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Iodosobenzene and persulfate oxygenation of saturated hydrocarbons catalyzed by diphosphino complexes of ruthenium(III)

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Abstract

Hydroxylation and/or ketonization of alkanes (adamantane, cyclo-octene, hexane) is achieved by using iodosobenzene or aqueous mono-persulfate at room temperature in the presence of catalytic amounts of ruthenium(III)–diphosphino complexes dissolved in dichloromethane. On the basis of the kinetic behavior, different oxidizing metal species are proposed for the oxidations with mono-persulfate and with iodosobenzene.

Introduction

The selective functionalization of alkanes by transition metal complexes remains a goal of considerable practical and fundamental importance and substantial progress over the past decade has been made in the basic understanding of factors that influence the viability of the initial intra- or inter-molecular addition of C–H bonds [1]. A number of recent reports has pointed out the potentiality of ruthenium salts and complexes as catalytic precursors for this important reaction in the presence of a variety of auxiliary oxidizing agents [2].

We previously reported that simple complexes of ruthenium(II) of the type $RuX_2(L)_n$, where L = phosphine, sulfoxide or nitrogen donors and X = chloride or other mononegative anions, are able to mediate the mild oxidation of saturated substrates, including alkanes, with hypochlorite and other oxidants [3]. Now we have examined the iodosobenzene and persulfate oxygenations of hexane, cyclo-octane and adamantane in the presence of ruthenium(III) diphosphino complexes of the type $[Ru^{III}Cl_2(LL)_2]BF_4$ (LL = 1,3-bis(diphenylphosphino)propane, DPP, or 1,2-bis(diphenylphosphino)ethane, DPE); the ruthenium(II) derivative $[Ru^{II}Cl(DPP)_2]PF_6$ was also examined for comparison.

Experimental

Organic analyses were made on an HP 5890 gas chromatograph equipped with FID, using a 30 m SE-30 capillary column (0.25 mm i.d.). The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV. $[RuCl(DPP)_2]PF_6$ was prepared as described in ref. 4.

$[RuCl_2(LL)_2]BF_4$ (LL = DPE, DPP)

The olive-green (LL = DPE) or light-green (LL = DPP) compounds were prepared by following literature procedures [5]. 0.66 mmol of *trans*-$[RuCl_2(LL)_2]$, dissolved in 50 ml of benzene, were reacted with 780 mg (6.7 mmol) of $NOBF_4$ and stirred for 30 min at room temperature (60 °C in the case of the DPE derivative). By addition of ethyl ether, the solid compounds precipitated and were recrystallized from methanol (yields 85%). Elemental analyses (C, H, Cl) are within 0.2%; magnetic moments (Gouy method), $\mu_{eff} = 2.1$ BM at 20 °C.

Procedure for the catalytic oxidations

A 1 ml aliquot of a CH_2Cl_2 solution containing 1 mmol of the substrates, 0.002 mmol of the complexes and a gas-chromatographic standard (5 mM decane) were stirred magnetically in a vial together with 1 ml of an aqueous solution of oxone (0.5 M in $KHSO_5$), as determined by iodometric titration, in the presence

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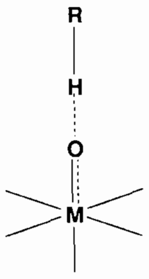
of benzyl-dimethyl-tetradecylammonium chloride (0.002 mmol) or with 22 mg (0.1 mmol) of solid PhIO. GLC analyses were performed on aliquots of the organic layer, withdrawn at appropriate times with a hypodermic microsyringe. Yields were determined after iodometric titration of residual oxidant. Reaction rates were determined at 22 °C for early stages of the reaction and were reproducible to within 15%.

Results and discussion

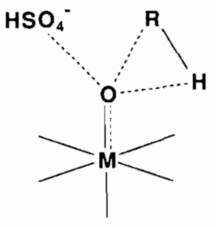
All our reactions with $KHSO_5$ took place in a two-phase system consisting of an organic phase (dichloromethane) containing the substrates and the catalysts and an aqueous solution containing the oxidizing agent at a concentration of 0.5 mol/l, in the presence of the phase transfer agent benzyl-dimethyl-tetradecylammonium chloride. All examined ruthenium complexes catalyzed the conversion of the alkanes to oxygenated derivatives with almost quantitative yields with respect to the oxidant PhIO and satisfactorily high yields to $KHSO_5$. H_2O_2 (30% aqueous solutions) underwent vigorous decomposition in the presence of the ruthenium catalysts with little oxygenation of the substrates; hypochlorite, although as effective as iodosobenzene for the oxygenation of the examined substrates, also led to the formation of significant amounts (up to *c.* 10%) of chloro derivatives, likely because of hypochlorous acid, a well-known chlorination agent for alkanes [6].

Typical oxidation rates for the examined substrates and product distribution are listed in Table 1 for the various catalyst–oxidant combinations. Whereas with persulfate the catalysts appear to be more effective than with iodosobenzene, selectivity does not significantly vary between the two oxidants: as commonly found in ruthenium-catalyzed oxidations, methyl groups are unaffected by the oxidation and methylene groups are converted into secondary alcohols and then very rapidly into ketones, the largely dominant products in the reaction mixtures. The observed ω-1 regioselectivity in the oxidation of hexane is typical of radical-chain substitution reactions, but is widely reported for many metal–oxo species, like cytochrome P-450 isozymes [7] and metal–porphyrin complexes [8]. Upon oxygenation of adamantane, large ratios of tertiary alcohol to total secondary products were found, which, together with the observed formation of minor amounts of 1,1-diadamantyl, point to a carbon-radical path, where oxidation happens in preference on the hydrogen carried by the bridgehead tertiary carbons. It should be noted that C3/C2 selectivity in adamantane functionalization appears definitely higher when the typical oxo-reagent PhIO (Table 1) is used and this can be an indication of the mechanism, since oxo–metals are usually expected to give fairly large tertiary to secondary selectivities [9].

The kinetic analysis, based on the measurement of the amount of carbonylic products formed in the oxidation of hexane, indicates an identical linear dependence of the reaction rates upon the concentration of the catalysts with both oxidants. However, different dependences on substrate concentration are observed for the iodosobenzene oxidation (first-order kinetics) and in the presence of persulfate (Fig. 1), where the reaction order is close to zero at least in the concentration range investigated; it should be noted that in the latter case the oxidation rates are markedly dependent upon the nature of the substrates examined, thus ruling out that the rate determining step simply consists in the formation of the oxidizing metal species. Significant k_H/k_D values, between 3 and 5, are measured for the oxidation of hexane over hexane-d_{14} by iodosobenzene, while no deuterium kinetic isotope effects are found in the presence of persulfate (D-KIE). The different kinetic behavior may suggest different mechanisms for the two reactions. The reactions with iodosobenzene behave as most oxygen transfers on saturated hydrocarbons by typical oxo–metal derivatives, where the hydrogen radical abstraction is generally regarded as the slow step [10], thus confirming that conventional oxo–metal species are formed upon reaction of the ruthenium(II) and ruthenium(III) complexes with PhIO. The absence of D-KIEs in the persulfate oxidations is in agreement with an early transition state, closer to a concerted rather than to a homolytic mechanism [11] (the apparent zero-order dependence in the substrates in saturation conditions, which apparently points to a reaction intermediate with a tightly bound substrate, remains without a reasonable explanation). A related divergent behavior of monopersulfate in the oxygenation of alkanes was recently observed for a series of manganese porphyrins and has been tentatively attributed to oxidizing metal species other than conventional oxo-metals **1a**, possibly peroxo–metal-like species **1b** containing the mono-persulfate moiety still coordinated to the metal [12].



1a



1b

Indeed, the reaction mixtures look completely different when iodosobenzene or persulfate are used:

TABLE 1. Catalytic oxygenation of alkanes by ruthenium complexes[a]

Oxidant	$[Ru^{III}Cl_2(DPP)_2]^+$		$[Ru^{III}Cl_2(DPE)_2]^+$		$[Ru^{II}Cl(DPP)_2]^+$	
	Rate[b]	Yield[c] (%)	Rate[b]	Yield[c] (%)	Rate[b]	Yield[c] (%)
Adamantane[d]						
$KHSO_5$	31	43 $C_3/C_2=4.1$	7	45 $C_3/C_2=4.4$	16	40 $C_3/C_2=4.5$
PhIO	1.6	99 $C_3/C_2=18$	0.2	75[e] $C_3/C_2=10$	0.3	99 $C_3/C_2=13$
Cyclo-octane[f]						
$KHSO_5$	3.5	40	2[g]	45	2.5	35
PhIO	0.7	85	0.5[h]	55[e]	0.7[g]	90
Hexane[i]						
$KHSO_5$	2.4	15[e]	1.2	15[e]	1.3	10[e]
PhIO	0.15	17[e]	0.04	<1[e]	0.03	20[e]

[a] All reactions run with alkane (1 mmol, except adamantane: 0.5 mmol) and the catalysts (0.002 mmol) in dichloromethane (1 ml) and solid PhIO (0.1 mmol) or $KHSO_5$ (0.5 mmol in 1 ml water) in the presence of benzyl-dimethyl-tetradecylammonium chloride (1:1 molar ratio to the catalysts), at 22 °C. Product distributions are quantified by GLC-MS analyses. [b] Initial conversion rates. Units: turnover h^{-1}. [c] Yields of alcohol and ketone, based on oxidant available, after 48 h. Units: % (mol). The ketone yields are the molar yields multiplied by 2, since 2 equiv. of oxidant are required to make 1 mol of ketone. [d] Products: 1-adamantanol and adamantanone in C_3/C_2 molar ratios (not statistically corrected). [e] Still running. [f] Products: cyclo-octanone and minor amounts of cyclo-octanol. [g] 3–5 h induction. [h] 20–30 h induction. [i] Products: 2-hexanone and minor amounts of 3-hexanone.

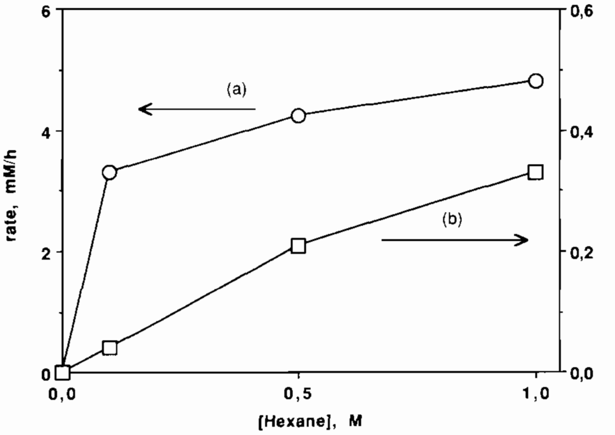


Fig. 1. Effect of substrate concentration on the oxygenation rate of hexane to 2-hexanone catalyzed by $[Ru^{III}Cl_2(DPP)_2]BF_4$ (2 mM, CH_2Cl_2, 22 °C) in the presence of: (a) aq. $KHSO_5$ 0.5 M (250-fold to the catalyst) and benzyl-dimethyl-tetradecylammonium chloride (1:1 to the catalyst); (b) PhIO (50-fold to the catalyst).

both the green $[RuCl_2(LL)_2]BF_4$ and the violet $[RuCl(DPP)_2]BF_4$ catalysts being rapidly converted into light-green (PhIO) or orange solutions ($KHSO_5$). The organometallic species maintain their integrity within two hours reaction, as shown by the negligible amounts of diphosphine oxide formed, <15%, as measured by the intensity of the $\nu(P{=}O)$ absorption at 1180 cm^{-1}; nevertheless we were not able to obtain direct evidence on the nature of the oxidized diphosphino complexes, since ^{31}P NMR spectra of the reaction mixtures only exhibit the singlet of free diphosphine oxide at 32 ppm, and broad and unresolved signals, likely due to the paramagnetism of the metal species. In the presence of persulfate complete degradation of the organic ligands occurs after *c.* 100 cycles with transformation of the catalysts into inactive dark-green species. Quite disappointingly, the ruthenium(II) and ruthenium(III) complexes behave substantially in the same way, apparently suggesting comparable oxidizing activities of the corresponding high-valent metal species or, alternatively, rapid conproportionation of the odd-valent ruthenium species arising from ruthenium(III) [2m], with formation of ruthenium(IV) or (VI) derivatives, as in the likely case of the ruthenium(II) precursor.

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