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Note

The oxygenation of cyclohexane under Gif^{IV} conditions – The catalytic behaviour of iron complexes

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Abstract

The catalytic oxygenation of cyclohexane to cyclohexanol (-ol) and cyclohexanone (-one) using a series of di- and trivalent iron-picolinate complexes under Gif^{IV} conditions (10:1 v/v pyridine–acetic acid, zinc powder at room temperature under aerobic atmosphere) proceeds with turnover numbers [defined as (moles of oxygenated products)/(moles of catalyst)] of 161–184 and -one:-ol ratios of 4.2–4.7. The corresponding values for the binuclear picolinate complex $[Fe_2(\mu\text{-}OMe)_2(pic)_4]$ (237 turnovers, -one:-ol ratio 7.2) are significantly higher. Iron complexes bearing functionalised pyridyl ligands exhibit turnover numbers and ketone selectivities of similar magnitude to, and in some cases higher than, the picolinate complexes.

Keywords: Gif catalysis; Iron; Picolinic acid; Cyclohexane; Turnover number; Oxygenation

1. Introduction

The catalytic functionalisation of C–H bonds in alkanes at ambient temperature and pressure attracts extensive and ongoing interest worldwide, with systems which mimic the dioxygen activation induced by iron-containing biological systems such as bleomycin, cytochrome P450 and methane monooxygenase receiving particular attention [1]. One prominent group of inorganic iron catalysts introduced by Sir Derek Barton for the oxygenation of cycloalkanes to cyclic ketones and alcohols is the Gif family of systems [2–5], which utilise iron salts with either atmospheric dioxygen or hydrogen peroxide as the oxidant at room temperature in pyridine. The preference for the formation of ketone over alcohol and the absence of over-oxidised products are attractive features of Gif catalytic systems. The mechanism of Gif chemistry provoked fierce debate for several years and much elegant analysis was conducted in order to resolve the issue. The consensus of opinion favours a pathway involving carbon- and oxygen-centred radicals, displacing Barton's original proposal of iron(V)-oxo intermediates which activated alkane C–H bonds via insertion [2,3].

Within this family of oxidant systems, Gif^{IV} [a heterogeneous mixture comprising an iron(II) salt and zinc powder in pyridine–acetic acid] is the most catalytically active manifold, with turnover numbers for the ketonisation of adamantane exceeding 2000 [6]. Several experimental parameters in Gif^{IV} reactions, such as the substrate:catalyst ratio, the rate of stirring and the particle size of the zinc, influence catalytic efficiency [7,8]. The use of pyridine as solvent is critical, reflecting its capacity to stabilise iron intermediates by co-ordination and its involvement in the radical chemistry which underpins Gif chemistry. Although several cycloalkanes have been investigated, with cyclohexane being particularly important as the precursor to adipic acid for Nylon manufacture [9,10], turnover numbers are greatest when the substrate is adamantane. An innovative approach to optimising the reaction parameters in Gif chemistry made use of the Plackett–Burman statistical design to the oxygenation of adamantane in acetonitrile–pyridine by a hexaazadiphenol macrocycle-diiron(III)

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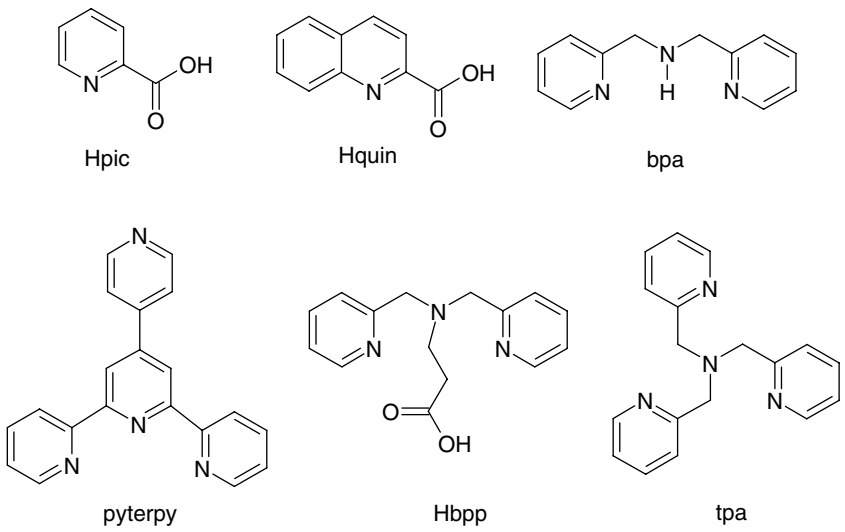

Fig. 1. Structures of pyridyl-containing ligands used in this study.

complex [11]. Application of the Plackett–Burman design enabled the successful optimisation of conditions from a small number of experiments, and moreover did not require an intimate knowledge of the mechanism.

Picolinic acid (Hpic) accelerates Gif-type catalysis and iron-picolinate complexes have been widely studied in Gif chemistry [12–15]. In particular, the $GoAgg^{III}$ system [comprising an iron(III) salt, Hpic and aqueous hydrogen peroxide in pyridine] [16,17] is a homogeneous counterpart of the Gif^{IV} manifold and exhibits mechanistic similarities with it. The use of $GoAgg^{III}$ catalysis to selectively oxidise complex natural products underlines the mildness and versatility of this system [18–22], and suggests that applications in fine chemical synthesis may exist.

We have recently reported [23] a UV–Vis and EPR spectroscopic study of the kinetics of the $GoAgg^{III}$ system and communicated [24] an improved synthesis of a complex, which Barton et al. described [25] as a key intermediate in $GoAgg^{III}$, $[Fe(pic)_2Cl_2]^-$. We describe in this paper the results of our studies on the Gif^{IV} oxygenation of cyclohexane to cyclohexanol and cyclohexanone, catalysed by iron complexes of picolinate and of polydentate ligands bearing pyridyl groups (Fig. 1). Iron salts have generally been used in Gif^{IV}; the capability of picolinate and related ligands to influence Gif chemistry encouraged us to study iron complexes with these ligands under Gif^{IV} conditions.

2. Experimental

2.1. General

Catalytic, work-up and gas chromatographic procedures were conducted under aerobic conditions. Solvents and reagents (analytical grade, Aldrich Chemical Co.) were used as received, apart from zinc powder (<10 μm mesh) which was activated with dilute hydrochloric acid [26]. The ligands 4′-(4-pyridyl)-2,2′:6′,2″-terpyridine (pyterpy) [27], 3-[bis(2-pyridylmethyl)amino]propanoic acid (Hbpp) [28,29], *N*,*N*′-bis(2-picolyl)amine (bpa) [30], and the complexes $[Fe(pyterpy)_2][ClO_4]_2$ [31], $[Fe(bpa)_2][BF_4]_2$ [32], $[\{Fe(bpp)(H_2O)\}_2(\mu\text{-}O)][ClO_4]_2$ [29], $[\{Fe(tpa)\}_2(\mu\text{-}O)][ClO_4]_4$ [tpa = tris(2-pyridylmethyl)amine] [33], $[Fe(quin)_2(py)_2]$ (Hquin = quinoline-2-carboxylic acid) [34], $[pyH][Fe(pic)_2Cl_2]$ [24], $[Fe_2(\mu\text{-}OMe)_2(pic)_4]$ [24], $[Fe(pic)_2]_n$ [13], $[Fe(pic)_3]$ [13], $[Fe(pic)_2(py)_2]$ [13], $[Cu(py)_4][ClO_4]_2$, $[Cu(pic)_2]\cdot 2H_2O$, $[Cu(tpa)(H_2O)][ClO_4]_2$ [35] and $[Fe(pic)_2(H_2O)_2]$ [13] were prepared by the literature methods and characterised using standard techniques (C/H/N microanalysis, IR, EI and FAB^+ mass spectrometry).

2.2. Catalytic reactions

The reactions were performed at 20 °C in round-bottom flasks (100 cm^3, B24 ground glass joint) and stirred with a 2 cm length rugby ball shaped stirrer bead. The mixture of catalyst (7 μmol), cyclohexane (1.07 cm^3, 10 mmol) and glacial acetic acid (2.3 cm^3, 40 mmol) in pyridine (28 cm^3) was stirred at 1000 rpm and the reaction was initiated by the addition of zinc powder (1.31 g, 20 mmol) in one portion. The flask was kept open to the atmosphere via the neck of the flask throughout the reaction. After 12 h, stirring was ceased, the unreacted zinc allowed to settle and a 2 cm^3 aliquot of the supernatant solution was removed using a Gilson pipette and neutralised with 20% v/v aqueous sulfuric acid (5 cm^3). The organic components were extracted into diethyl ether (3×5 cm^3), the combined ethereal extract was washed with saturated aqueous sodium bicarbonate solution (1×5 cm^3) and dried over anhydrous magnesium sulfate. The flasks were stoppered during this extraction process to minimise evaporation of the solvent. An accurately measured aliquot (1 cm^3) of the dried ethereal extract was removed and analysed by GC.