CHEMISTRY LETTERS, pp. 387-390, 1981.

THERMAL DECOMPOSITION OF ^{17}O-LABELED t-BUTYL o-METHYLTHIO- AND o-PHENYLTHIOPEROXYBENZOATES STUDIED BY ^{17}O NMR. THE SULFURANYL RADICAL STRUCTURE OF THE o-THIOBENZOYLOXY RADICALS

Warō NAKANISHI, Toshihiko JO, Kunio MIURA, Yoshitsugu IKEDA,
Tadashi SUGAWARA,* Yuzo KAWADA,* and Hiizu IWAMURA*

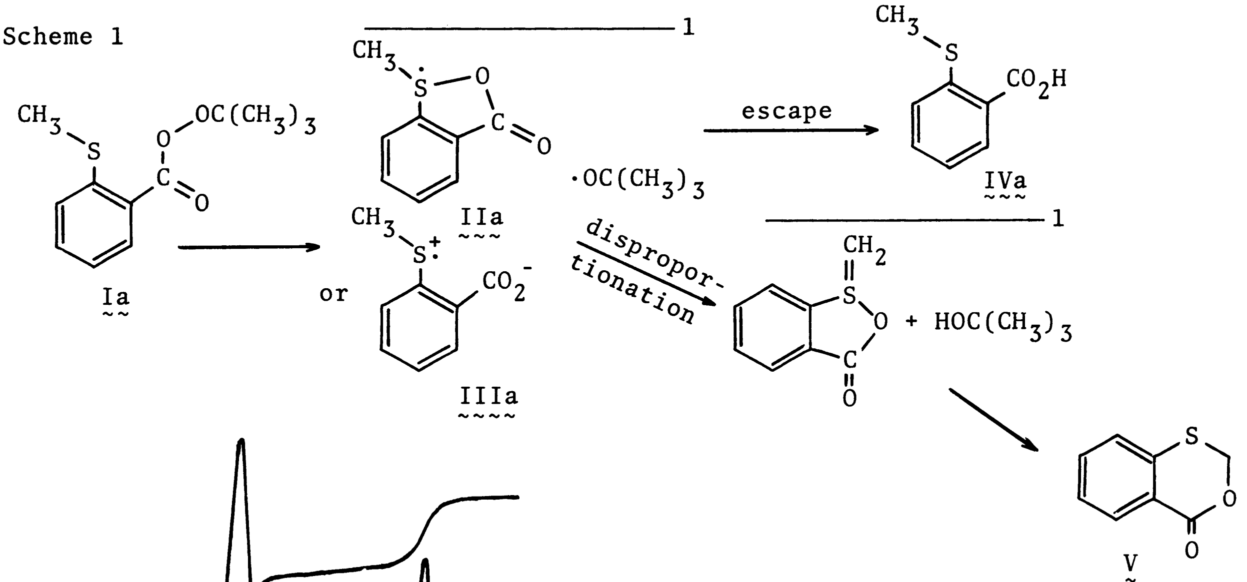
Department of Chemistry, Faculty of Education, Wakayama University,
Masago-cho, Wakayama 640, and *Division of Applied Molecular Science,
Institute for Molecular Science, Myodaiji, Okazaki 444

t-Butyl o-methylthio- and o-phenylthioperoxybenzoates-[C=^{17}O] were prepared and decomposed thermally in chlorobenzene. The oxygen labels were detected by ^{17}O NMR spectroscopy preferentially at the carbonyl oxygen of 3,1-benzoxathian-4-one and diphenyl 2,2'-dithiodibenzoate, demonstrating the bridged sulfuranyl radical structures for the o-thiobenzoyloxy radicals.

Bentrude and Martin have proposed that the participation of a neighboring sulfur atom is responsible for the enhanced rate (by a factor of 10^4) of the homolytic O-O bond cleavage in t-butyl o-methylthioperoxybenzoate (Ia).$^{1)}$ More recently we have shown by the CIDNP and CNDO/2 MO studies that, not only in the transition state for the decomposition but also in the intermediate o-methylthiobenzoyloxy radical, the anchimerically assisted structure IIa with considerable spin density at the sulfur atom is preferred to the classical benzoyloxy radicals.$^{2)}$ However, the possibility of a zwitterionic structure IIIa has not been rigorously excluded. ^{17}O NMR spectroscopy has now revealed that the identity of the carbonyl oxygen is rather well kept during the thermal decomposition of t-butyl o-methylthio- and o-phenylthioperoxybenzoates (Ia* and Ib*), ruling out the non-bridged structure for the intermediate radicals. We also point out that, in contrast to the ^{18}O tracer technique widely used to elucidating structures and reaction mechanisms in organic chemistry, the ^{17}O labeling coupled with ^{17}O NMR determination has the strong advantage as a non-destructive method; by employing chemical shifts and integration of signal intensities, the site and distribution of the isotopes in the product molecules can be determined directly.$^{3)}$

t-Butyl o-methylthioperoxybenzoate enriched with ^{17}O selectively at the carbonyl group (Ia*) was prepared by the reaction of ^{17}O-labeled o-methylthiobenzoic acid (IV*)$^{5)}$ with 1,1'-carbonyldiimidazole in THF followed by treatment with t-butylhydroperoxide at low temperature.$^{6)}$ t-Butyl o-phenylthioperoxybenzoate-[C=^{17}O] (Ib*) was prepared similarly. Five and three tenth g of Ia* were decomposed in 69 ml of chlorobenzene at 76 °C, and 0.327 g of ^{17}O-labeled 3,1-benzoxathian-4-one was isolated. As shown in Figure 1, the ^{17}O NMR spectrum of the lactone contained two signals.[7] The downfield signal (365 ppm from external D_2O) was assigned to the carbonyl oxygen and the highfield one (159 ppm) to the ether oxygen.[8] They were found to be in the integration ratio of 66 : 34. The ratio was 50 : 50 when the ^{17}O NMR spectrum of V in natural abundance was measured. Thus the oxathianone-[C=^{17}O] (V*) and -[ether-^{17}O] (V*') were formed in the ratio of 66 : 34 when Ia* was decomposed under the conditions described above. As shown in Table 1, the formation of V* in preference to V*' is more favored as the temperature of decomposition is lowered.

Scheme 1



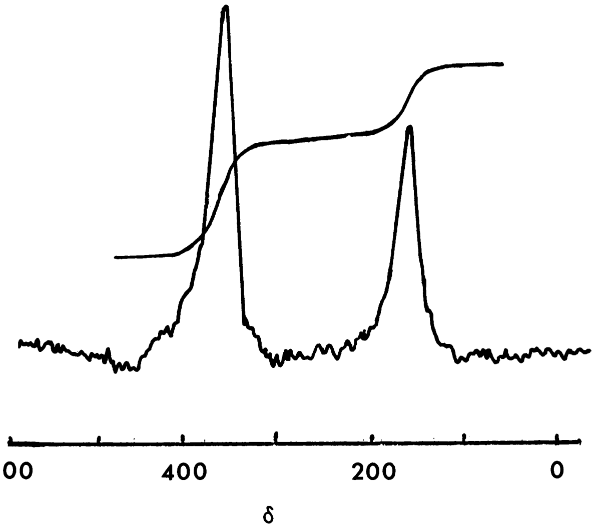


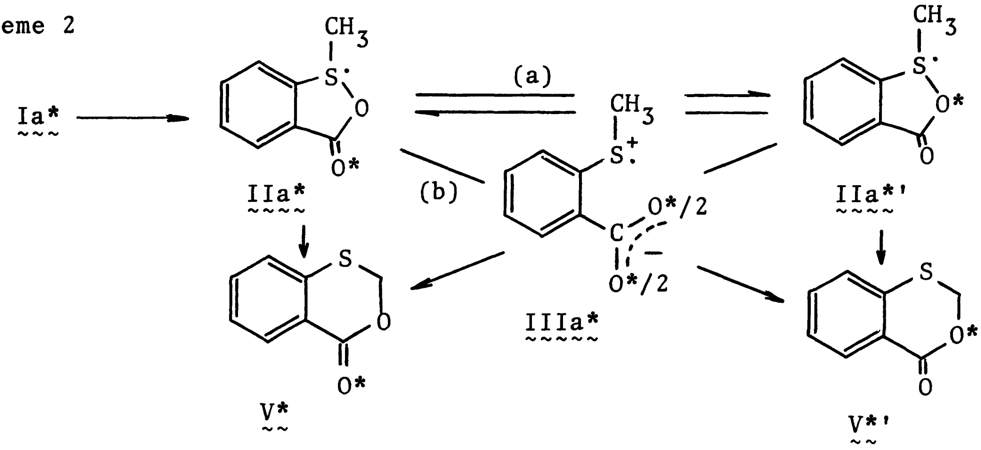
Figure 1. ^{17}O NMR spectrum (10.782 MHz) of V* and V*' derived from the thermal decomposition of Ia* at 76.0 °C.

Table 1. Population of the ^{17}O label in V and the temperature of decomposition of Ia*.

decomposition temperature	V* δ 365	V*' 159
76.0 °C	66	34
62.0	69	31
40.0	74	26

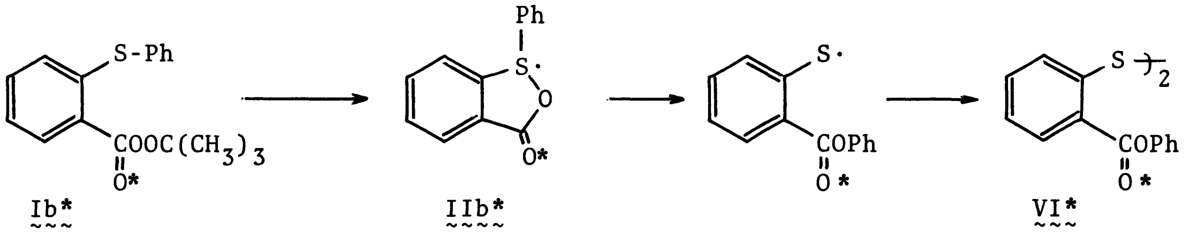
Thermal decomposition of Ia produces IVa and V as the escape and disproportionation products, respectively, of the primary radical pair formed by the O-O bond cleavage of Ia (Scheme 1).[1,2] If the structure of o-methylthiobenzoyloxy radical is IIa, V* can be exclusively formed from decomposition of Ia*. Structure IIIa should operationally lead to scrambling of the label between the two oxygen atoms, although there may be some life-time before the requisite rotation of the ϕ-CO_2^- bond takes place. The results in Table 1 indicate that the identity of the carbonyl oxygen can be kept through the reaction path to lactone V and that there is a competitive channel available for the scrambling of the oxygen label which has the higher activation energy of the reaction than the retentive path by 2.3 kcal mol^{-1}. Therefore we conclude that the o-methylthiobenzoyloxy radical should be represented as IIa. The scrambling of the label between the carbonyl and endocyclic oxygens may take place either before or during the course of the Pummerer-type rearrangement (a or b in Scheme 2). Zwitterionic radical IIIa is supposedly an intermediate or a transient species in these scrambling processes.

Scheme 2



A similar study has been carried out on the decomposition of t-butyl o-phenylthioperoxybenzoate-[C=^{17}O] (Ib*)$^{5)}$ which gives among many other products diphenyl 2,2'-dithiodibenzoate VI* as shown in Scheme 3. The contribution of the induced decomposition which could be another mechanism for the retention of the oxygen label is negligible in this reaction.$^{1)}$ Here we encountered a typical example demonstrating the limitation of the ^{17}O NMR method. Due to quadrupolar relaxation of ^{17}O nuclei, line broadening of the signal gets serious as the size of molecules increases.$^{8)}$ Whereas the signal due to the ^{17}O-rich carbonyl oxygen was easily determined, it was difficult to get a reasonable s/n for the ^{17}O-poor ether oxygen of VI*. Population of the ^{17}O label was therefore determined on phenyl thiosalicylate obtained by the cleavage of VI* into two halves by the method of Overman et al.$^{9)}$ Integration of the peaks at δ 363 and 191 for the carbonyl and ether oxygens gave a ratio of 71 : 29 for the sample obtained by the decomposition of Ib* at 52.0 °C. Here again sulfuranyl radical structure IIb* for the o-thiobenzoyloxy radical was supported.

Scheme 3



References and Notes

1) W. G. Bentrude and J. C. Martin, J. Am. Chem. Soc., 84, 1561 (1962); J. C. Martin, in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, 1973, Chapt. 20.

2) W. Nakanishi, S. Koike, M. Inoue, Y. Ikeda, H. Iwamura, Y. Imahashi, H. Kihara, and M. Iwai, Tetrahedron Lett., 81 (1977).

3) For a mechanistic study of the anchimerically assisted bond cleavages, for example, Martin and Koenig investigated the distribution of ^{18}O in 3-benzhydrylphthalide obtained from the decomposition of the labeled peroxyester by comparing the content of the ^{18}O isotope before and after the saponification/relactonization procedure.[4)] The decomposition of t-butyl o-(2,2-diphenylvinyl)peroxybenzoate labeled with ^{18}O in the carbonyl position was found to give the phthalide with 88 % retention of the identity of the carbonyl oxygen.

4) J. C. Martin and T. W. Koenig, J. Am. Chem. Soc., 86, 1771 (1964).

5) The chloride of **IV** (55 mmole) was hydrolyzed with 1 ml of water-[^{17}O] (20 atom % enriched, Prochem) and 55 mmole of sodium hydroxide in 100 ml of dioxane containing a catalytic amount of 18-crown-6 under reflux for several hours. Each oxygen in **IV** is, therefore, estimated to be enriched by ca. 5 atom %. Contribution from the natural abundance isotope to the ^{17}O NMR spectra is less than 1 %. ^{1}H and ^{13}C NMR spectra and the melting points of the ^{17}O-enriched compounds were the same as those of the unlabeled ones.

6) R. Hecht and C. Rüchardt, Chem. Ber., 96, 1281 (1963).

7) ^{17}O NMR spectra were measured on a Varian FT-80A spectrometer at 10.782 MHz, using a 90° pulse of 0.02 s. A spectral width was 8000 Hz with 323 data points, the Fourier number being kept at 16384. The labeled sample (ca. 300 mg) was dissolved in chloroform-d and the temperature of the probe was set at 60 °C in order to obtain a better s/n of the signals due to narrower half-band widths. A reasonable s/n of ca. 8 of the spectra was obtained by 1 h's accumulation (the number of transients accumulated was 10^5) for enriched samples of this size of molecules. Three to four such data were averaged; the reproducibility of the relative peak areas was ± 2 %.

8) T. Sugawara, Y. Kawada, M. Katoh, and H. Iwamura, Bull. Chem. Soc. Jpn., 52, 3391 (1979); T. Sugawara, Y. Kawada, and H. Iwamura, Kagaku no Ryoiki, 34, 35 (1980).

9) L. E. Overman, J. Smoot, and J. D. Overman, Synthesis, 59 (1974).

(Received December 26, 1980)