Inorganica Chimica Acta, 44 (1980) L107–L109
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Catalytic Oxidations with Molecular Oxygen in the Presence of Cobaloxime(II) Derivatives

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Received September 21, 1979

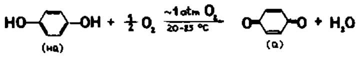
Bis(dimethylglyoximato)cobalt(II), referred to also as cobaloxime(II), and its derivatives are known to react reversibly with molecular oxygen in aprotic solvents [1]. Among the reaction products transient species can be observed, which are regarded as different μ-peroxo and superoxo compounds [1]. Although there have been extensive studies of oxygenation reactions in the presence of other cobalt complexes [3–6], little attention has been devoted to the use of cobaloximes as catalysts for the activation of molecular oxygen [2]. We now wish to report on the catalytic oxidation of some substrates in the presence of cobaloxime(II) derivatives.

Experimental

Oxygen uptake was measured by gas volumetry. Analytical grade chemicals were used throughout. Benzene and acetone were dried over molecular sieves. $Co^{II}(Hdmg)_2(Ph_3P)_2$ and $Co^{II}(Hdmg)_2py$ (where Hdmg is the monoanion of dimethylglioxime) were prepared according to standard procedures [1]. All reaction products were identified by GLC. The yields were determined by comparing the GLC peak areas with those of authentic samples. As hydrazobenzene decomposes quantitatively into aniline and azobenzene in the injector of the gas chromatograph, residual hydrazobenzene was determined by measuring the amount of aniline formed upon its decomposition. The ESR spectra were obtained using a JES-ME-3X type spectrometer.

Results

We have found that, in an atmosphere of air or O_2, under mild conditions, $Co(Hdmg)_2(Ph_3P)_2$ and $Co(Hdmg)_2py$ catalyze the oxidation of hydroquinone, triphenylphosphine and hydrazobenzene, added in a 5–50-fold excess over the catalyst. These oxidation reactions are described by the following stoichiometric equations:



(1)

$$Ph_3P + \frac{1}{2}O_2 \xrightarrow[20\text{–}25\ ^\circ C]{\sim 1\ \text{atm}\ O_2} Ph_3P{=}O \qquad (2)$$

$$\underset{(HAB)}{Ph{-}NH{-}NH{-}Ph} + \frac{1}{2}O_2 \xrightarrow[20\text{–}25\ ^\circ C]{\sim 1\ \text{atm}\ O_2} \underset{(AB)}{Ph{-}N{=}N{-}Ph} + H_2O \qquad (3)$$

Oxidations in Aprotic Media

In aprotic solvents, such as benzene and acetone, the yields of the oxidation products in eqs. (1)–(3) are excellent or quantitative in most cases (Table I), which agrees well with the amount of oxygen absorbed by the solutions. The catalytic effect of cobaloxime(II) derivatives is clearly demonstrated by the yields and reaction times in comparison with those of the blank experiments listed in the last 3 rows of Table I. Careful GLC investigations have shown that no products other than those given in eqs. (1)–(3) are detectable during the reactions. Also, when $Co(Hdmg)_2(Ph_3P)_2$ is used as catalyst for reactions (1) or (3), coordinated Ph_3P is only oxidized after all the HQ or HAB has been converted to product, *i.e.* the oxidation of Ph_3P does not interfere with the catalytic oxidation of either substrate.

The O_2 absorption curves for the above substrates were not influenced by prior addition of the corresponding oxidation product to the reaction mixture. The cobaloxime(II) complexes used in this work do not catalyze the oxidation of allyl alcohol and cyclohexene under the mild conditions employed. These compounds remained unreactive in the presence of HAB, HQ and Ph_3P or their oxidation products.

According to the data in Table I, the catalytic activity of cobaloxime(II) complexes depends on the nature of the axial base. $Co(Hdmg)_2(Ph_3P)_2$ proved to be a more effective catalyst than $Co(Hdmg)_2py$; lower yields are observed with longer reaction times in the case of pyridine cobaloxime(II). After a substrate has been consumed in a run, the reaction can be re-started by adding a new portion of substrate.

Oxidations in Methanol

To gain further insight into the nature of cobaloxime(II)-catalyzed oxidations, the reactions were also carried out in methanol. The oxidation of HAB is quantitative in methanol too but the reactions are faster than in benzene and acetone. The oxidation of HQ reveals some interesting features, not observed in benzene and acetone: it appears to be oxidized both

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TABLE I. Catalytic Oxidation of Various Substrates in Acetone (T = 23.5 °C; $P_{O_2} \approx 1$ atm).

Catalyst	Catalyst conc. (*M*)	Substrate	Substrate conc. (*M*)	Product yield[a] in mol % of substrate added (reaction time[d], hr)
$Co(Hdmg)_2(Ph_3P)_2$	2×10^{-2}	Ph_3P	0.1	85 (12)
	2×10^{-2}	HQ[b]	2×10^{-2}	100 (0.5)
	2×10^{-2}	HQ[b]	0.1	100 (4.5)
	2×10^{-3}	HQ[b]	0.1	100 (7.5)
	2×10^{-3}	HAB[b]	0.1	100 (2)
	2×10^{-2}	Ph_3P[c]	0.1	80 (20)
	2×10^{-3}	Ph_3P[c]	0.1	20 (20)
$Co(Hdmg)_2py$	2×10^{-3}	HQ	0.1	10 (20)
	2×10^{-3}	HAB	0.1	100 (3)
No catalyst added		Ph_3P	0.1	5 (48)
		HQ	0.1	15 (24)
		HAB	0.1	80 (36)

[a] Determined by GLC. [b] Ph_3P oxidized after full conversion of the substrate. [c] In benzene solution. [d] End of increase in yield.

TABLE II. Oxidation of Various Substrates in Methanol (T = 23.5 °C; $P_{O_2} \approx 1$ atm).

Catalyst	Catalyst conc. (*M*)	Substrate	Substrate conc. (*M*)	Overall amount of O_2 absorbed (mol O_2/mol substr.)	Reaction time[a] (min)
$Co(Hdmg)_2(Ph_3P)_2$	2×10^{-3}	HAB	0.1	0.5	20
	2×10^{-3}	HQ	0.1	0.20	40
	2×10^{-2}	HQ	2×10^{-2}	2.5	20
	2×10^{-2}	HQ + Q (quinhydrone)	2×10^{-2}	2.25	30
	2×10^{-2}	Q	2×10^{-2}	2.0	140
$Co(Hdmg)_2py$	2×10^{-2}	HQ	2×10^{-2}	1.1	200
No catalyst added		HAB	0.1	0.35	24 hours
		HQ	0.1	0.05	24 hours

[a] End of detectable O_2 absorption.

more extensively and rapidly in methanol, provided that a sufficiently high catalyst concentration is ensured (with 1% catalyst, the reaction stops after the uptake of only 40% of the O_2 required for complete oxidation to *p*-benzoquinone). According to gas volumetric measurements, the maximum amount of absorbed O_2 is 5 times greater in methanol than in acetone (at a cobaloxime(II) to HQ mol ratio of 1:1). Quinhydrone (1:1 adduct of HQ and *p*-benzoquinone) shows the stoichiometry expected for the behaviour of its individual components.

These results indicate that *p*-benzoquinone (formed during the reaction or added initially) undergoes further oxidation in methanol. However, probably because of the formation of non-volatile quinone oligomers, we have been unable to detect either *p*-benzoquinone or its oxidation products by GLC at a substrate to catalyst mol ratio of 1:1.

Discussion

According to Schrauzer and Lian Pin Lee [1], the interaction of cobaloxime(II) complexes with dioxygen involves the initial equilibria (axial base omitted):

$$\mathrm{Co^{II}(Hdmg)_2 + O_2 \rightleftharpoons \underset{(\mathit{I})}{(Hdmg)_2CoO_2}} \qquad (4)$$

$$\mathrm{(Hdmg)_2CoO_2 + Co^{II}(Hdmg)_2 \rightleftharpoons (Hdmg)_2CoO_2Co(Hdmg)_2} \qquad (5)$$

followed, after longer times, by further, more complicated steps. The above mononuclear superoxo and dinculear μ-peroxo complexes are similar to those detected in numerous other cobalt-based oxygen carrier systems [4–6].

The catalytic oxidations reported in this paper seem to involve both oxygen transfer (Ph_3P) and dehydrogenation (HAB and HQ), though no definitive evidence can at this stage be provided for either reaction path. If oxygen complexes are the active species, the mononuclear superoxo compound is a more likely candidate since considerable steric hindrance is expected against the approach of either substrate to any dinuclear μ-peroxo complex. The superoxo complex may in principle transfer an O-atom to Ph_3P. However, the fate of the second oxygen cannot be rationalized in aprotic media without loss of the catalytic activity. The dehydrogenation of HAB can be visualized by assuming stepwise H-atom transfer to *I*, resulting in the formation of azobenzene (AB) and H_2O_2:

$$(Hdmg)_2CoO_2 + HAB \longrightarrow (Hdmg)_2Co + AB + H_2O_2 \qquad (6)$$

followed by

$$H_2O_2 + HAB \longrightarrow AB + H_2O \qquad (7)$$

In benzene and acetone, similar steps can be written for HQ. Accordingly, both H_2O_2 and *I* may be involved as oxidants in the catalytic cycle. Recently, Sen and Halpern have shown [7] that H_2O_2 is responsible for the air oxidation of Ph_3P in the presence of $Pt(Ph_3P)_3$ in ethanol.

The role of *I* in the catalytic process is supported by the fact that its characteristic ESR signal does not appear in the presence of an oxidizable substrate.

Oxidation of the substrates by cobaloxime(III) complexes, formed via O_2-oxidation of cobaloxime(II), can be excluded as no oxidation is observed upon the addition of a substrate to a cobaloxime(II) solution exposed to air for several days.

Work is in progress to elucidate the nature of the active species and the mechanistic patterns involved.

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