The formation of nitroxyl radicals in reactions of dimethyldioxirane with 2,2,6,6-tetramethylpiperidine and 2,2,5,5-tetramethyl-3-imidazoline-3-oxide derivatives

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The oxidation of secondary and tertiary amines, derivatives of 2,2,6,6-tetramethylpiperidine and 2,2,5,5-tetramethyl-3-imidazoline-3-oxide, by dimethyldioxirane results in the formation of nitroxyl radicals, which induce the decomposition of dimethyldioxirane. Chemiluminescence in the IR and visible regions during the reaction of dimethyldioxirane with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl was observed.

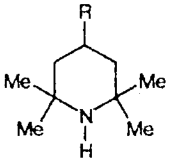
Key words: dimethyldioxirane, secondary amines, nitroxyl radicals, chemiluminescence.

The chemistry of dioxiranes has undergone intense development during the last decade. Oxidation reactions involving dioxiranes occur under mild conditions, rapidly, and selectively. The reactions of secondary amines with dimethyldioxirane (**1**) have been described previously.[1—3] Nitrons[1,2] or nitroxyl radicals[3] (depending on the structure of amine) are formed in quantitative yield in the presence of a twofold excess of **1**. In this work, we studied the reactions of dimethyldioxirane with derivatives of 2,2,6,6-tetramethylpiperidine and 2,2,5,5-tetramethyl-3-imidazoline-3-oxide and with 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl.

Experimental

Synthesis of dimethyldioxirane, its identification, and analysis were carried out according to the procedure described previously.[4] Nitroxyl radicals were identified and analyzed quantitatively by ESR using an SE/X 2544 spectrometer. 2,2,6,6-Tetramethyl-4-hydroxypiperidine-1-oxyl, 2,2,6,6-tetramethyl-4-oxopiperidine-1-oxyl, and 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide-1-oxyl were used as the standards for quantitative analysis.

Oxidation of 2,2,6,6-tetramethyl-4-hydroxypiperidine (**2**), 2,2,6,6-tetramethyl-4-oximepiperidine (**3**), 2,2,6,6-tetramethyl-4-oxopiperidine (**4**), 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-3-oxide (**5**), 2,2,4,5,5-pentamethyl-3-imidazoline-3-oxide (**6**), 1-hydroxy-2,2,5,5-tetramethyl-3-imidazoline-3-oxide (**7**), and 1,2,2,4,5,5-hexamethyl-3-imidazoline-3-oxide (**8**) was carried out in ESR ampoules. The starting concentrations of compounds **2**—**8** and **1** were varied within $(2.5—5) \cdot 10^{-3}$ mol L^{-1} and $(5—7.5) \cdot 10^{-3}$ mol L^{-1}, respectively. Acetone was used as the solvent (25 °C). After the reagents were mixed, the ampoule was placed in the resonator of the ESR spectrometer, and a change in the radical concentration in time was measured.



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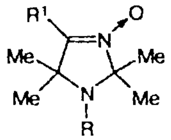

5—8

Compound	R	Compound	R	R¹
2	OH	**5**	H	Ph
3	N—OH	**6**	H	Me
4	=O	**7**	OH	Me
		8	Me	Me

Stoichiometry of the reaction of dimethyldioxirane (1) with the nitroxyl radical (2a) was studied by spectrophotometry on a Specord UV—VIS instrument. Solutions of **1** and **2a** in acetone were placed into a quartz 3-mL cell. The concentrations of **1** and **2a** after mixing were $5.2 \cdot 10^{-2}$ and $(2—3) \cdot 10^{-2}$ mol L^{-1}, respectively. The change in the concentration of **1** was monitored spectrophotometrically (λ_{max} = 335 nm). The concentration of **2a** was determined by ESR after the reaction had been completed.

Chemiluminescence in the visible and IR spectral regions was detected by the known procedures.[5,6] A solution of nitroxyl radical **2a** in acetone-h_6 or -d_6 was placed in the reactor, and a solution of **1** was added with vigorous stirring. The concentrations of **1** and **2a** in the reactor were $2.7 \cdot 10^{-2}$ and $5.2 \cdot 10^{-2}$ mol L^{-1}, respectively. Luminescence was detected automatically on a K-101 self-recorder.

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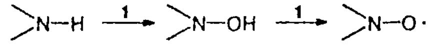
Results and Discussion

The ESR signal was observed during the oxidation of amines **2**—**8** by dimethyldioxirane. The radicals were identified as nitroxyls based on the shape of the signal (triplet) and values of the splitting constant a_N (Table 1).[7—9] Most likely, no oxidation of amines **5**—**8** to the nitron group resulting in the formation of nitroxyl radicals occurs, since the a_N values for these radicals should be[10] 12.7—13.1 G. According to the data in Table 1, the yield of nitroxyl radicals depends on the ratio of the reagents. The oxidation of 2,2,5,5-tetramethylpyrroline-3-carboxamide by an equivalent amount of dimethyldioxirane gives[3] hydroxylamine, whose reaction with **1** results in the formation of the nitroxyl radical. We oxidized both amine **6** and the corresponding hydroxylamine **7** (see Table 1). In both cases, the reaction product is the nitroxyl radical. These results suggest that the oxidation of secondary amines to nitroxyl radicals occurs through the intermediate formation of hydroxylamine.



The oxidation of amine **8** first affords the secondary amine, which then is oxidized according to the same scheme.[11,12]

A low yield of nitroxyl radicals at a high excess of an oxidant is likely associated with their subsequent oxidation by dimethyldioxirane, which is indicated by the data on the kinetics of radical accumulation and stoichiometry of the reaction of **1** with **2a**.

Table 1. Yields and splitting constants (a_N) of nitroxyl radicals during oxidation of amines **2**—**8** by dimethyldioxirane (acetone, 25 °C)

Amine	$[\mathbf{2}$—$\mathbf{8}]_0 : [\mathbf{1}]_0$	$[{=}NO^{\cdot}]_\infty : [\mathbf{2}$—$\mathbf{8}]_0$	a_N/G
2	1 : 1	42	15.19
	1 : 2	100*	
	1 : 3	92	
3	1 : 1	36	15.19
	1 : 2	100*	
	1 : 3	43	
4	1 : 1	12	14.23
	1 : 2	98*	
	1 : 3	27	
5	1 : 1	5	14.04
	1 : 3	25	
6	1 : 1	13	14.04
	1 : 3	4	
7	1 : 1	15	14.04
	1 : 3	18	
8	1 : 1	20	14.04
	1 : 3	13	

* See Ref. 3.

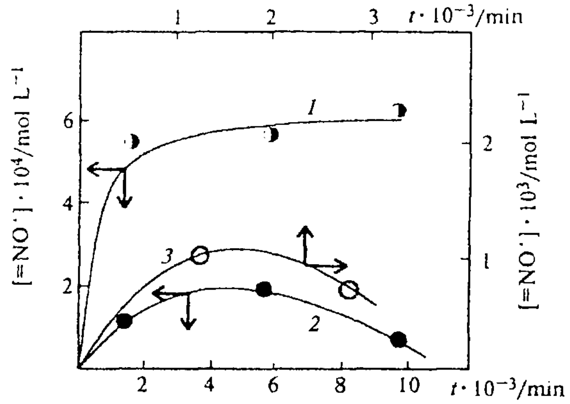
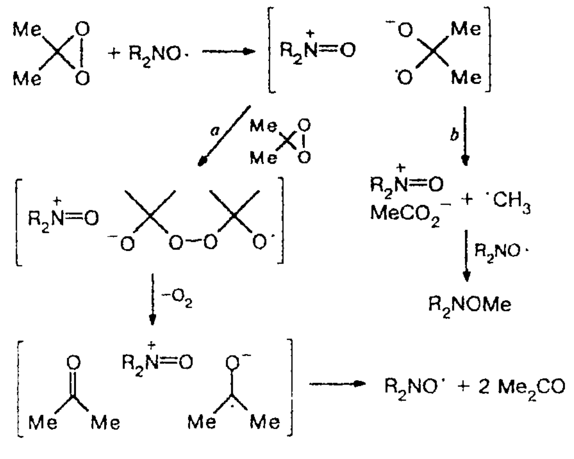


Fig. 1. Kinetic curves of accumulation of nitroxyl radicals during the oxidation of compounds **4** and **6** in acetone at 25 °C: *1*, $[\mathbf{6}]_0/[\mathbf{1}]_0 = 1 : 1$, $[\mathbf{6}]_0 = 5 \cdot 10^{-3}$ mol L^{-1}; *2*, $[\mathbf{6}]_0/[\mathbf{1}]_0 = 1 : 3$, $[\mathbf{6}]_0 = 2.5 \cdot 10^{-3}$ mol L^{-1}; and *3*, $[\mathbf{4}]_0/[\mathbf{1}]_0 = 1 : 3$, $[\mathbf{4}]_0 = 2.5 \cdot 10^{-3}$ mol L^{-1}.

It follows from the analysis of the kinetic curves (Fig. 1) that the consumption of nitroxyl radicals occurs along with their accumulation, which agrees with the known[13,14] ability of nitroxyl radicals to react with peroxide compounds. At the same time, dioxiranes are prone to induced decomposition under the action of free radicals.[4] We established that the rate of decomposition of **1** increases 58—86 times in the presence of (2—3) · 10^{-2} mol L^{-1} of compound **2a**. The stoichiometry of the reaction changes ($[\mathbf{1}]_0 : [{=}NO^{\cdot}]_0 = 2.7$—$5.1$). In this reaction, we detected chemiluminescence in the visible and IR spectral regions (Fig. 2). Replacement of acetone-h_6 by acetone-d_6 results in an increase in the intensity of IR luminescence. Bubbling of O_2 through the reaction mixture results in an enhancement of the luminescence intensity in the visible region. The detection region of chemiluminescence (1000—1300 nm) and the character of the influence of the solvent on the luminescence intensity indicate that singlet oxygen is the emitter of IR luminescence.[15,16] The formation of

Scheme 1



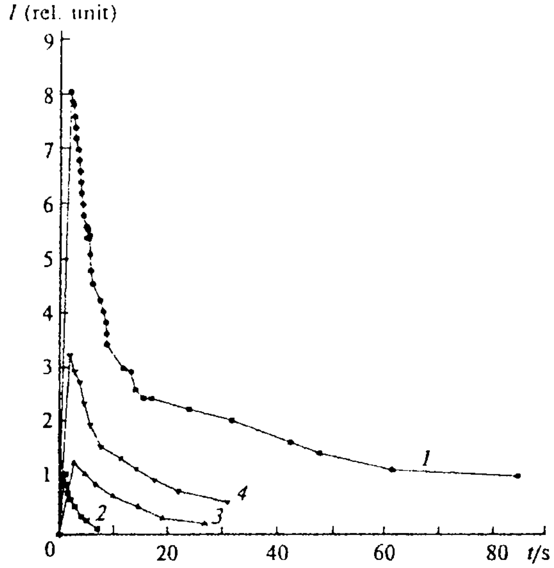


Fig. 2. Change in time of the intensity of chemiluminescence appearing during the reaction of 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl with dimethyldioxirane in the IR region when acetone-d_6 (*1*) and acetone-h_6 (*2*) are used as the solvents and in the visible region without (*3*) and with bubbling O_2 (*4*).

$^1O_2$ (route *a*) is explained in terms of Scheme 1 proposed previously.[17]

Chemiluminescence in the visible region (see Fig. 2) is most likely the result of recombination of peroxide radicals, which are formed with the diffusional rate constant in the reaction of methyl radicals (route *b*) with O_2 dissolved in the solution.

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