

Alkane oxygenation with H₂O₂ catalysed by FeCl₃ and 2,2'-bipyridine

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Abstract—The H₂O₂–FeCl₃–bipy system in acetonitrile efficiently oxidises alkanes predominantly to alkyl hydroperoxides. Turnover numbers attain 400 after 1 h at 60 °C. It has been assumed that bipy facilitates proton abstraction from a H₂O₂ molecule coordinated to the iron ion (these reactions are stages in the catalytic cycle generating hydroxyl radicals from the hydrogen peroxide). Hydroxyl radicals then attack alkane molecules finally yielding the alkyl hydroperoxide.

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Iron ions surrounded with certain *N*-containing ligands can activate molecular oxygen and they play an extremely important role in nature, particularly in oxidations of alkanes and other hydrocarbons (see reviews^{1–7}). Surprisingly, in vitro 'simple' iron derivatives are usually poor catalysts for hydrocarbon oxidations with hydrogen peroxide.^{8,9} Iron complexes containing *N*-ligands exhibit higher catalytic activity in comparison with 'simple' salts, and amines added to the reaction solutions either accelerate oxidations or/and significantly change their selectivity.^{10–28}

In the course of our systematic studies of iron-catalysed hydrocarbon oxygenations with peroxides^{4,5,7,12,23,24,27,28} we decided to explore the possibility of enhancing the efficiency of the reaction by addition of certain amines (see a review on the dramatic role of additives in metal-catalysed hydrocarbon oxygenations in solutions⁴). In the present paper we report that 2,2'-bipyridine (bipy) added to iron(III)

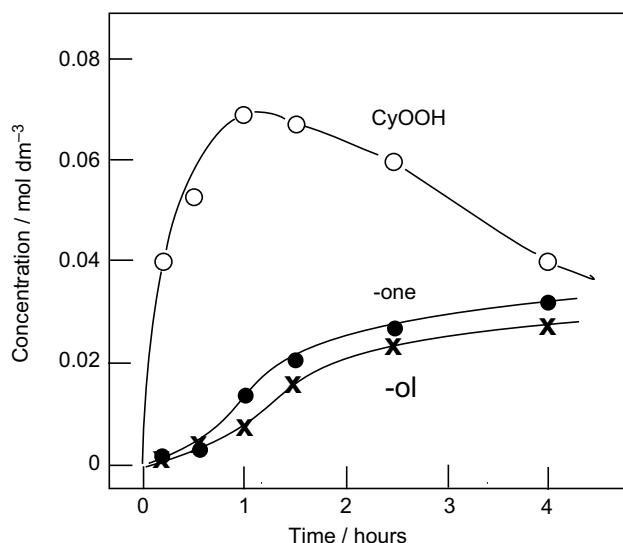


Figure 1. Cyclohexane (0.55 mol dm⁻³) oxidation with 35% aqueous H₂O₂ (1.2 mol dm⁻³) catalysed by FeCl₃ (5 × 10⁻⁴ mol dm⁻³) and bipy (5 × 10⁻³ mol dm⁻³). Accumulation of cyclohexyl hydroperoxide (ROOH), cyclohexanol (-ol) and cyclohexanone (-one) (concentrations of -ol and -one were measured twice before and after reduction of the reaction mixture with PPh₃) with time is shown. The temperature was 60 °C, and the solvent was acetonitrile.

Keywords: Alkanes; Alkyl hydroperoxides; Biomimetics; Homogeneous catalysis; Hydrogen peroxide; Hydroperoxidation; Iron complexes; Oxygenation.

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chloride used as a catalyst dramatically accelerates oxidation of alkanes with hydrogen peroxide in acetonitrile solution. The oxidations were carried out in air in thermostated (60 °C) Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 5 mL. In our experiments, aqueous solutions of hydrogen peroxide were used: either 35% ('Fluka') or 70% ('Peróxidos do Brasil'). The catalyst, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and the co-catalyst, bipy, were introduced into the reaction mixture in the form of stock solutions in acetonitrile. After given time intervals, samples (about 0.2

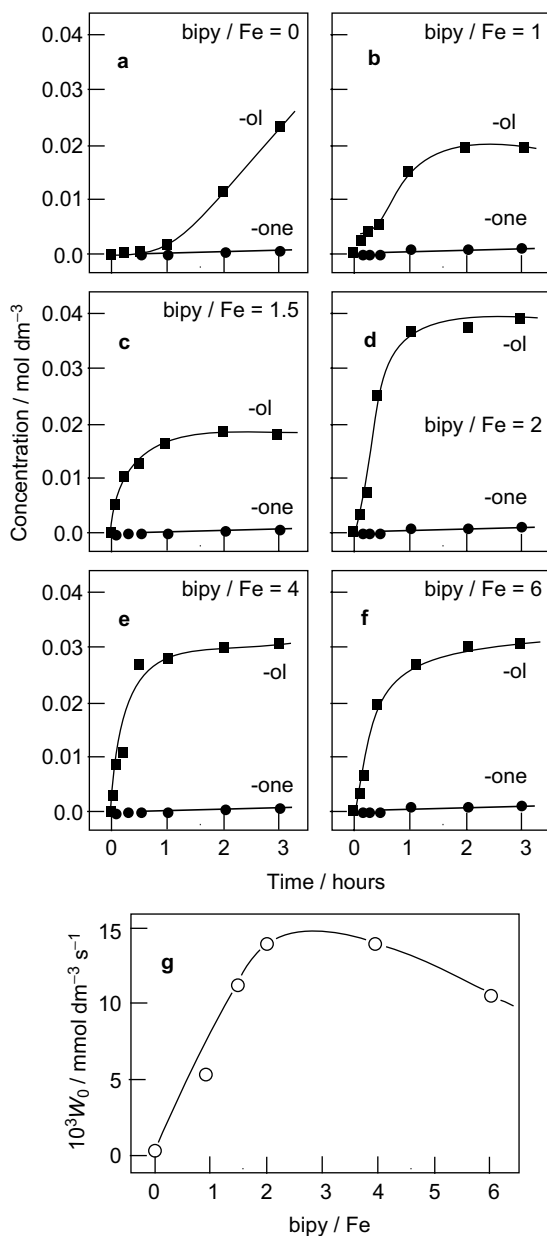


Figure 2. Cyclohexane (0.5 mol dm^{-3}) oxidation with 70% aqueous H_2O_2 (0.5 mol dm^{-3}) catalysed by FeCl_3 ($1 \times 10^{-4} \text{ mol dm}^{-3}$) at various concentrations of added bipy. Accumulation of cyclohexanol (-ol) and cyclohexanone (-one) (concentrations were measured after reduction of the reaction mixture with PPh_3) (graphs a–f) and dependence of initial rate of formation of oxygenates W_0 on the bipy/Fe ratio (graph g) are shown. The temperature was 60 °C, the solvent was acetonitrile.

mL) were taken. Samples of the reaction solutions were usually analysed by GC (instruments 'HP Series 6890' and 'DANI-86.10'; fused silica capillary columns) twice, before and after addition of an excess of solid triphenylphosphine. Triphenylphosphine reduces hydrogen peroxide to water and the alkyl hydroperoxide to the corresponding alcohol, and the comparison of the reaction chromatograms before and after the reduction allowed us to estimate the real concentrations of the alkyl hydroperoxide, formed from the alkane, as well as the concentrations of the alcohol and the ketone. This method was developed and used by us previously.^{4,5,7,12,23,24,27–30} In the kinetic studies presented below, we measured the concentrations of the cyclohexanone and cyclohexanol only after reduction with PPh_3 because in this way we obtained more precise values of the initial reaction rates.

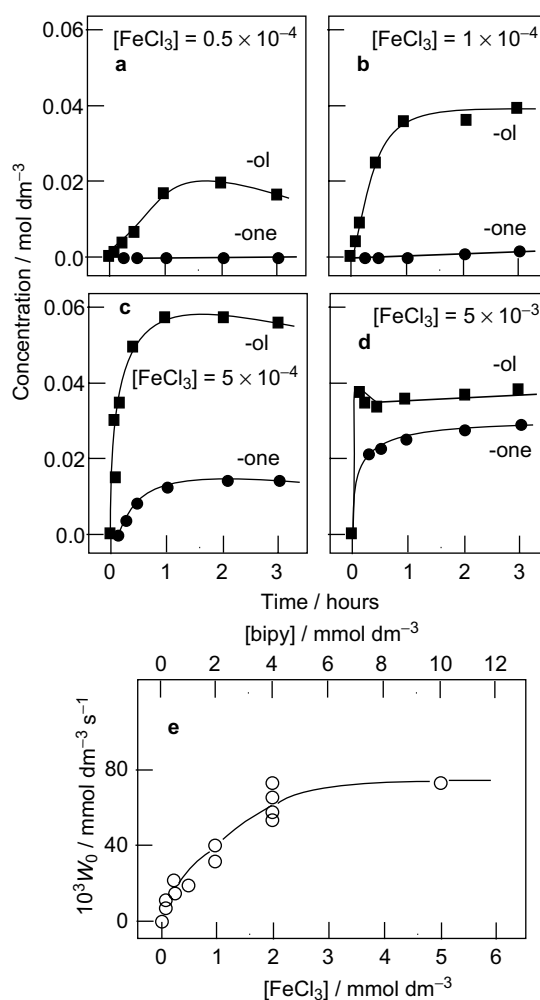


Figure 3. Cyclohexane (0.5 mol dm^{-3}) oxidation with 70% aqueous H_2O_2 (0.5 mol dm^{-3}) catalysed by the ' FeCl_3 -bipy' system at various concentrations of both FeCl_3 and bipy at constant ratio bipy/ $\text{FeCl}_3 = 2$. Accumulation of cyclohexanol (-ol) and cyclohexanone (-one) (concentrations were measured after reduction of the reaction mixture with PPh_3) (graphs a–d) and dependence of initial rate of formation of all oxygenates W_0 on the concentration of FeCl_3 and bipy (graph e) are shown. The temperature was 60 °C, the solvent was acetonitrile.

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