CHEMISTRY LETTERS, pp. 167-170, 1989.

Spin Trapping Studies of Peroxyl Radicals. Detection of the Reactive Intermediates for Oxidation Generated from $O_2^{-\bullet}$ and Sulfonyl, Sulfinyl, and Phosphoryl Chlorides

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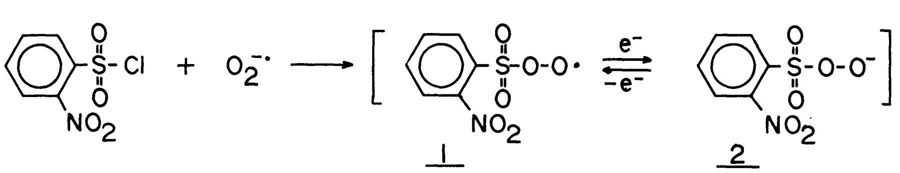
The spin trapping studies by ESR have demonstrated that $O_2^{-\bullet}$ efficiently reacts with 2-nitrobenzenesulfonyl chloride, 2-nitrobenzenesulfinyl chloride, and diphenylphosphoryl chloride, to result in the formation of their peroxyl radicals, some of which have been key intermediates for site-selective oxidation of certain organic molecules and argued whether they exist as anion and/or radical form.

In recent decades, superoxide anion radical, $O_2^{-\bullet}$, has received increasing attention in research fields of both biology and chemistry.1,2) It is believed that $O_2^{-\bullet}$ is a strong oxidant. However, as pointed out by Sawyer and Valentine,1) $O_2^{-\bullet}$ is not much reactive as an oxidant in organic solvents. Our previous studies have revealed that $O_2^{-\bullet}$ reacts with 2-nitrobenzenesulfonyl chloride in acetonitrile under mild conditions to form a 2-nitrobenzeneperoxysulfur intermediate 1 or 2 which is an excellent oxidizing reagent.3-6) Here a question has been raised whether the active intermediate involve a radical 1 or anion species 2 which can be formed by one electron transfer from $O_2^{-\bullet}$ to 1. In the present work, we have carried out the spin trapping studies by ESR in order to identify the reactive intermediates responsible for the oxidations. The spin trapping method has been proved of great use for elucidation of reaction mechanisms involving radical species.7,8)



Pure 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) was used. The use of DMPO as a spin trapping reagent has the advantage that the β-hydrogen of the DMPO spin adduct exhibits hyperfine coupling very sensitive to the nature of the trapped radical.[9)] Acetonitrile was purified by fractional distillation after drying over P_2O_5. The ESR spectra were recorded on a JEOL JES-FE3AX X-band spectrometer.

An acetonitrile solution of $O_2^{-\cdot}$ was prepared by dissolving KO_2 (0.1 mmol) and 18-crown-6 (0.12 mmol) in dry acetonitrile (3 ml). Two hundred µl of the acetonitrile solution of $O_2^{-\cdot}$ was added dropwise to the acetonitrile solution (600 µl) containing organic chloride (0.02 mmol) and DMPO (0.13 mmol). The resulting solution was transferred into a quartz cell for ESR measurements. The procedures mentioned above were performed at -20 °C under dry nitrogen to avoid moisture and thermal decomposition of the DMPO spin adducts. The ESR spectra were measured immediately after warming the sample solution to room temperature.

We initially measured the ESR spectrum of the DMPO spin adduct of $O_2^{-\cdot}$. A mixture of $O_2^{-\cdot}$ and DMPO in the acetonitrile solution successfully gives an ESR spectrum which exhibits hyperfine splitting due to the nitrogen and the β-hydrogen of the DMPO spin adduct: a_N = 14.2 G and a_H = 12.0 G. These values are in good accord with those reported for the DMPO spin adduct of $O_2^{-\cdot}$ or $HO_2^{\cdot}$, a_N = 14.3 G and a_H = 11.7 G,[9)] which fact indicates that the acetonitrile solution of KO_2 and 18-crown-6 contains $O_2^{-\cdot}$ dissociated from KO_2. The DMPO spin adduct disappeared with a half life of ca. 10 min. Figure 1 shows the ESR spectra of the DMPO spin adduct yielded by the reaction of $O_2^{-\cdot}$ and 2-nitrobenzenesulfonyl chloride. The major species observed at ca. 5 min after completion of the reaction shows the ESR spectrum which has the hyperfine coupling constants, a_N = 12.8 G a_H = 10.1 G. Since these values are very different from those reported for the DMPO spin adducts of $O_2^{-\cdot}$, $HO_2^{\cdot}$, and $^{\cdot}OH$,[9,10)] we conclude that DMPO efficiently trapps the radical produced by the reaction of $O_2^{-\cdot}$ and 2-nitrobenzenesulfonyl chloride. The rate of the reaction of $O_2^{-\cdot}$ with DMPO is suggested to be significantly slower than of the reaction of $O_2^{-\cdot}$ with 2-nitrobenzenesulfonyl chloride, because of no detection of the DMPO spin adduct of $O_2^{-\cdot}$. The DMPO spin adduct gradually decomposed at room temperataure: the half life is ca. 7 min.

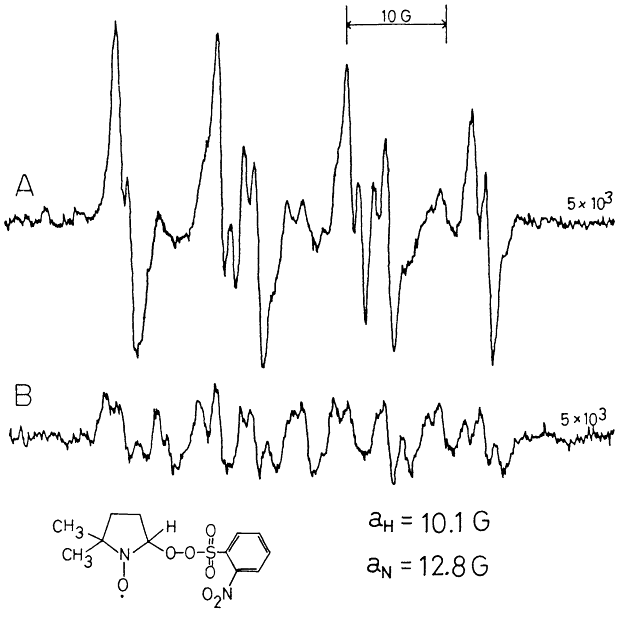
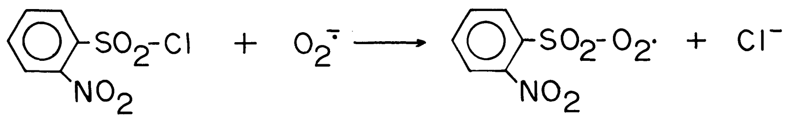
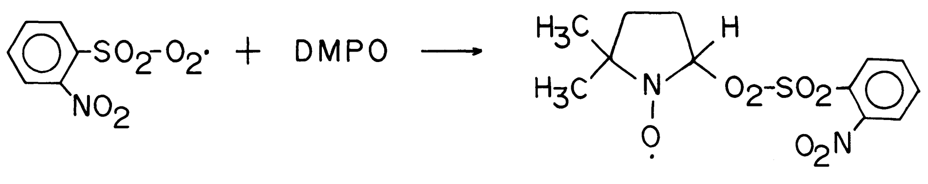
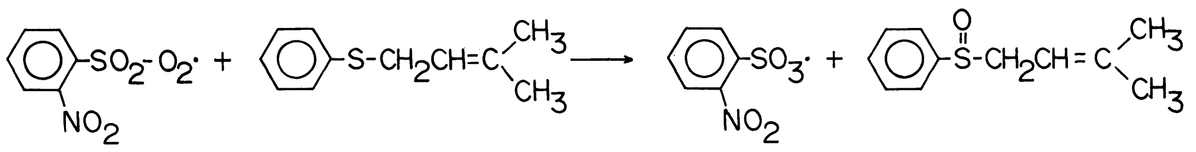


Fig. 1. ESR spectra observed at 5 (A) and 15 min (B) after addition of DMPO to a mixture of $O_2^{-\cdot}$ and 2-nitrobenzenesulfonyl chloride in acetonitrile.

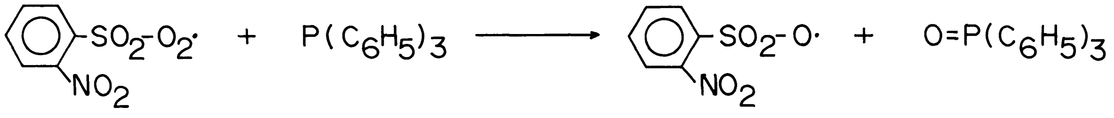




The reaction scheme described above is further supported by the fact mentioned below. 2-Methyl-2-butenylphenyl sulfide (MBPS) was used as a quencher of the peroxysulfonyl radical as shown below.



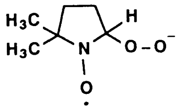
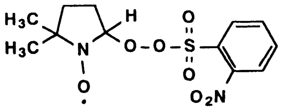
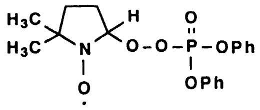
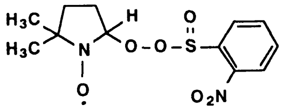
When $O_2^{-\cdot}$ in an acetonitrile solution was added to the mixture of DMPO, MBPS, and 2-nitrobenzenesulfonyl chloride in acetonitrile, the ESR signal ascribable to the DMPO spin adduct of the peroxysulfonyl radical could not be detected. On the other hand, the oxidation product, 2-methyl-2-butenylphenyl sulfoxide, was clearly detected with thin layer chromatography. Since $O_2^{-\cdot}$ was innocuous to MBPS, the peroxysulfonyl radical was considered to oxidize MBPS to the sulfoxide. Probably, the peroxysulfonyl radical preferentially reacts with MBPS, and therfore, the DMPO spin adduct of the peroxysulfonyl radical becomes undetectable. The use of triphenylphosphine as the quencher gave the same result: the formation of the DMPO spin adduct was suppressed by the addition of triphenylphosphine due to a loss of the peroxyl radical according to the reaction as shown below.



The spin trapping studies were also carried out for the reaction systems, $O_2^{-\cdot}$ + 2-nitrobenzenesulfinyl chloride, and $O_2^{-\cdot}$ + diphenylphosphory chloride. In Table 1 are shown the hyperfine coupling constants obtained for the DMPO spin adducts of the peroxyl radicals, which structures are also depicted.

There have been reported a number of DMPO spin adducts and their hyperfine coupling constants have been compiled and listed.[11] The coupling constants of

Table 1. Hyperfine coupling constants of the DMPO spin adducts of the peroxyl radicals

DMPO spin adducts	Values	DMPO spin adducts	Values
	a_H = 12.0 G a_N = 14.2 G		a_H = 10.1 G a_N = 12.8 G
	a_H = 10.3 G a_N = 12.6 G		a_H = 10.0 G a_N = 12.8 G

the DMPO spin adducts are known to vary depending on the nature of the trapped radicals,[9] and are summarized as a_N = 14-16 G and a_H = 19-23 G for C-radicals, a_N = 13-14 G and a_H = 6-9 G for O radicals, a_N = 13-16 G and a_H = 11-18 G for S radicals, and a_N = 12-15 G and a_H = 10.0-12 G for alkylperoxyl radicals.[11] The DMPO spin adducts of the peroxyl radicals detected in the present work have the coupling constants, a_N = 12.6-12.8 G and a_H = 10.0-10.3 G, in agreement with those of the DMPO spin adducts of alkylperoxyl radicals.

The spin trapping studies with the use of DMPO have revealed that organic chlorides readily react with $O_2^{-\bullet}$ to give their peroxyl radicals. Taking account of the results obtained by our previous studies[3-6] and the studies on quenching of the peroxyl radicals with MBPS and triphenylphosphine, we conclude that the peroxysulfonyl radical derived from the reaction between $O_2^{-\bullet}$ and 2-nitrobenzenesulfonyl chloride is one of the most reactive intermediates responsible for oxidation of organic molecules.

Authors thank Drs. M. Kohno and K. Yamamoto of JEOL Ltd. for their kind donation of DMPO and for the generous support from the Korean Science and Engineering Foundation.

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(Received November 7, 1988)