Tetrahedron. Vol. 29, pp. 4299 to 4302. Pergamon Press 1973. Printed in Great Britain

ELECTRON SPIN RESONANCE SPECTRA OF α-SULFONYL IMINOXY RADICALS

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(*Received in the UK 7 August 1973; Accepted for publication 6 September 1973*)

Abstract—*Syn*- and *anti*-α-sulfonyl iminoxy radicals have been generated *in situ* by lead tetra-acetate oxidation of α-oximino sulfones. The ESR spectra of the geometrical isomers have been assigned and the ^{14}N and ^{1}H hyperfine splitting constants are discussed in terms of the proposed structures.

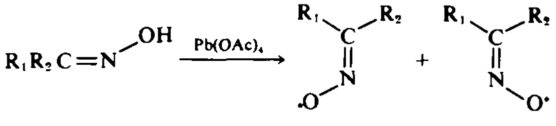
A number of iminoxy radicals have been produced as transient intermediates in various types of reactions. Detailed examination of their ESR spectra[1-4] has indicated that these species can be best represented as hybrids of the structures A and B in which the unpaired electron is contained in an MO derived from a nitrogen sp^2 orbital and an oxygen p orbital. Since this MO is orthogonal to the molecular π system, iminoxy radicals should be described as σ radicals.[5,6]

In the course of our investigations of the chemistry of α-nitrosulfones, we recently prepared a series of α-oximino sulfones.[7] We now report ESR spectral evidence for the *in situ* conversion of these types of oximes into a new class of radicals in which a sulfonyl group is attached to the iminoxy function.

RESULTS AND DISCUSSION

The treatment of the oximes **1-7** under static conditions with lead tetra-acetate in CH_2Cl_2 at 0° according to the method of Lown[8] results in the formation of paramagnetic species with halflives of several minutes. ESR spectral data are listed in the Table.

The spectra are assigned to α-sulfonyl iminoxy radicals **8–14** on basis of the following: (i) the large and characteristic[4-6] nitrogen hyperfine splitting constants (hfc's) of *ca* 30 gauss and (ii) the simultaneous observation to ESR spectra due to two geometricalty isomeric iminoxy radicals,† referred to as *syn*-sulfonyl (**8a–14a**) and *anti*-sulfonyl (**8b–14b**), with hfc's that can be interpreted on basis of the proposed structures (*vide infra*). Others[6] have also observed that oxidation of oximes with lead tetraacetate usually leads to both isomeric iminoxy radicals, irrespective of the configuration of the oxime used.‡



1–7 **8a–14a** **8b–14b**

The assignment of hfc's to *syn*- and *anti*-sulfonyl iminoxy radicals (Table) is largely based on analogy with ESR data of related iminoxy radicals and on internal consistency in the assignments within the series **8a–14a** and **8b–14b**. Fig 1 shows the low field nitrogen lines of the iminoxy radicals obtained from

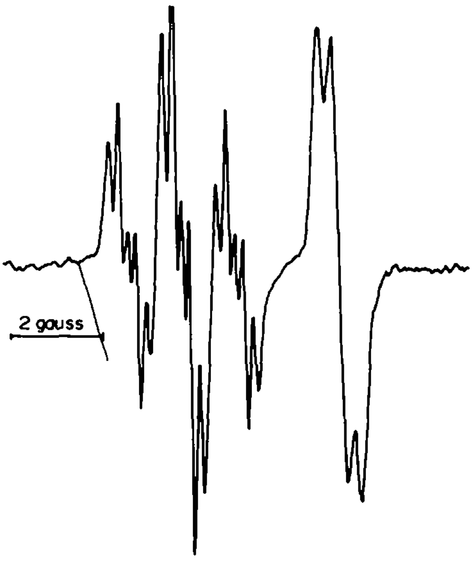


Fig 1. Low field nitrogen lines of the iminoxy radicals **8a** - **8b** derived from **1**.

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†Except for **4**, see Table.

‡The oximes **1–7** probably have *anti*-configurations in solution.[7]

Table. Hyperfine splitting constants[a] of α-sulfonyl iminoxy radicals, $R_1R_2C{=}N{-}O$ in CH_2Cl_2 at 0°

	Oxime		Iminoxy Radical							
			syn-Sulfonyl				*anti*-Sulfonyl			
	R_1	R_2		a_N	$a_{o\text{-}H}$	a_H (other)		a_N	$a_{o\text{-}H}$	a_H (other)
1	p-$CH_3C_6H_4SO_2$	C_6H_5	**8a**	29·7	0·3 (2H)		**8b**	32·9	1·17 (2H)	0·20 (2H), 0·35 (1H)
2	p-$CH_3C_6H_4SO_2$	p-$CH_3OC_6H_4$	**9a**	29·8	0·3 (2H)		**9b**	33·0	1·10 (2H)	
3	p-$CH_3C_6H_4SO_2$	p-ClC_6H_4	**10a**	29·6	0·3 (2H)		**10b**	33·0	1·08 (2H)	
4	p-$CH_3C_6H_4SO_2$	2,6-$Cl_2C_6H_3$	**11a**	30·3					not observed	
5	$C_6H_5CH_2SO_2$	C_6H_5	**12a**	29·7	0·3 (2H)		**12b**	32·9	1·17 (2H)	0·20 (2H), 0·35 (1H)
6	p-$CH_3C_6H_4SO_2$	CH_3	**13a**	29·4		1·59 (3H)	**13b**	31·6		1·23 (3H)
7	p-$CH_3C_6H_4SO_2$	C_2H_5	**14a**	29·0		1·67 (2H), 0·3 (3H)	**14b**	31·8		1·20 (3H)

[a] In gauss. The spectra were measured on a Varian E-4 apparatus fitted with a Varian A 1268 variable temperature controller.

oxime **1**. One of these lines is further split into a triplet with a small coupling constant (0·3 gauss). The hyperfine splitting of the other line is more complex and the hfc's (see Table) were evaluated using computer simulation (Fig 2). Similar aromatic proton splittings are observed in one of the iminoxy radicals derived from **5**. This suggests that the spectra exhibiting hyperfine interaction with all phenyl protons should be assigned to those isomers in which the phenyl ring is positioned in the *syn*-position with respect to the iminoxy O atom (**8b** and **12b**, respectively). The splitting of 1·17 gauss is apparently due to coupling with both *ortho*-protons and is comparable to the hfc (1·4 gauss) found for the two *ortho*-protons of one aromatic ring in the ESR spectrum of the iminoxy radical derived from benzophenone oxime.[6] The substantial splittings due to the *para*-proton in **8b** and **12b** are noteworthy since, to our knowledge, *para*-splittings of this magnitude have not been observed previously in phenyl iminoxy radicals. The $a_{m\text{-H}}/a_{p\text{-H}}$ ratio is probably indicative of some spin density in the aromatic π system.

The geometrical isomers **8a** and **12a** exhibit only a very small coupling with two aromatic protons, probably the *ortho*-protons. Analogous results are obtained for the iminoxy radicals formed from **2** and **3**, although in the spectra of the *anti*-sulfonyl isomers **9b** and **10b** no coupling with the *meta*-protons of the R_2 aromatic ring could be detected. The data in the Table show that it is consistently found that the *syn*-sulfonyl isomers possess smaller a_N values (29–30 gauss) than the *anti*-sulfonyl iminoxy radicals (31–33 gauss). It is tentatively proposed that this is due to a small destabilization of resonance hybrid B in the *syn*-form because of unfavourable electrostatic interaction between the negatively charged iminoxy oxygen atom and the sulfonyl oxygen lone pairs.

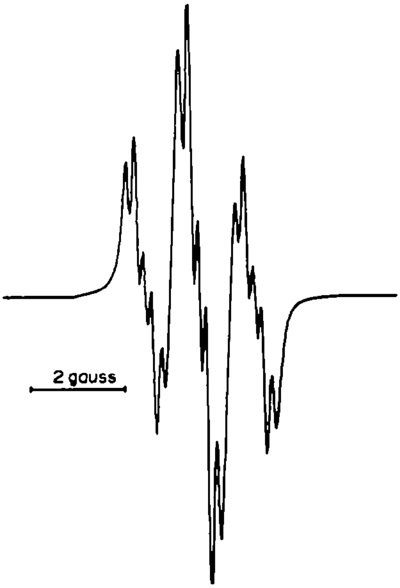

Fig 2. Computer simulated low field nitrogen line of **8b**.

Note, however, that the a_N values of the sulfonyl iminoxy radicals are in the same range as those commonly found for dialkyl, alkyl aryl or diaryl iminoxy radicals. The absence of a significant substituent effect of the strongly electron withdrawing sulfonyl moiety on the nitrogen hfc's is in accord with the σ-character of these species and may be contrasted with the effect induced by substitution of electronegative groups on the a_N values of nitroxides.[9,10] Upon oxidation of **4**, only the *syn*-sulfonyl iminoxy radical was observed as deduced from the a_N value (30·3 gauss). Repulsive interaction between the iminoxy oxygen atom and the *ortho*-chloro atoms could be invoked to explain a much higher population of the *syn*-sulfonyl isomer as compared with the *anti*-form.

The ESR spectra of the iminoxy radicals derived from **5** reveal that there is no observable transmission of spin density through or over the sulfonyl group as evidenced by the absence of hyperfine splitting of the α-sulfonyl methylene protons. This situation differs from the one for α-sulfonyl nitroxides[10,11] and anion radicals derived from alkyl aryl sulfones[12,13] where such hyperfine interaction was easily resolved.

The ESR spectrum obtained upon oxidation of **6** is shown in Fig 3. Clearly two overlapping spectra are involved with a_N values of 29·4 and 32·2 gauss, respectively. The high field nitrogen lines (Fig 4) show that each nitrogen line is further split due to interaction with three protons. The rather small difference between the proton hfc's in both isomers does not permit an assignment of the geometrical forms.* Therefore, the *syn*- and *anti*-forms were assigned on basis of their nitrogen couplings. Following the arguments of Norman and Gilbert,[6] the similarity of the methyl proton coupling constants in **13a** and **13b** may be the result of the operation of two mechanisms for the transmission of spin density, namely spin polarization and direct overlap of the orbital containing the unpaired electron and the hydrogen 1s orbital. These mechanisms will induce

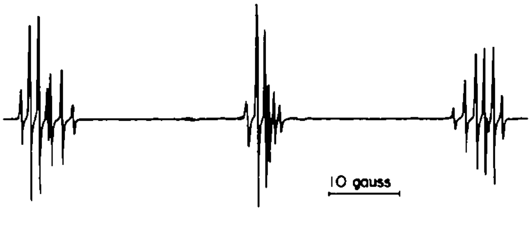

Fig 3. ESR spectrum obtained upon oxidation of **6**.

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*Both iminoxy radicals derived from $CH_3COC(=NOH)CH_3$ show nearly equal α-methyl proton splittings of *ca* 1·4 gauss.[6]

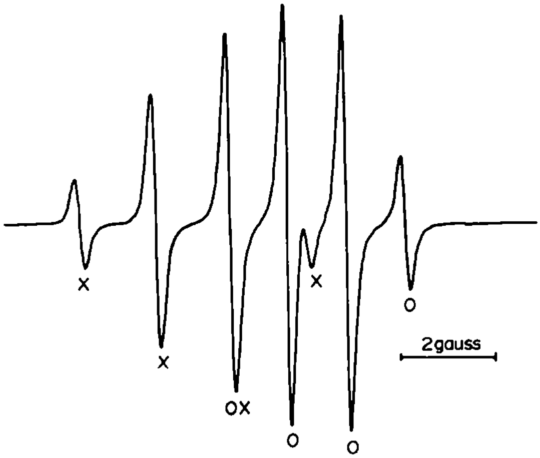

Fig 4. High field nitrogen lines of **13a** and **13b**.

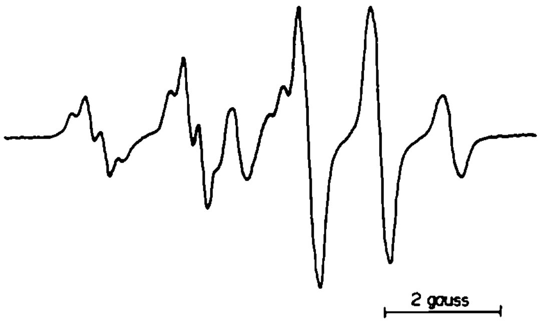

Fig 5. High field nitrogen lines of **14a** and **14b**.

spin densities of opposite sign at the methyl hydrogen nuclei. The geometry of **13a** implies that spin polarization will be largely responsible for the methyl splitting. In **13b** both mechanisms will be operative resulting in a reduced $a_H^{CH_3}$ as compared with **13a**. The absence of methylene proton splittings in the *anti*-sulfonyl iminoxy radical **14b** (high-field nitrogen line is shown in Fig 5) is understandable assuming that the operation of both coupling mechanisms has resulted in complete nullification of spin density at that site. In the *syn*-form **14a** splittings due to all ethyl protons appear, since now spin polarization will dominate in the transmission of spin density.

In **13b** no splitting due to the *ortho*-protons of the aromatic ring was found in contrast to the observation[6] of *ortho*-H-splittings of 0·71 gauss in the corresponding iminoxy radical with $R_1 = C_6H_5CO$ instead of p-$CH_3C_6H_4SO_2$. The sulfonyl group in **13b** prevents the radical from adopting a coplanar conformation necessary for effective, long-range spin transmission.

Finally we note that upon oxidation of several oximes (**1–3**, **6**) a weak ESR spectrum of a third radical was detected, often with varying intensity. These spectra showed nitrogen hfc's of 7·5–8·0 gauss and the radical derived from **6** had $g = 2{\cdot}00629 \pm 0{\cdot}00001$. Caragheorgheopol *et al.*[14] have also detected radicals with $a_N = 7{\cdot}3 - 8{\cdot}0$ gauss, especially upon oxidation of sterically hindered oximes, however with higher g-values (2·0069). These ESR spectra were attributed to the presence of acyl nitroxides. In our case the origin of these radicals is as yet obscure.

Acknowledgement—We are indebted to Mr. D. van Leusen for providing us with the oxime 4 and to drs. J. H. Lichtenbelt for supplying the computer programme and for technical advice.

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