

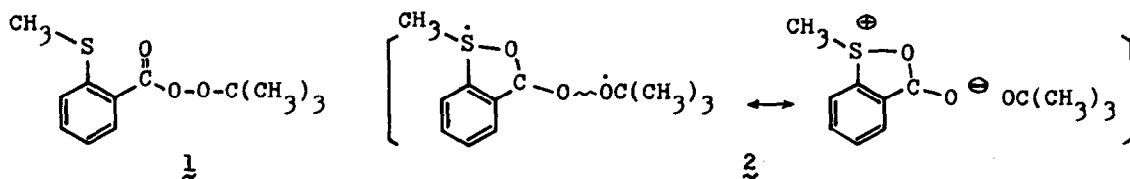
ON THE STRUCTURE OF o-METHYLTHIOBENZOYLOXY RADICAL
AS REVEALED BY CIDNP SPECTRA AND CNDO/2 MO CALCULATIONS ¹⁾

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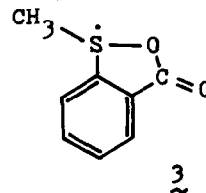
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Acceleration of a homolytic O-O bond cleavage by participation of a neighboring sulfur atom has been very clearly established in tert-butyl o-methylthioperoxybenzoate (1) which decomposes ca. 10^4 times as fast as the parent peroxybenzoate at 60°C in chlorobenzene. The rate-determining step for the cleavage is described by the anchimerically assisted structure 2.²⁾



We wish to report that the free o-methylthiobenzoyloxy radical itself is better represented as bridged sulfuranyl radical 3 in which most of the spin density is localized at the sulfur atom rather than in the carboxyl.

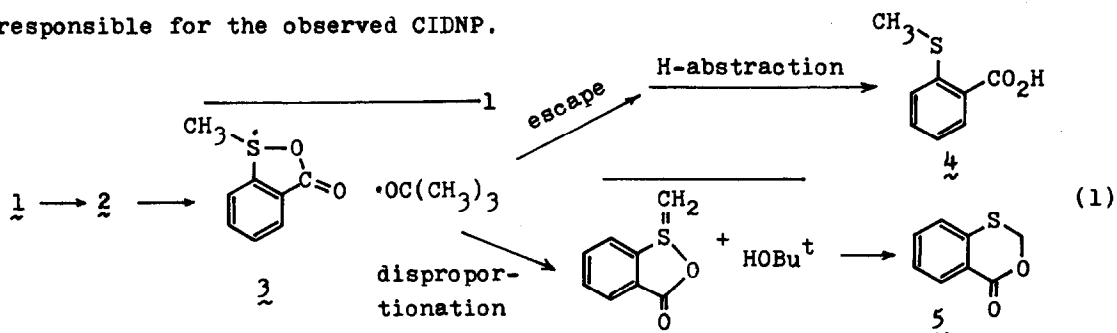


CIDNP Results and Discussion When the

solutions of 5 mg of 1 in 0.5 ml of chlorobenzene, o-dichlorobenzene, tetrachloroethylene and trans-decalin were heated at 90~95°C in a ¹H NMR probe,³⁾ strong emission (E) and enhanced absorption (A) signals were observed at δ 2.38

and 5.21, respectively. By adding small amounts of the authentic samples to the completed reaction mixture and observing increase in the corresponding signal intensities, we found that the methyl protons of *o*-methylthiobenzoic acid (4) was in E and the methylene protons of 3,1-benzoxathian-4-one (5) was in A. The singlets due to acetone and *tert*-butyl alcohol were not spin-polarized. No CIDNP was detected in the aromatic protons for the reactions run in tetrachloroethylene and *trans*-decalin.⁴⁾ The ¹³C experiments on 1 were carried out on a solution of 150 mg of 1 in 1 ml of *o*-dichlorobenzene at 80°C.³⁾ The methylene carbon due to 5 was in strong E at δ 68.7. The S-methyl carbon (δ 15.5) of 4 was in A and there were some weak polarization signals yet to be assigned in the aromatic carbons. There was no polarization signal in the C=O carbon region.

All the results, especially strong polarization in the S-methyl-derived moieties and no polarization in the carbonyl carbons in 4 and 5, appear to indicate that hyperfine interaction of the methyl protons and carbon is quite large and that the considerable spin density is localized at the sulfur atom and not in the carboxyl group in the *o*-methylthiobenzoyloxy radical. The CIDNP spectra are reasonably explained only when the radical has structure 3 (or 6). In reference to the Kaptein rule,⁵⁾ Eq. 1 is proposed as the reaction scheme responsible for the observed CIDNP.



The signs for hyperfine coupling are expected to be plus for the β -H and minus for the α -C in the methyl group of S-centered radical 3. The *g* values can be higher for the *tert*-butoxyl (*g* = 2.009) than the benzoyloxy 3.⁶⁾ The opposite signs of polarization found in the S-methyl group of 4 and the methylene group of 5 are reasonably ascribed to the different mode of formation of these products; 4 is an escape product while 5 may be formed by cage-disproportionation followed by rearrangement.

CNDO/2 Molecular Orbital Calculations We have examined the odd electron spin distribution and valence structure of the o-methylthiobenzoyloxy radical by the open-shell CNDO/2 SCF-MO.⁷⁾ Calculations were performed on various geometries based on sets of standard bond lengths and angles.⁸⁾ A typical result is shown in Figure 1. The half-filled molecular orbitals are about 80% localized on the $3p_z$ orbital of the sulfur atom. The Wiberg's bond indices which can be used as a good measure of bond orders in the all-valence-electron SCF-MO methods show that there is a definite bonding of the order 0.886 between the sulfur and one of the oxygen(1) atoms at a distance of 1.88 Å. The bonding is possible only by expansion of valence octets of the sulfur atom. Its hybrid orbitals directed to the methyl, phenyl ring and oxygen atom are $s^{0.1}p^{2}d^{1.06}$, $s^{0.26}p^{2}d^{0.52}$ and $s^{0.013}pd^{1.60}$, respectively. Thus the sulfur atom is approximately p^2d hybridized with the lone pair of electrons in the s and the odd electron in the p_z orbitals. In another geometry which may be considered as a good model for no-bond structure $\tilde{6}$, the Wiberg's bond index for the $S \cdots O(1)$ is still 0.394 at the distance of 2.48 Å apart, suggesting a strong bonding character between these two atoms.⁹⁾ We conclude that the free o-methylthiobenzoyloxy radical should in fact be a bridged sulfuranyl radical.¹⁰⁾

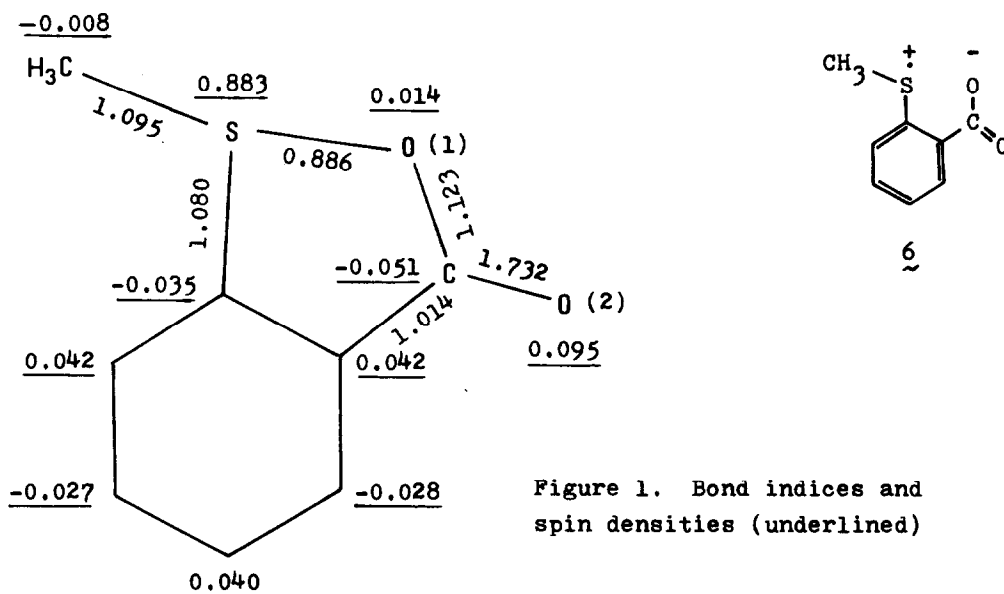


Figure 1. Bond indices and spin densities (underlined)

References and Notes

- 1) Part XI of Studies of Reaction Mechanisms with All-valence Electron Semi-Empirical SCF MO Theories. For Part X, see: H. Iwamura, H. Kihara, S. Misumi, Y. Sakata, and T. Umemoto, *Tetrahedron Lett.*, 615 (1976).
- 2) W. G. Bentrude and J. C. Martin, *J. Amer. Chem. Soc.*, 84, 1561 (1962).
- 3) The ^1H NMR spectra were obtained on a JEOL JNMC-60HL (60 MHz) spectrometer. The ^{13}C NMR were obtained on a Varian CFT-20 Pulse Fourier Transform spectrometer (20.1 MHz). A 8 μs pulse was applied with an acquisition time of 0.909 s over the spectrum width of 4.5 KHz. The number of data points was 8 K.
- 4) A similar CIDNP experiment on the *p*-methylthioperoxybenzoate gave negative results; the ^1H signals due to acetone, tert-butyl alcohol and a methylthio signal at δ 2.40 of the product increased monotonically at 155 °C.
- 5) See for example: A. R. Lepley and G. L. Closs, "Chemically Induced Magnetic Polarization," Wiley, New York, N. Y. (1973).
- 6) The experimental *g* factor of benzoyloxy is 2.0117 (N. J. Karch, E. T. Koh, B. L. Whitsel, and J. M. McBride, *J. Amer. Chem. Soc.*, 97, 6729 (1975)). Diminution in the *g* value would be expected when excitation of the odd electron to an empty *d* orbital is available. There is an argument that the *tert*-butoxyl radical has probably a very short electron relaxation time due to large *g*-tensor anisotropy and therefore ESR observation of this radical in solution is difficult. The radical may not be able to be a component of a radical pair responsible for CIDNP effect (J. den Hollander, PhD thesis of University of Leiden, 1976). However, there are some reports in which the pair containing *tert*-BuO \cdot does produce CIDNP (P. D. Bartlett and N. Shimizu, *J. Amer. Chem. Soc.*, 97, 6253 (1975)).
- 7) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y. (1970). Since one-center atomic exchange integrals are neglected, no spin density is introduced into the σ -orbitals.
- 8) $\angle\text{OCO} = 124^\circ$, $\angle\text{CCO}(1) = 109^\circ$, $\text{C-O}(1) = 1.34 \text{ \AA}$ and $\text{C-O}(2) = 1.26 \text{ \AA}$ were adopted for the carboxyl. $\text{CH}_3\text{-S} = 1.82 \text{ \AA}$, $\text{Ar-S} = 1.80 \text{ \AA}$ and $\angle\text{CSC} = 99^\circ$ were assumed for the methylthio group.
- 9) Optimization of the geometry with respect to the CNDO/2 energy has not been carried out. This model is less stable than the one in Fig. 1 by more than 50 kcal/mole. While the energy depends considerably on the choice of geometry, the spin distribution does not differ much from those given in Fig. 1 and appears less sensitive to geometry.
- 10) The conclusion is consistent with the formation of a stable sulfurane from di-*tert*-butyl 2-phenylthiobenzene-1,3-dicarboperoxoate (J. C. Martin and M. M. Chau, *J. Amer. Chem. Soc.*, 96, 3319 (1974)).