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Aerobic photochemical oxygenation of alkanes sensitized by pyrazine derivatives

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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 cocatalyst of a dark reaction[6]) is an efficient photosensitizer. In fact, irradiation of a solution containing cyclohexane (0.46 mol L^{-1}) and pyrazine-2-carboxylic acid (**1**; $4 \cdot 10^{-4}$ mol L^{-1}) in MeCN for 4 h afforded cyclohexanol (**2**), cyclohexanone (**3**), and cyclohexyl hydroperoxide (**4**) (their total concentration was $2.2 \cdot 10^{-3}$ 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 °C with running water was irradiated in air with the full light of a 125 Wt luminescence lamp, $\lambda > 300$ nm. Methyl pyrazine-2-carboxylate (**5**) exhibits much higher activity ($3.7 \cdot 10^{-4}$ 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 ($1.8 \cdot 10^{-4}$ mol L^{-1}; a glass vessel, **2** : **3** : **4** = 1 :1 : 2.2). It is significant that the activity of pyrimidine is substantially lower ($0.5 \cdot 10^{-4}$ 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:

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

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

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Low-temperature reactions of CO_2 in the presence of iron-titanium intermetallide

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Involving CO_2, which is one of the most easily accessible sources of carbon raw materials, in organic and petrochemical synthesis is being held back by the lack of effective and selective catalytic systems. At present, elaboration of these systems receives much attention.[1,2] In this connection, the development of scientific fundamentals of power-consuming processes of the transformation of CO_2 into fuel compounds or in compounds meant for petrochemical synthesis is of interest.

In this communication we present the results of hydrogenation of CO_2 in the presence of $TiFe_{0.9}Zr_{0.05}Mn_{0.05}$ intermetallide, which is capable of chemisorbing H_2 to form a hydride phase, which reversibly decomposes under relatively mild conditions.[3]

The experiments were carried out in a stainless-steel reactor using a flow-loop type setup (p_{CO_2} = 8 atm, T = 293 to 623 K, a batch of intermetallide was 20 g (5 cm^3)). A specimen with granules of diameter 2—5 mm was used. After preliminary activation of the catalyst in an H_2 flow for 10 h at 373 K, the system was filled with hydrogen, pressure was increased to 100 atm, and the system was kept for 10 h.

The quantity of chemisorbed H_2, determined by manometry based on the pressure drop, was 0.013 mol per g of intermetallide. Hydrogen was displaced with an excess of CO_2, the setup was switched to the circulation conditions, and then the reaction zone was heated to a specified temperature. The turnover frequency of the reaction gas through the layer of intermetallide was 0.25 L (g Cat h)$^{-1}$.

In the studies on the effect of the temperature on the conversion of CO_2, a fresh sample of the catalyst was taken for each run. The dependence of the accumulation of reaction products on the duration of experiment was studied in three experimental cycles with the same batch of the catalyst. Each cycle included three steps, *viz.*, activation of intermetallide by treating it with H_2 at 373 K, saturation of intermetallide with H_2 (p = 100 atm, T = 293 K, 10 h), and circulation of the gas mixture through the intermetallide layer.

Gaseous and liquid reaction products (CO, hydrocarbons, and H_2O) were analyzed by gas chromatography.

From the data presented in Table 1, one can see that CO and CH_4 are formed even at ambient temperature. Noticeable conversion of CO_2 into gas products

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