

Aerobic photochemical oxygenation of alkanes sensitized by pyrazine derivatives

G. V. Nizova and G. B. Shul'pin*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156

Photochemical transformations of saturated and alkylaromatic compounds under the action of molecular oxygen to give oxygen-containing products usually occur in the presence of sensitizers. The key step of these reactions is abstraction of a hydrogen atom from a substrate by a photoexcited species of the sensitizer or an electron transfer to this species with subsequent or synchronous abstraction of a proton (see, for example, Refs. 1–3).

When we continued our studies dealing with photooxygenation of alkanes sensitized by organic compounds,^{4,5} we unexpectedly found that pyrazine-2-carboxylic acid (which we previously used as a co-catalyst of a dark reaction⁶) is an efficient photosensitizer. In fact, irradiation of a solution containing cyclohexane (0.46 mol L^{-1}) and pyrazine-2-carboxylic acid (**1**; $4 \cdot 10^{-4} \text{ mol L}^{-1}$) in MeCN for 4 h afforded cyclohexanol (**2**), cyclohexanone (**3**), and cyclohexyl hydroperoxide (**4**) (their total concentration was $2.2 \cdot 10^{-3} \text{ mol L}^{-1}$; the **2** : **3** : **4** ratio was 1 : 1 : 1.5). In all experiments, a MeCN solution, placed in a glass vessel cooled to $-15 \text{ }^\circ\text{C}$ with running water was irradiated in air with the full light of a 125 Wt luminescence lamp, $\lambda > 300 \text{ nm}$. Methyl pyrazine-2-carboxylate (**5**) exhibits much higher activity ($3.7 \cdot 10^{-3} \text{ mol L}^{-1}$ of products was obtained after irradiation for 4 h; **2** : **3** : **4** = 1 : 1 : 1.5), and unsubstituted pyrazine is less active ($1.8 \cdot 10^{-3} \text{ mol L}^{-1}$; a glass vessel, **2** : **3** : **4** = 1 : 1 : 2.2). It is significant

that the activity of pyrimidine is substantially lower ($0.5 \cdot 10^{-3} \text{ mol L}^{-1}$, **2** : **3** : **4** = 1 : 1 : 4.6); some other heterocyclic compounds (imidazole, picolinic acid, phenanthroline) or anthranilic acid do not sensitize oxygenation at all. The dependence of the initial rate of the reaction (defined as the concentration (*C*) of products after irradiation for 1 h) on the concentration of ester **5** is characterized by the following values:

$[5] \cdot 10^{+3} / \text{mol L}^{-1}$	0	0.4	0.8	3.9
$[C] \cdot 10^{+3} / \text{mol L}^{-1}$	0	1.0	1.5	4.8

Oxidation of *n*-hexane in the presence of compound **1** gives products resulting from oxidation at the C(1), C(2), or C(3) atom in a ratio of 1 : 35 : 32. In the case of 2-methylhexane, primary, secondary, and tertiary C–H bonds are oxidized at relative rates of 1, 16, and 100, respectively. These data indicate that oxidation in the presence of the sensitizer found is much more selective than aerobic photooxidation through the action of hydroxyl radicals. In fact, when oxidation is carried out by hydrogen peroxide in MeCN, the corresponding values are 1 : 10 : 7 for *n*-hexane and 1 : 6 : 30 for 3-methylhexane (see Ref. 7). However, the observed selectivity parameters are lower than those for anthraquinone-sensitized oxygenation (1 : 55 : 57 in oxidation of *n*-hexane and 1 : 43 : 55 for 3-methylhexane).⁸ It is likely that the process of oxygenation in the presence of pyrazine begins with abstraction of a hydrogen atom of alkane by photosensitized heterocyclic species and

addition of this hydrogen atom to one of the nitrogen atoms.

The work was carried out with financial support from the International Science Foundation (Grant Nos. MMS 000 and MMS 300), INTAS (Grant 93-1226), and the Russian Foundation for Basic Research (Project No. 93-03-05226).

References

1. M. Chanon, M. Julliard, J. Santamaria, and F. Chanon, *New J. Chem.*, 1992, **16**, 171.
2. M. Julliard, *New J. Chem.*, 1994, **18**, 243.
3. M. Mella, M. Freccero, and A. Albini, *J. Chem. Soc., Chem. Commun.*, 1995, 41.
4. G. B. Shul'pin, M. M. Kats, and G. V. Nizova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2653 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 2395 (Engl. Transl.)].
5. G. B. Shul'pin, M. M. Kats, and P. Lederer, *Zh. Obshch. Khim.*, 1989, **59**, 2742 [*J. Gen. Chem. USSR*, 1989, **59** (Engl. Transl.)].
6. G. B. Shul'pin and G. Süss-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, No. 7.
7. G. B. Shul'pin and G. V. Nizova, *React. Kinet. Catal. Lett.*, 1992, **48**, 333.
8. G. V. Nizova and G. B. Shul'pin, *Neftekhimiya [Petroleum Chemistry]*, 1994, **34**, 364 (in Russian).

Received May 22, 1995