PHOTOOXIDATION OF ALKYLBENZENES AND CYCLOHEXANE BY ATMOSPHERIC OXYGEN IN ACETONITRILE SENSITIZED BY o-PHENANTHROLINE

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Electron phototransfer [1] from alkylaromatic and saturated hydrocarbons may lead to activation of the C–H bonds in these compounds [2]. Thus, aromatic nitriles have been used as sensitizers for the photooxidation of hydrocarbons [3].

We have found that irradiation of a solution of $0.95 \cdot 10^{-3}$ mole alkylbenzene, 10^{-6} mole o-phenanthroline, 0.05 ml H_2SO_4, and 0.05 ml water in 24 ml acetonitrile at 10°C for 4 h using the total emission of a high-pressure 1000-W mercury lamp in a glass vessel ($\lambda > 310$ nm) gives the following products (yield relative to the starting compound, %, in parentheses): from toluene) C_6H_5CHO (22) and $C_6H_5CO_2H$ (5), from ethylbenzene) $C_6H_5COCH_3$ (55) and $C_6H_5 \cdot CH(OH)CH_3$ (19), from p-$CH_3C_6H_4CH_3$) p-$CH_3C_6H_4CHO$ (48) and p-$CH_3C_6H_4CO_2H$ (11), from $(C_6H_5)_3CH$) $(C_6H_5)_3COH$ (48) and $(C_6H_5)_2CO$ (32), and from $C_6H_5CH(CH_3)_2$) $C_6H_5C(CH_3)_2OH$ (23) and $C_6H_5COCH_3$(6). Under analogous conditions using 2,2'-dipyridyl as the sensitizer, the yield of C_6H_5CHO from toluene is three times less than in the case of o-phenanthroline (the photoactivity of 2,2'-dipyridyl was discussed by Kachanova [4]). On the other hand, 4,4'-dipyridyl, pyridine, α-picolinic acid, and imidazole are inactive in the oxidation.

The irradiation of $1.9 \cdot 10^{-3}$ mole cyclohexane in 6 ml acetonitrile in the presence of 10^{-6} o-phenanthroline, 0.05 ml H_2SO_4, and 0.05 ml water for 4 h at 10°C gives $7.3 \cdot 10^{-6}$ mole cyclohexanol and $1.2 \cdot 10^{-5}$ mole cyclohexanone. Hexane is not oxidized. The proposed reaction mechanism involves electron transfer from the hydrocarbon to photoexcited protonated o-phenanthroline with subsequent formation of a hydrocarbon radical, which reacts ith the O_2 molecule.

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