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SHORT COMMUNICATIONS

EVIDENCE FOR FORMATION OF 2-NITROBENZOYLPEROXY RADICAL GENERATED FROM 2-NITROBENZOYL CHLORIDE AND SUPEROXIDE: SPIN TRAPPING OF THE PEROXYRADICAL INTERMEDIATE AND ITS OXIDIZING ABILITIES

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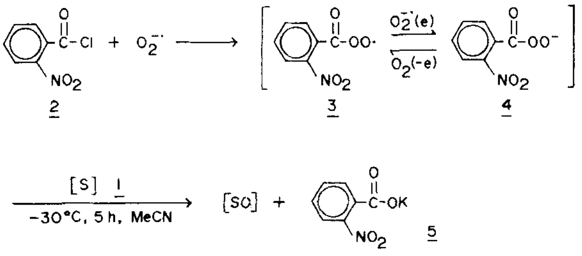
2-Nitrobenzoyl chloride was reacted with superoxide in acetonitrile to form 1 2-nitrobenzoylperoxy radical intermediate which showed a stronger oxidizing ability than that from superoxide, as confirmed by ESR spin trapping studies.

Superoxide ($O_2^{-\cdot}$) has received increasing attention in the fields of both biology and chemistry.[1,2] Recently, the accumulation of information on the physical and chemical properties of superoxide has promoted the study of organic reactions using superoxide. During a study on the activating reactions of superoxide,[3-5] a 2-nitrobenzoylperoxy intermediate (**3**), generated from 2-nitrobenzoyl chloride and superoxide, was found to be a more powerful oxidant than superoxide itself. This work is the first to demonstrate a carbonyl peroxy radical such as **3** by spin trapping studies using ESR. Various sulphides were readily oxidized to the corresponding sulphoxides by addition of 2-nitrobenzoyl chloride to a reaction mixture of the substrates and potassium superoxide at −30 °C in acetonitrile. Triphenylphosphine and triphenyl phosphite were oxidized to triphenylphosphine oxide and triphenyl phosphate, respectively, in excellent yields under the same conditions. As evidence of the participation of radicals in the chemical reaction, diphenylmethane was also converted to the benzophenone in 62% yield.



In a general procedure (run 5 in Table 1), a solution of 2-nitrobenzoyl chloride (257 mg, 1·5 mmol) and triphenyl phosphite (155 mg, 0·5 mmol) in dry acetonitrile (3 ml) was added to a heterogeneous solution of potassium superoxide (320 mg, 4·5 mmol) in dry acetonitrile (3 ml) at −30 °C with continuous vigorous stirring. After stirring for 5 h at −30 °C, the reaction mixture ws filtered and the solid collected was washed

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Table I. Oxidation of various substrates (S) by the 2-nitrobenzoylperoxy intermediate at −30 °C

$$\mathbf{2} + KO_2 + (S)\mathbf{1}^{-30\,°C,\ 5\ h,\ MeCN}(SO) + \mathbf{5}$$

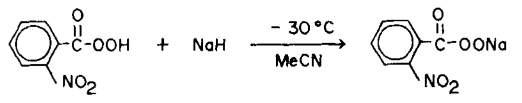
Run No.	Substrate (**1**)	Ratio **2**/**1**	Product	Yield (%)[a]
1	C_6H_5SMe	1·5	C_6H_5SOMe	95[b]
2	*p*-ClC_6H_4SMe	1·5	*p*-ClC_6H_4SOMe	96[b]
3	*p*-$CH_3OC_6H_4SMe$	1.5	*p*-$CH_3OC_6H_4SOMe$	87
4	$(C_6H_5)_3P$	3·0	$(C_6H_5)_3P{=}O$	97
5	$(C_6H_5O)_3P$	3·0	$(C_6H_5O)_3P{=}O$	95
6	$C_6H_5CH_2C_6H_5$	5·0	$C_6H_5COC_6H_5$	62

[a] Isolated yields.
[b] Determined by ^{1}H NMR.

twice with 10 ml of acetonitrile and then twice with 10 ml of chloroform.

Concentration and separation by preparative TLC [Merk silica gel 60 GF_{254}, diethyl ether–hexane (2 : 1, v/v)] gave pure triphenyl phosphate (155 mg, 95%). The products obtained were identified by comparing their IR and ^{1}H NMR spectra with those of authentic samples. The results obtained are summarized in Table 1.

The 2-nitrobenzoylperoxy intermediate (**3** or **4**) which is used in these reactions may be formed by nucleophilic attack of superoxide anion on the carbon atom of the carbonyl group of 2-nitrobenzoyl chloride. Here the question is raised as to whether the active intermediate involves a radical **3** or anion **4**, which can be formed by one-electron transfer from $O_2^{-\cdot}$ to **3**. There have been discussions on the generation of peroxy radicals or anionic intermediates from carbonyl halides and superoxide[6,7] and by photolysis of α-diketones in the presence of oxygen.[8] In order to establish whether the active species of the 2-nitrobenzoylperoxy intermediate has a radical or anionic character for the oxidation of various substrates, the reactivity of the 2-nitrobenzoylperoxy intermediate was compared with that of the 2-nitrobenzoylperoxy anionic intermediate **4** prepared *in situ* by the following method. The 2-nitrobenzoylperoxy anionic intermediate **4** was prepared by addition of 2-nitroperoxybenzoic acid (**6**) to a solution of sodium hydride in acetonitrile at −30 °C. After stirring for 2 h at −30 °C, the solution of the 2-nitrobenzoylperoxy anionic intermediate **4**, which is relatively stable at −30 °C but decomposes at room temperature, was used in the above reactions. When **4** was used, no benzophenone or methyl phenyl sulphoxide was obtained under the same conditions as for **3**, which gave 62% benzophenone (run 6 in Table 1) and 95% methyl phenyl sulphoxide (run 1). From these results it may be postulated that as the reactivity of the 2-nitrobenzoylperoxy intermediate is different from that of the 2-nitrobenzoylperoxy anionic intermediate (**4**), the 2-nitrobenzoylperoxy radical intermediate (**3**) plays an important role in the oxidation of various substrates.



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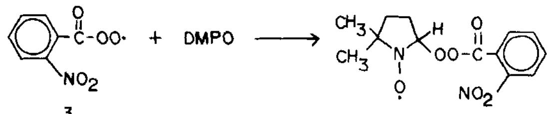
In this work, to detect the 2-nitrobenzoylperoxy radical intermediate (**3**), which is expected to be a real reactive intermediate responsible for the oxidations, the spin trapping method, which is indirect technique for the detection and identification of low concentrations of free radicals or short-lived radicals, was applied.[9–11] Pure 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) was



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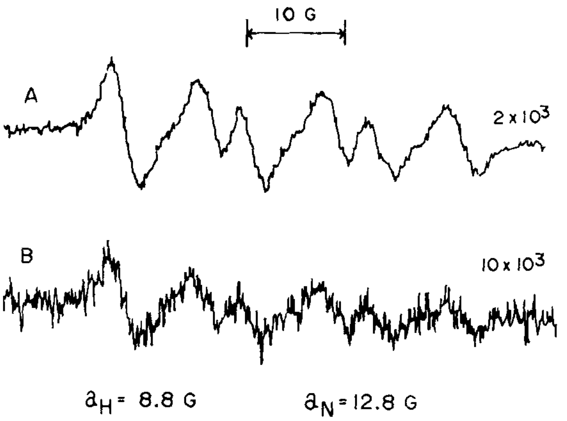

Figure 1. ESR spectra observed (A) 1 and (B) 4 min after addition of DMPO to a mixture of $O_2^{-\cdot}$ and 2-nitrobenzoyl chloride in acetonitrile

used as a trapping reagent and the ESR spectra were recorded on a JEOL JES-FE 3AX X-band spectrometer. An acetonitrile solution of $O_2^{-\cdot}$ was prepared by dissolving KO_2 (7·1 mg, 0·1 mmol) in the presence of 18-crown-6 (31·7 mg, 0·12 mmol) in dry acetonitrile (3 ml). A 200-μl volume of the acetonitrile solution of $O_2^{-\cdot}$ was added dropwise to an acetonitrile solution (600 μl) containing 2-nitrobenzoyl chloride (3·7 mg, 0·02 mmol) and DMPO (14·7 mg, 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.

The ESR spectra of the DMPO spin adduct (**7**) obtained by the reaction of $O_2^{-\cdot}$ and 2-nitrobenzoyl chloride are shown in Figure 1. The major species observed in the ESR spectrum ca 1 min after completion of the reaction shows hyperfine coupling constants $a_N = 12{\cdot}8$ G and $a_H = 8{\cdot}8$ G. These values are different from those reported for the DMPO spin adducts of $O_2^{-\cdot}$ ($a_N = 14{\cdot}2$ G and $a_H = 12{\cdot}0$ G), $HO_2^{\cdot}$, and $^{\cdot}OH$.[12,13] The reaction of $O_2^{-\cdot}$ with DMPO is suggested to be significantly slower than that of $O_2^{-\cdot}$ with 2-nitrobenzoyl choride, because no DMPO spin adduct of $O_2^{-\cdot}$ was detected. Judging from the results of the oxidizing ability of the peroxy intermediate and of spin trapping, it may be concluded that the radical species **3** rather than **4** is involved in these oxidations.

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