

Photochemical Degradation of 2,2,5,5-Tetramethyl-4-phenyl-3-imidazoline-1-oxyl

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Abstract—The photochemical degradation of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl has been studied in solution at room temperature and in glassy matrices at 77 K. Nitrogen(II) oxide is split from the starting radical during the reaction. The quantum yield of the reaction constitutes ~0.2 in a liquid solution at 298 K and ~0.001 in glassy matrices at 77 K. The kinetics of the solid-phase reaction have a stepped character.

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Nitroxyl radicals are used as paramagnetic labels and probes for studying the chemical and physical properties of various media (solutions, solid matrices, biological systems, and others) [1]. Additional possibilities appear when the probe can experience photochemical transformations: if so, the probe reactivity will depend on its surrounding. Various mechanisms of photochemical transformations of nitroxyl radicals are discussed in the literature: (1) formation of an oxaziridine cycle, (2) reaction with the solvent, and (3) splitting of an NO molecule. The first two mechanisms have been observed experimentally and studied quite well. When exposed to light, 2-*H*-2,2-dimethyl-4-phenylimidazole-1-oxide isomerizes to 1,3-diaza-6-oxabicyclo[3.1.0]-4-phenylhexane [2]. 2,2,6,6-Tetramethylpiperidine-1-oxyl under irradiation in either a liquid solution or a glassy matrix reacts with solvent molecules [3, 4].

The splitting of nitrogen(II) oxide remains the least studied mechanism of the photochemical degradation of nitroxyl radicals. This reaction has not been proven experimentally, although it is considered possible by analogy with the splitting of a CO molecule for ketones [3]. Nitroxyl radical 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl degrades in benzene under irradiation according to this mechanism [5].

The authors carried out long-term photolysis, after which isopropyl phenyl ketone was isolated from the

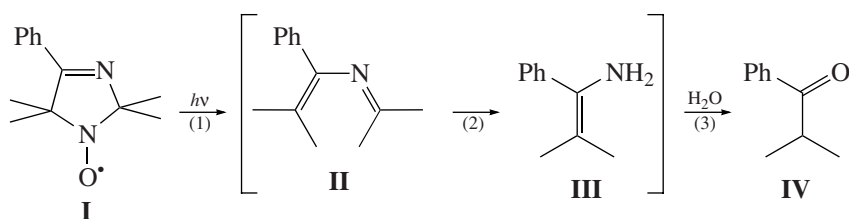
system. On this basis, it was suggested in [5] that the reaction occurs in three stages, as shown by the scheme below. However, the rationale for the suggested scheme is unclear: products (compounds **II** and **III**) have not detected experimentally. In addition, water (which was necessary for the specified processes to occur) was not added to the system during the experiment described in [5].

This work elucidates whether reactions can occur according to the scheme and determines the kinetic laws and efficiency of the photochemical degradation of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl.

EXPERIMENTAL

The stable nitroxyl radical 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl (compound **I**) was synthesized and kindly supplied to us by Professor I.A. Grigor'ev.

The solvents used were heptane, toluene, and 2-methyltetrahydrofuran (MTHF) of chemically pure grade. Heptane and toluene were dried over calcined molecular sieves. To free MTHF from peroxides, it was stored over alkali and twice distilled. Samples for photolysis were prepared in quartz ampoules with an inner diameter of 3 mm, into which a solution of the radical was placed. Samples were freed from oxygen in four or



Scheme 1.

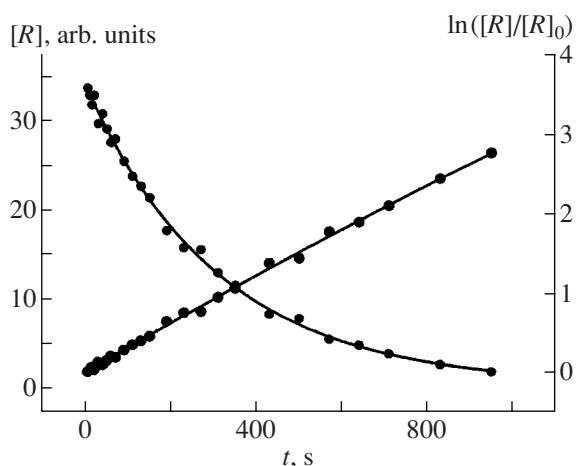


Fig. 1. Area S under the ESR spectrum of a solution of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl in toluene at 298 K under 365-nm irradiation vs. time.

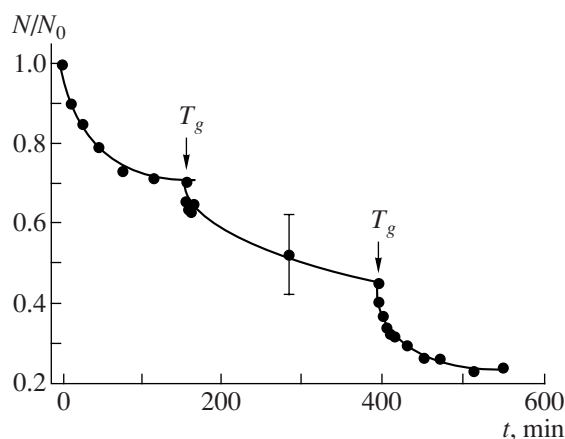


Fig. 2. Radical concentration vs. time during the photolysis of compound **I** in glassy toluene at 77 K under 365-nm irradiation. Arrows mark annealing of a sample at the glass-transition temperature of toluene (114 K).

five freezing/evacuating/defrosting cycles. In the last two cycles, evacuating was to a residual pressure of 10^{-3} mm Hg.

The light source used was a DRS-500 high-pressure mercury lamp equipped with quartz lenses, a water filter, and a 365-nm standard glass light filter. The light intensity ($\sim 3 \times 10^{16}$ photons/s per sample) was determined using ferrioxalate actinometry [6].

ESR spectra were recorded on a Varian E3 spectrometer (3-cm range). The number of paramagnetic centers was determined by double integration of ESR spectra with reference to a $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ single crystal, for which the number of paramagnetic centers is known. The determination precision was 10%. Annealing was carried out as follows: a sample was exposed for 5 min to a nitrogen gas flow, whose temperature was controlled with an accuracy of ± 1 K.

The absorbance of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl was 55 L/(mol cm) in toluene and 48 L/(mol cm) in MTHF, as we determined experimentally. Optical absorption spectra were recorded on a Specord M40 spectrometer in cylindrical quartz ampoules with the optical length equal to 0.3 cm.

The products of photochemical degradation of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl were studied by chromatography/mass spectrometry. After photolysis was over, the sample was dried in air; then, it was dissolved in acetonitrile. Analysis was carried out on an HP5973 mass spectrometer and a GC 6890 gas chromatograph. A silicone capillary column was used with the DB-5 phase (length, 30 m; inner diameter, 0.25 mm; thickness, 0.25 μm). The temperature schedule was as follows: 70°C (3 min)–150°C (1 min)–280°C (10 min).

RESULTS AND DISCUSSION

When a solution of compound **I** at room temperature is irradiated at 365 nm in either toluene or MTHF, its ESR spectrum only contains the signal from the starting 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl. The rate curve for the photolysis of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl is shown in Fig. 1 as the concentration of the radical versus time. One can see that the kinetics of photochemical degradation of the radical at room temperature obey a first-order equation. The quantum yield of the reaction Φ , derived from a log anamorphose, was 0.16. The quantum yield of the photochemical degradation of compound **I** in MTHF at room temperature was determined in the same manner ($\Phi = 0.21$).

For glassy solutions of compound **I** that were frozen at 77 K, the amplitude of the ESR signal decreases under irradiation. Spectra of other radical species were not detected during the reaction. At a certain moment, the reaction rate starts to drop anomalously and rapidly during photolysis at 77 K (Fig. 2), and a kinetic stop is observed.

In order to elucidate the reason for this phenomenon, we annealed a sample at the glass-transition temperature of toluene (114 K); then, the sample was cooled to 77 K and again photolyzed. The results of this experiment are illustrated by Fig 2. The reactivity of the unreacted compound is recovered during annealing. Thus, the kinetics of the photochemical reaction have a stepped character.

Similar kinetic laws, referred to as kinetic nonequivalence, were earlier observed for other thermal [7, 8] and photochemical [9, 10] reactions. Such kinetic laws are due to the fact that chemically identical molecules in a solid phase can have different energy barriers to the reaction. Possible reasons for kinetic nonequivalence include the macroscopic heterogeneity of a sample, particle–particle distance distribution, distribution over

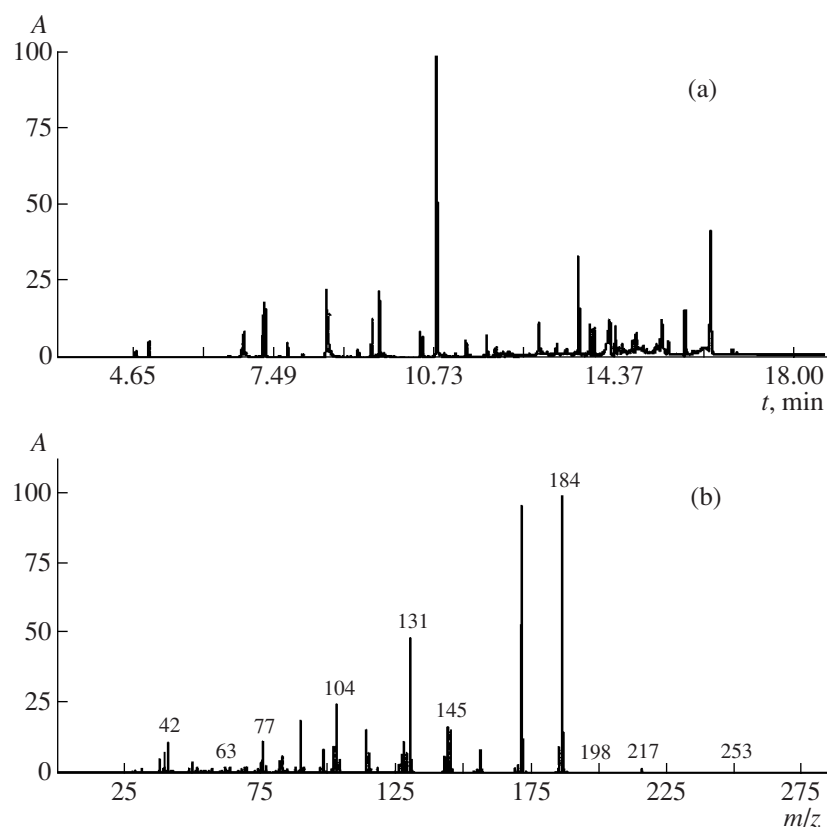


Fig. 3. Pattern (a): the chromatogram of photolysis products. Pattern (b): the mass spectrum of the strongest peak (187, the molecular ion peak for compound **I**).

the free volume required for the reaction to occur, and other factors. In the case at hand, the geometric size of reaction products is likely larger than the size of the starting radical. Only those molecules around which there is the required free volume can enter the reaction. Under these conditions, the existence of distribution of molecules with respect to some kinetic parameter, the quantum yield in our case, is manifested in the reaction kinetics. The distribution-average quantum yield is determined from the initial segment of the rate curve. The quantum yield of the photochemical degradation of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl in glassy matrices at 77 K determined from the initial segment of rate curves, Φ , is 0.006 for toluene and 0.001 for MTHF. These quantities are far smaller than the quantum yields of radical degradation at room temperature. This difference is evidently due to the hindrances created by solid matrices to the motion required for a molecule to degrade to fragments. The rather great difference between the quantum yields in the two glasses is noticeable. Two hypotheses can explain this difference: (1) the lifetimes of an excited state in these matrices are different; (2) the free volume in toluene is larger, despite the high rigidity of this matrix.

The pathway of the photochemical reaction of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl was determined using the chromatography/mass spectrometry

of reaction products. Photolysis at either room temperature or 77 K yields qualitatively identical product mixtures. The chromatogram of the photolysis products obtained at room temperature and the mass spectrum of its strongest peak are displayed in Fig. 3.

Figure 3a makes it clear that the peak with the retention time equal to 10.83 min is the strongest signal in the chromatogram. The mass spectrum of this compound (Fig. 3b) contains the peak of a molecular ion of the degradation product of the radical with splitting of nitrogen oxide (compound **II**; molecular mass, 187 g/mol). Other, weaker peaks were identified on the basis of their mass spectra as propyl phenyl ketone (retention time, 9.52 min), isopropyl phenyl ketone (retention time, 7.81 min), and benzoic acid amide (retention time, 8.61 min). These minor products evidently result from the hydrolysis of the primary product of the photochemical reaction. Hydrolysis likely occurs during sample preparation for chromatography/mass spectrometry analysis, namely, while the sample is left for drying in air for several days.

To summarize, our analysis shows that compound **II**, which is produced by nitrogen oxide splitting from the starting radical, is the major product of the photochemical degradation of 2,2,5,5-tetramethyl-4-phenyl-3-imidazoline-1-oxyl.

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