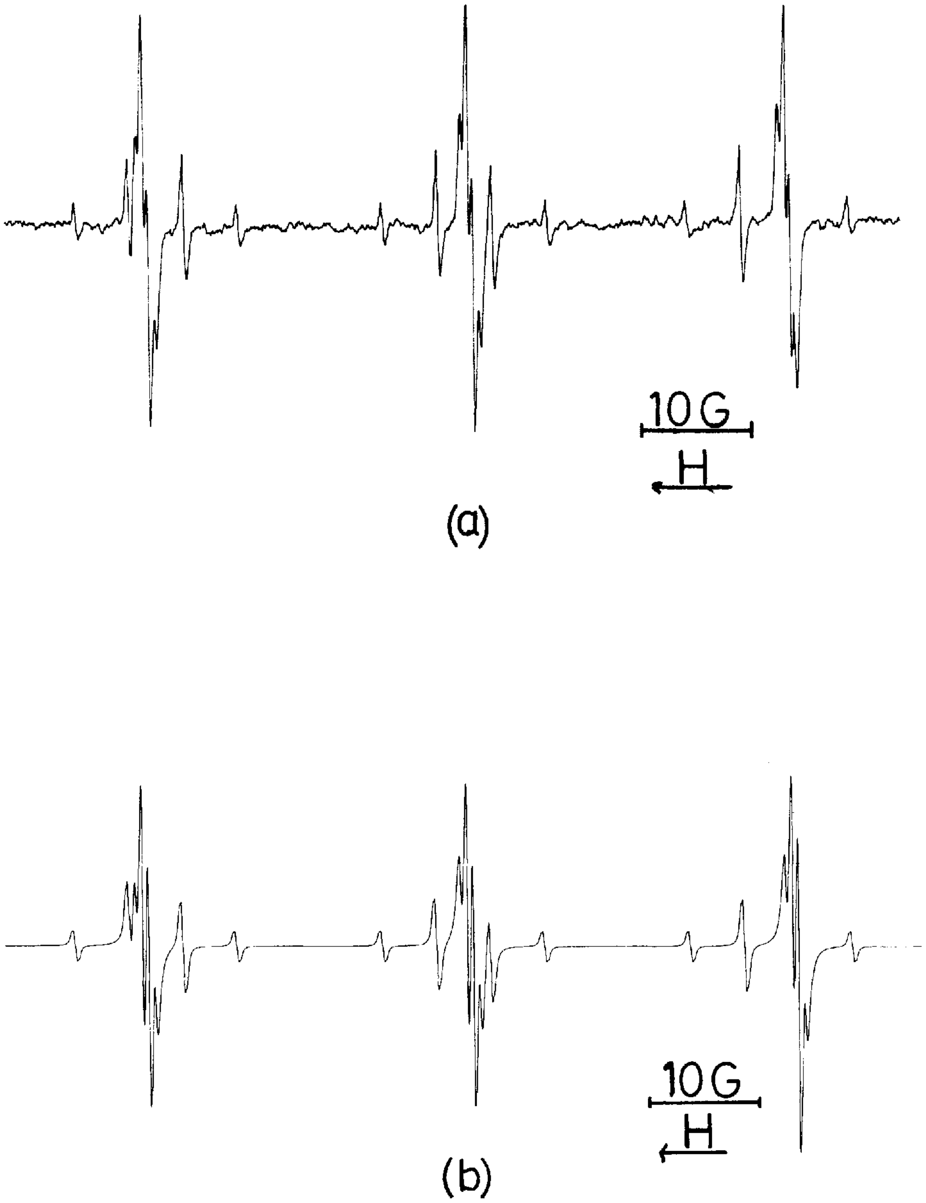

Fig. 1. E.s.r. spectra of $CH_3COC(=NO)COCF_3$ radicals in chloroform containing trace of ethanol.

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 $=N-OH$ --- F_3C- interaction. Baker and Shulgin[6] have obtained some i.r. evidence of similar unexpected preferred position of the o-trifluoromethyl phenol via some strong intramolecular OH --- F_3C- 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.

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