Formation of stable carbonyl oxide by photooxidation of (phenyl)(2-thienyl)diazomethane

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Formation of (phenyl)(2-thienyl)carbonyl oxide, which has the longest lifetime among known carbonyl oxides, has been registered by flash photolysis in acetonitrile at room temperature. It is consumed in the pseudomonomolecular reaction with the parent diazo compound.

Key words: kinetics, flash photolysis, carbonyl oxides, diazo compounds, oxygen.

Carbonyl oxides (R_2COO) are key intermediates in ozonolysis of olefins.¹ Photooxidation of diazo compounds, so called the "triplet mechanism" of carbonyl oxides generation, is a convenient method for the preparation of carbonyl oxides² (Scheme 1).

Scheme 1

$$R_2CN_2 \xrightarrow{h_V} {}^{1}R_2C: \longrightarrow {}^{3}R_2C: \xrightarrow{O_2} R_2COO$$

The "singlet mechanism" of generation of carbonyl oxides suggests an interaction of the singlet oxygen with a diazo compound.² In this case, the use of a singlet sensitizer, for example, methylene blue (MB), is necessary (Scheme 2).

Scheme 2

$$MB \xrightarrow{hv} MB^{\star} \xrightarrow{O_2} MB + {}^{1}O_2 \xrightarrow{R_2CN_2} R_2COO + N_2$$

Aromatic carbonyl oxides in solution are characterized by optical absorption in the visible range of the spectrum, the maximum of which is in the region 390–450 nm.^{3,4} Kinetic regularities of consumption of these species in the absence of oxidizing substrates rather strongly depend on the nature of substituents at the carbonyl oxide group. The influence of a substituent character on the mechanism of termination of carbonyl oxides can be of two main kinds. First, strong electron-donating groups (amino, methoxy) in the aromatic core decrease an activation energy of the isomerization of carbonyl oxides into dioxiranes.^{5–7} Such carbonyl oxides are consumed in the monomolecular process, whereas a bimolecular termination is characteristic of most aromatic carbonyl oxides.^{3,4} Secondly, such substituents as bromo,⁴ methyl,^{3,8} *tert*-butyl⁹ in *ortho*-position relatively to the carbonyl oxide group sharply increase the lifetime of the carbonyl oxides. Thus, the halflife time of unsubstituted diphenylcarbonyl oxide in acetonitrile at room temperature is $\sim 10^{-2}$ s, while for 2-bromodiphenylcarbonyl oxide it increases by two orders of magnitude.⁴ Sterically hindered dimesitylcarbonyl oxide (the halflife time at room temperature in acetonitrile is ~ 0.4 s³ or ~ 4 s⁸) and (6-*tert*-butyl-2,3,4-trimethylphenyl)phenylcarbonyl oxide (the halflife time in CCl₃F—(CBrF₂)₂ (1 : 1) at 267 K is 4.5 min⁹) are the most stable out of known by far carbonyl oxides. Both these carbonyl oxide are consumed according to the first order kinetic law.

In the present work, an absorption spectrum of (phenyl)(2-thienyl)carbonyl oxide (1) in acetonitrile has been obtained by the flash photolysis at room temperature and kinetic features of its decay have been studied. It was found that the pseudomonomolecular termination observed for this carbonyl oxide turned out to be its reaction with the parent diazo compound, by the decrease in concentration of which, the time of consumption of compound 1 can be prolonged to 20 min or more.

The flash photolysis of acetonitrile solution of (phenyl)(2-thienyl)diazomethane (2) in the presence of oxygen results in the optical absorption in the wavelength region 350-420 nm, which disappears with time. In the absence of oxygen, the signal in the mentioned wave region is also absent. This gives us a reason to suggest that it corresponds to carbonyl oxide 1. A similar signal is also registered during the flash photolysis of the diazo compound 2-methylene blue system, which was mentioned above as the singlet pathway for the generation of carbonyl oxides. The absorption spectrum of carbonyl

Published in Russian in Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 3, pp. 666-668, March, 2008.

1066-5285/08/5703-679 © 2008 Springer Science+Business Media, Inc.

oxide 1, recorded for the concentration of the parent diazo compound 2 being $6 \cdot 10^{-4}$ mol L⁻¹, is not changing in time (Fig. 1). This demonstrates that only one species absorbs the light under these conditions. The absorption maximum of carbonyl oxide 1 is at 375 nm. A decrease in time of optical density by 90% and more can be well described by the first order kinetic equation (Fig. 2, graph 2):

$$A - A_{\infty} = (A_0 - A_{\infty})\exp(-k^{\text{eff}}t), \qquad (1)$$

where A_0 is the initial optical density of carbonyl oxide 1; A_{∞} is the final optical density, caused by absorption of the reaction products; k^{eff} is effective rate constant of consumption of carbonyl oxide 1.

The time of complete consumption of carbonyl oxide 1 decreases with the increase in the initial concentra-



Fig. 1. Optical spectrum of carbonyl oxide 1 in acetonitrile, recorded with concentration of the starting diazo compound $[2]_0 = 6 \cdot 10^{-4} \text{ mol } \text{L}^{-1}$ immediately after the flash (1), after 0.5 (2), 1 (3), and 1.5 s (4).



Fig. 2. Kinetic curves of consumption of carbonyl oxide 1 in acetonitrile at $[2]_0 = 5 \cdot 10^{-7}$ (*I*) and $1 \cdot 10^{-3}$ mol L⁻¹ (*2*) (the solid line represents theoretical description of the curve by the equation (1)).

tion of diazo compound 2 in the system and this value varies from a few seconds to 20 min, while the $[2]_0$ value changes in the range from $1 \cdot 10^{-3}$ to $5 \cdot 10^{-7}$ mol L⁻¹ (see Fig. 2). The k^{eff} value is linearly dependent from the concentration of diazo compound 2 in the range $(1-100) \cdot 10^{-5}$ mol L⁻¹ (Fig. 3). From the slope of this relationship, we obtained the rate constant of the reaction of carbonyl oxide 1 with the parent diazo compound: $k_{1+2} = (1.37 \pm 0.04) \cdot 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$. At $[\mathbf{2}]_0$ being $< 1 \cdot 10^{-5}$ mol L⁻¹, the kinetic curves of consumption of carbonyl oxide 1 no more can suffice to the equation (1) (see Fig. 2, graph 1). This can be rationalized in view of the starting concentration of carbonyl oxide 1 being comparable with the concentration of diazo compound 2 and, along with consumption of carbonyl oxide 1 in the reaction with the parent diazo compound 2, by all appearances, another channel for the termination of this species is involved. Obviously, this is a very slow process.

It can be suggested that the obtained carbonyl oxide **1** is stabilized by the interaction of the terminal oxygen atom of the carbonyl oxide group and the neighboring sulfur atom.



This hypothesis will be verified in our further research.

We studied the products of the decay reaction of carbonyl oxide 1 using for this purpose the "singlet pathway" for the generation of carbonyl oxide 1 under steady-state photooxidation conditions of acetonitrile solution of diazo compound 2 ($[2]_0 = 2 \cdot 10^{-4} \text{ mol L}^{-1}$, methylene



Fig. 3. The effective rate constant of consumption of 1 versus the starting concentration of diazo compound 2.

blue was the sensitizer $(1 \cdot 10^{-5} \text{ mol } \text{L}^{-1})$, irradiation with the light of $\lambda > 540$ nm). Analysis of the reaction mixture by HPLC showed that (phenyl)(2-thienyl)ketone (3) was the only reaction product (it was identified by comparison with the authentic sample). Proceeding from this and taking into account the observed kinetic features, it can be concluded that when diazo compound 2 is presented in a large excess as compared with the concentration of carbonyl oxide 1, the only reaction takes place in the system, namely, the interaction of carbonyl oxide 1 with its precursor (Scheme 3).

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In the following study, we are going to clarify the mechanism of termination of carbonyl oxide 1 under conditions when diazo compound is absent in the system.

This work was financially supported by the Division of Chemistry and Materials Science of the Russian Acad-

emy of Sciences (Program "Theoretical and Experimental Study of the Nature of Chemical Bond and Mechanisms of the Most Important Chemical Reactions and Processes") and the Ministry of Education and Science of Russian Federation (Analytical Department Specially Purposed Program "Development of the Scientific Potential of the Higher School" (2006-2008)", Project code RNP 2.2.1.1.6332).

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Received November 30, 2007: in revised form January 19, 2008

