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Preliminary communication

Oxidation of furfural with H_2O_2 in the presence of a photogenerated iron catalyst

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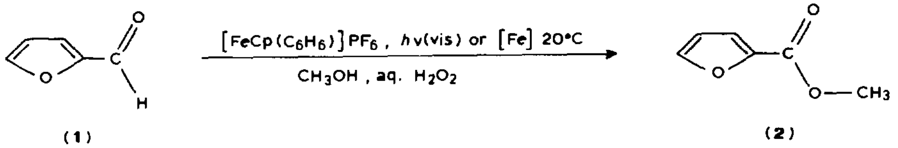
Abstract

Visible irradiation of a methanolic solution of furfural containing dilute aqueous H_2O_2 and $[FeCp(C_6H_5R)]PF_6$ (**1**: R = H, Cl or CH_3) as catalyst yields methyl 2-furoate quantitatively. After photodecomplexation, the inorganic $Fe^{II,III}$ catalyst can be isolated and recycled several times with unchanged activity in dark reactions at 20 ° C.

Transition metal complexes that can liberate a large number of coordination sites such as metal-arene sandwiches have potential for catalytic activity. In designing a research program in this direction, we turned our attention to the photolability of the cations $[FeCp(arene)]^+$ towards visible light [1,2] as a potential source of catalysts [3]. The finding of new oxidation catalysts is important, especially those for transformation of cheap raw materials such as furfural.

In a typical procedure 0.5 mmol of $[FeCp(C_6H_6)]PF_6$ is irradiated for 2 h with a 200 W visible lamp in a Schlenk tube containing also 50 ml of CH_3OH, 10 ml of aqueous H_2O_2 (29 mmol), and 1.66 ml of furfural (20 mmol). The reaction was then continued in the dark with addition of 1 ml of aqueous H_2O_2 every day. Monitoring of the formation of methyl 2-furoate (**2**), by GLC (SE30 column) or by ^1H NMR [4] (CO_2CH_3: 3.9 ppm, $CDCl_3$) indicates that reaction was complete after 4 days. Standard work up and distillation provided **2** (90%) pure as indicated by ^1H NMR spectroscopy and elemental analysis (see eq. 1). In the absence of iron catalyst, the procedure gave < 5% of **2**.



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Although this type of oxidation of furfural is well-known [5], various other classical catalysts, including metalloporphyrins, are inactive or less active under the conditions we used. After the reaction, a catalyst species can be isolated in the solid state: concentration of the methanolic solution, precipitation with ether and washing with ether gives a white amorphous powder, which was dried in vacuo. This powder redissolves very slowly when stirred with CH_3OH if aqueous H_2O_2 is added (1 day, 20 ° C), and the catalyst is again active when dissolved. The same activity as before is observed for the oxidation of furfural in the dark at 20 ° C, and the catalyst can be recycled at least twice without loss of activity. The nature of the active species and that of the white powder are not yet known. The active solution shows, when frozen at 4.2 K, an ESR spectrum with $g = 4.422$ and 1.93 (half height width: 132 and 550 G, respectively). The Mössbauer spectra of the white powder show the presence of both inorganic Fe^{II} and Fe^{III} and the absence of a π-complex. Elemental analysis of C, H and Fe indicates a C/H ratio of ca. 1 and a CH/Fe ratio of ca. 10. Attempts to grow crystals were unsuccessful. It it possible that the species is an oxo-iron cluster of large nuclearity. Structural investigations and development of other types of catalysis using the concept described above, with this system as well as other metal species, are in progress.

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