Brief Communications

Formation of radicals during dimethyldioxirane decomposition

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Thermal decomposition of dimethyldioxirane is followed by the formation of radicals registered by ESR spectroscopy using a *C*-phenyl-*N*-*tert*-butylnitrone spin trap. The intensity of the ESR signal increases linearly with increasing temperature; the dependence is extreme in character.

Key words: organic peroxides, dimethyldioxirane; spin trap.

Dioxiranes are a new class of efficient oxidative reactants.[1] There is almost no information on the kinetics and mechanism of their decomposition. In the present work ESR techniques with a *C*-phenyl-*N*-*tert*-butylnitrone (PBN) spin trap were used to show for the first time that the thermal decomposition of dimethyldioxirane is followed by the generation of radicals.

Experimental

Oxone ($KHSO_4 \cdot 2KHSO_5 \cdot K_2SO_4$). Oleum (27 mL, 20 % concentration) was added dropwise for 1 h to 16.5 mL of conc. H_2O_2 (92—95 %) at −5 °C (NaCl—ice cooling mixture). A 50 % solution of K_2CO_3 (36 mL) was added dropwise for 1 h at 0 °C to the Caro's acid (H_2SO_5) that formed. The crystals that precipitated were filtered off, washed three times with EtOH, and dried for 4—5 h in a vacuum-desiccator.

Dimethyldioxirane.[2] Acetone (13 mL), $NaHCO_3$ (12 g), and H_2O (20 mL) and then oxone (25 g) were placed into a 250 mL flask equipped with a mechanical stirrer and an air condenser in series with two traps cooled to −75 °C (acetone—carbon dioxide mixture). The reaction was run under argon in a water pump vacuum (160 Torr) with vigorous stirring for 1 h. The slightly yellow solution of dioxirane in acetone that accumulated in the cooled trap was separated from water crystals and dried with $MgSO_4$ for 1 h at −75 °C. Dimethyldioxirane was identified by ^{13}C NMR (a Bruker AM-300 spectrometer) by the characteristic signal (101.35 ppm) of a carbon atom bound to a peroxo group as well as by spectrophotometry on a Specord M40 instrument (Carl Zeiss, Jena). The quantitative analysis of dimethyldioxirane was performed spectrophotometrically (λ = 335 nm, ε = 10 L mol^{-1} cm^{-1}).

PBN and 2-methyl-2-nitrosopropane (MNP) were used as spin traps. The synthesis and purification of MNP was performed following the known procedure,[4] and the PBN was purified by recrystallization from hexane. Solutions of dimethyldioxirane and a trap in acetone cooled to −80 °C were placed into an ESR ampule and blown with argon for ~4 min. Special care was taken to prevent direct light. The above procedure of Ar blow-out does not provide total elimination of oxygen, but allows one to avoid spectral line broadening. The concentrations of dimethyldioxirane, PBN, or MNP in an ampule were 0.03, 0.045, and 0.03—0.3 mole L^{-1}, respectively. In some experiments with MNP, the solution was kept for 1—5 min at 40—60 °C, cooled quickly, and placed into the spectrometer resonator (−50—50 °C). ESR spectra were recorded on an SE/X2544 spectrometer.

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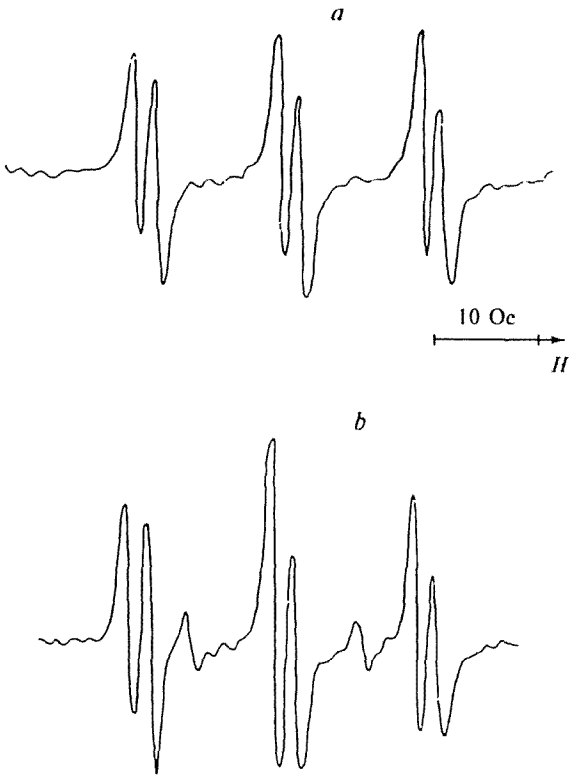
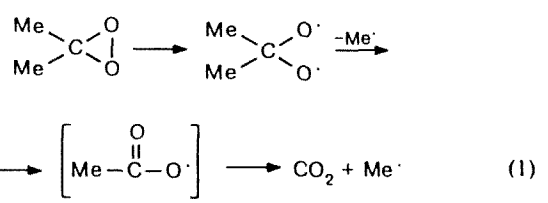


Fig. 1. The ESR spectra of the dimethyldioxirane—PBN system (dimethyldioxirane : PBN = 0.03 : 0.45) at 40 °C ~5 min (*a*) and ~15 min (*b*) after the specimen was placed in the spectrometer resonator.

Results and Discussion

An ESR signal characteristic of adducts with PBN, a triplet of doublets with a_N = 13.5 Oe and a_H = 2.0 Oe (Fig. 1, *a*) is observed when a mixture of dimethyldioxirane and PBN in the spectrometer resonator is heated to 0—56 °C. One can assume that the appearance of this triplet of doublets is due to the formation of an adduct of PBN with a ($RO_2^{\cdot}$) peroxide radical.[5,6] Formation of radicals might proceed as a result of following reactions:[7]



The Me radical reacts readily with the O_2 ($k \approx 5 \cdot 10^9$ mole^{-1} L s^{-1})[8] that is available in the solution to yield an oxide radical:

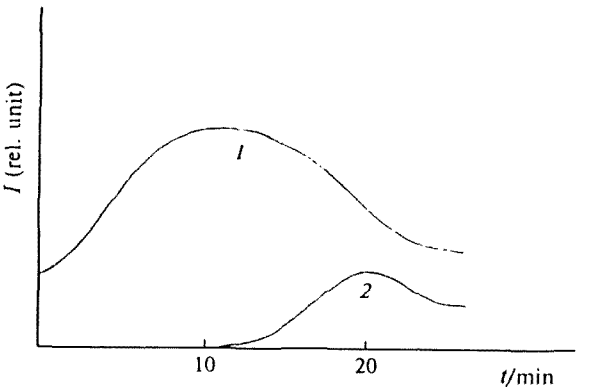
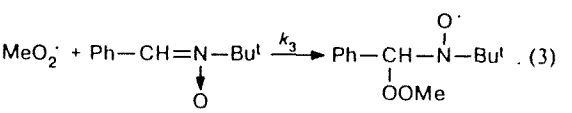
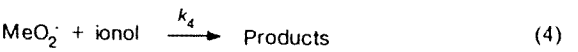


Fig. 2. The time dependence of the ESR signal intensity at 40 °C: for the triplet of doublets with a_N = 13.5 Oe and a_H = 2.0 Oe (*1*); for the triplet with a_N = 8.1 Oe (*2*).

The latter is trapped by PBN:



The introduction of ionol (an inhibitor of free-radical processes) in the ratio PBN : ionol = 1 : 2 results in a sharp decrease in the intensity of the signal due to the competing reaction:



($W_4/W_3 = 10^2$—10^3). The following values of the rate constants were used in calculations:[9,5] $k_4 \approx 10^4$ mole^{-1} L s^{-1}, $k_3 = (0.4$—$2) \cdot 10^2$ mole^{-1} L s^{-1}. The signal intensity increases linearly with increasing temperature, and the concentration of radicals amounts to ~10^{-4} mole L^{-1} at 56 °C. The time dependence of the signal intensity (at constant temperature) is of an extreme character (Fig. 2). For example, the maximum intensity of the triplet of doublets a_N = 13.5 Oe and a_H = 2.0 Oe is reached after 10 min at 40 °C; simultaneously, a triplet with the splitting of a_N = 8.1 Oe appears (see Fig. 1, *b*), whose amplitude reaches its maximum value after 20 min (see Fig. 2). The signal with a_N = 8.1 Oe corresponds to the benzoyl-*tert*-butylnitroxyl radical, which, according to previously published papers,[5,6 10,11] can form as a result of rearrangement of an adduct of peroxide radicals with PBN. This fact, as well as the results of the experiments with the addition of ionol, are evidence of the presence of accepting peroxide radicals. One can rule out the possibility of the formation of benzoyl-*tert*-butylnitroxyl radicals during oxidation of the trap by dioxirane, since it should appear just after the reactants are mixed.

In the case of MNP we failed to detect radicals, which might be associated with the low stability of the

radical adducts with the above trap under experimental conditions.[12,13]

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O,N-Dimethylation of 5,6-dihydroxynicotinic acid

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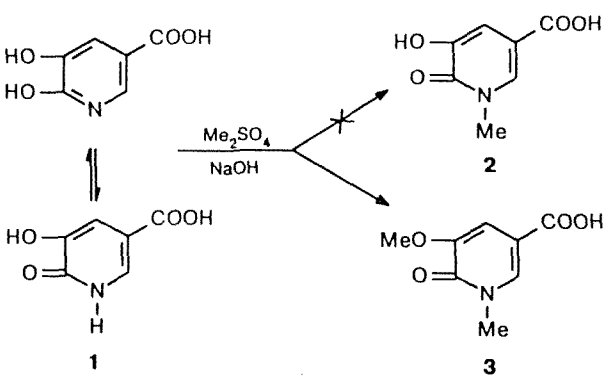
An *O,N*-dialkylation product, 1-methyl-5-methoxy-6-oxo-1,6-dihydropyridine-3 carboxylic acid, is formed in the reaction of 5,6-dihydroxynicotinic acid with dimethylsulfate.

Key words: 5,6-dihydroxynicotinic acid, dimethyl sulfate, *O,N*-dialkylation.

Studies of the alkylation of 3-hydroxypyridine derivatives containing functional groups are not only of theoretical interest, but are also of practical interest. *O*- or *N*-alkylation of 3-hydroxypyridine is known to be possible, depending on the reaction conditions and the type of alkylating agent.[1] Thus, the *N*-alkylation of non-substituted 3-hydroxypyridine occurs if dimethyl sulfate is used,[2] while 3-methoxypyridine is formed in the reaction with diazomethane.[3] Only *N*-methylation[4] occurs in the reaction of 5-hydroxynicotinic acid and its methyl ether with dimethylsulfate. Alkylation of 4,5-dihydroxypicolinic acid and 3,4-dihydroxy-6-methylpyridine with dimethyl sulfate in a basic medium results in the formation of an *O,N*-dimethyl derivative.[5] Taking into account the above data, one could expect either a product of monoalkylation at the N atom (**2**) or an *O,N*-dialkyl derivative (**3**) produced in the reaction of 5,6-dihydroxynicotinic acid (**1**) with Me_2SO_4.



Alkylation **1** with dimethyl sulfate in a basic medium was performed following the known procedure.[4] It was established that *O,N*-methylation with the formation of compound **3** proceeds under these conditions. The structure of **3** was confirmed by mass spectrometry and NMR spectroscopy.

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