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HOMOGENEOUS CATALYSIS BY TRANSITION METAL COMPLEXES. SELECTIVE OXIDATION OF CYCLOHEXENE BY MIXED-CATALYSTS CONTAINING RHODIUM(II) COMPLEXES

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Summary

The oxidation of cyclohexene catalyzed by mixtures of rhodium(II) carboxylates and epoxidation catalysts (V, Mo) has been studied at 55°C under 1 atm of oxygen. The main product of oxidation is 1,2-epoxycyclohexene-3-ol (II), the yield of which depends strongly on the catalytic system used. The best yields (ca. 70% at 15% conversion) are attained with mixtures of electron-deficient rhodium carboxylates and a vanadium cocatalyst. The proposed mechanistic scheme involves two distinct steps: initially autooxidation of the olefin occurs to yield cyclohexenyl hydroperoxide, which is used to epoxidize preferentially 2-cyclohexen-1-ol.

Introduction

The homogeneous autooxidation of olefins is known to be catalyzed by a variety of metal complexes. Although the free-radical character of this reaction as well as the prior formation of allylic hydroperoxide are well established [1], the recent discovery that mixtures of low-valent group VIII metal complexes and of an epoxidation catalyst (Mo, V and W derivatives) lead to quite a different ratio of products [2], with in some cases anomalously high formation of epoxides, has led to speculation about direct activation of dioxygen.

Since the discovery of more or less reversible oxygen-adducts of low valent Rh complexes [1,3], the latter metal has been widely tested as a catalyst for selective oxidation of both olefins and hydrocarbons. However, to the best of our knowledge, the use of rhodium(II) derivatives has never been reported, except as possible intermediates in Haber-Weiss schemes [4].

Rhodium(II) carboxylates look, however, interesting for the following reasons.

(a) They are stable diamagnetic bimetallic species (d^7) with only one vacant site of coordination per metal [5], and preliminary tests have shown some of them to be stable toward oxygen [6] (vide infra).

(b) Complexes with more or less electron-withdrawing or -donating carboxylate groups are readily synthesized, permitting control of the electron density at the metal centers.

We now report on the unusual selectivities obtained in the cyclohexene oxidation with mixtures of rhodium(II) carboxylates and of typical epoxidation catalysts. The following carboxylates of rhodium(II) were chosen as representative of this class of compounds: $Rh_2(O_2C{-}CH_3)_4$ (A), $Rh_2(O_2C{-}Ad)_4$ (B) (Ad = 1-adamantyl group), $Rh_2(O_2C{-}CF_3)_4$ (C), $Rh_2(O_2C{-}C_6F_5)_4$ (D). The last two examples constitute examples of electron deficient complexes.

Results

The course of the reaction was followed by the rate of oxygen uptake (1 atm, 55°C) and by direct GLC analysis of the reaction mixture.

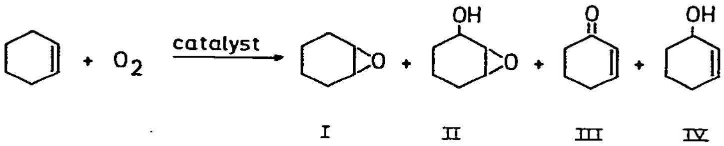
In the absence of the epoxidation catalyst, the above mentioned carboxylates promote typical autooxidation reactions, the main compounds formed, besides polymers, being 2-cyclohexen-1-one (III) and 2-cyclohexen-1-ol (IV). This reaction is inhibited by the addition of radical scavengers (hydroquinone) and the rate of oxygen absorption is proportional to the amount of metal; however, it strongly depends on the rhodium complex used, the slowest absorption being observed with the electron deficient complexes and the fastest with B. In the case of C, the catalyst is recovered unchanged after several hours at 55°C under an oxygen atmosphere, while some additional C=O stretching absorptions at 1700 cm^{-1} are apparent in the infrared spectrum of the solid recovered from reactions involving B.

The addition of an epoxidation catalyst always produces an overall decrease of the reaction rate (Fig. 1), with variable induction times before the oxygen absorption starts, together with a dramatic change in the product distribution. Then, besides the usual autooxidation products III and IV, cyclohexene oxide (I) and 1,2-epoxycyclohexane-3-ol (II) are also formed in fair amounts (Scheme 1).

II has been identified by IR, NMR and mass spectrometry and corresponds to the description of the literature [7]. It is not a common oxidation product of cyclohexene; it was previously prepared by Lyons with $CpV(CO)_4$ (55% at 30% conversion) [8] and by Allison et al. with sodium naphthenate (24% at 15% conversion) [9], but neither of the two above reports mentions the simultaneous formation of non-negligible amounts of I.

Tables 1, 2 and 3 give the relative yields of I, II and (III + IV) as obtained by

SCHEME 1



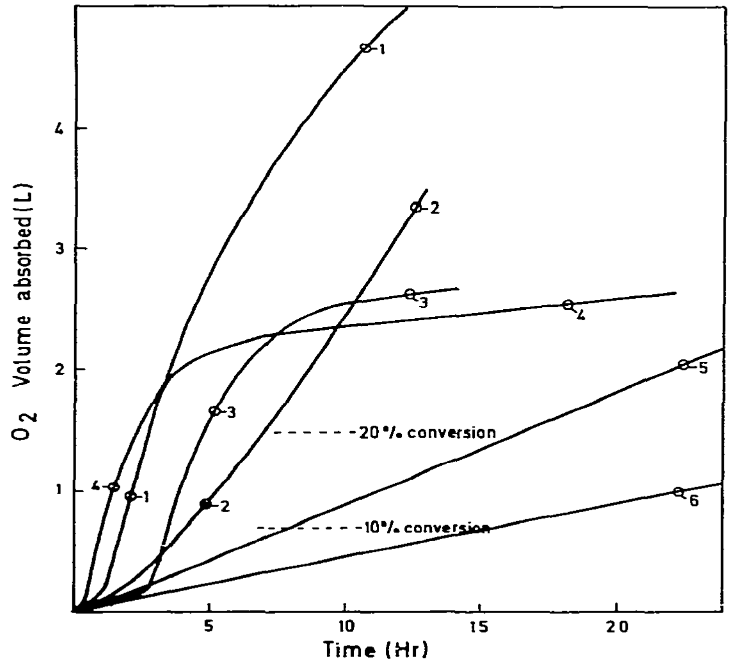


Fig. 1. Rates of oxygen uptake: cyclohexene 30 ml, benzene 30 ml; 55 ± 2°C. (1) B alone, 1.12×10^{-3} mol l^{-1}; (2) C alone, 1.08×10^{-3} mol l^{-1}; (3) A + $Vo(Acac)_2$, 1.1×10^{-3} mol l^{-1} in each metal; (4) B + $Vo(Acac)_2$; (5) C + $Vo(Acac)_2$ in trichlorethane; (6) C + $Vo(Acac)_2$, 1.1×10^{-3} mol l^{-1} and D + $Vo(Acac)_2$.

electronic integration of the GLC data of the reaction mixtures for different pairs and ratios of mixed catalysts, while Fig. 1 illustrates the kinetics of O_2 uptake for some of those reactions. It is apparent that the selectivities strongly depend on the rhodium derivatives used. The overall selectivity for I and II somewhat changes with time, with catalysts including A or B. This is not the case with

TABLE 1

OXIDATION OF CYCLOHEXENE BY $Rh_2(O_2C—Ad)_4$ (B)—EPOXIDATION CATALYST (E)
Concentration of B: 1.0×10^{-3} mol l^{-1}, solutions of cyclohexene 50% (v/v) in benzene.

Epoxidation catalyst (E)	Ratio B/E	Conversion (%)	Selectivity (%)		
			I	(III + IV)	II
$MoO_2(Acac)_2$	1	15	18	73	6(1.5) [a]
		20	21	73	6(1) [a]
$VO(Acac)_2$	1	15	15	52	30
		25	17	48	36
	0.5	15	16	50	34
		25	18	46	35
	0.25	15	18	41	39
		35	16	52	32
$V(Acac)_3$	1	10	17	55	28
		20	16	49	36

[a] *trans*-Isomer.

TABLE 2

OXIDATION OF CYCLOHEXENE BY $Rh_2(O_2C—CF_3)_4$ (C)—EPOXIDATION CATALYST (E)
Concentration of C: 1.1×10^{-3} mol l^{-1}, solution of cyclohexene 50% (v/v) in benzene except for runs 7 and 8 in trichloroethane.

Epoxidation catalyst (E)	Ratio C/E	Conversion (%)	Selectivity (%)		
			I	(III + IV)	II
(1) $MoO_2(Acac)_2$	1	8	42	49	7(+2) [a]
(2) $VO(Acac)_2$	1	10	20	28	52
		15	18	28	54
(3)	0.5	5	20	36	44
		10	20	32	48
		15	19	26	55
(4)	2	7	20	24	54
		15	19	23	56
		25	17	24	56
(5) $V(Acac)_3$	1	5	19	24	56
		10	20	25	55
		15	14	16	62
(6) $V(Acac)_3 + CF_3COOH$(1/1)	1	15	17	24	52
(7) $V(Acac)_3$ in $C_2H_3Cl_3$	1	10	22	20	57
		20	20	22	57
		30	22	21	57
(8) $Vo(Acac)_2$ in $C_2H_3Cl_3$	1	15	26	25	49
(9) $W(CO)_6$	1	15	3	60 [b]	2
(10) $Mo(CO)_6$	1	15	2.5	70 [b]	1

[a] *trans*-Isomer. [b] Solutions containing large amounts of peroxides (>15%).

C or D for which the selectivities do not vary much with time or with the ratios of rhodium to the cocatalyst within the limits tested.

It is noteworthy that the more selective reactions also show the slower rate of oxygen uptake and that C- and D-containing mixed catalysts show practically overall identical rates and selectivities (Fig. 1). As usual, the rate of oxygen

TABLE 3

SOME OTHER RHODIUM(II) CATALYSTS
Conditions and concentrations as in Table 2.

	Ratio of catalysts	Conversion (%)	Selectivity (%)		
			I	(III + IV)	II
$Rh_2C_6F_5 + VO(Acac)_2$	1	10	16	22	62
		15	14	16	70
$RhCl_2[P(o\text{Tolyl})_3]_2 + VO(Acac)_2$	1	8	20	42	35
		20	23	32	40
$RhCl_2[P(o\text{Tolyl})_3]_2 + MoO_2(Acac)_2$	1	15	40	51	6(+1)
		30	39	43	13(+3)
$Rh_2(O_2C—CH_3)_4 + VO(Acac)_2$	1	12	22	44	33
		30	26	38	36

uptake is greater in polar chlorinated solvents such as 1,1,3-trichloroethane (compare curves 5 and 6 in Fig. 1). The epoxyalcohol II is produced in fair amount only with vanadium epoxidation catalysts ($VOAcac_2$ and $VAcac_3$), and then II is formed with a *cis* stereoselectivity larger than 95%.

In contrast, molybdenum cocatalysts (MoO_2Acac_2) are poor promoters for the formation of II (yields <5%), and they lead to a low stereoselectivity (ratio *cis* II to *trans* II = 4), but the yields of I increase up to 30—35%.

The efficiency and selectivity of systems including $W(CO)_6$ or $Mo(CO)_6$ is even poorer, the major feature is then an accumulation of hydroperoxide in the solution, as shown by iodometric titration.

Other rhodium(II) carboxylates, including rhodium acetate, methoxyacetate, pivalate, $RhCl_2[P(o\text{-Tolyl})_3]_2$, and $RhCl_3$ all display similar features, viz. faster oxygen absorption than D and C, but overall poorer selectivity (Table 3).

The most selective systems are thus those constituted by an electron deficient rhodium(II) complex together with a vanadium epoxidation catalyst. With these, yields of I and II are, respectively, in the 15—20% and 50—60% range at 10 to 30% conversion, but the yield of II drops at higher conversion. This makes the reaction potentially attractive for the preparation of II, since it also allows recovery of I.

Titrations of the "active oxygen" in the reaction medium proved the peroxide content to be low throughout the reaction. Polymer formation is also low, especially with the most selective catalysts, with which the yields of the non volatile products remain below 5% at 25% conversion.

Discussion

The major feature of the mixed catalytic systems described in this work is their unusual selectivity, a selectivity which seems to be controlled essentially by the electronic nature of the substituents of the rhodium(II) carboxylates. Since under our conditions no (or very little) oxidation occurs in the absence of the rhodium catalysts, they clearly do take part in the oxidation process.

The previously proposed scheme for "mixed catalysts", which formally requires formation of equivalent amounts of 2-cyclohexen-1-ol and epoxide, is not applicable (Scheme 2). An intramolecular rearrangement of an intermediate hydroperoxide or the preferential epoxidation of 2-cyclohexen-1-ol to form II would not be subject to this limitation. It is well known that the V and Mo catalysts we have used are effective for the epoxidation of olefins with hydroperoxides. In order to check the feasibility of a cyclohexenyl hydroperoxide rearrangement under our conditions, we submitted solutions of the latter in cyclohexene (the hydroperoxide was determined to be 80% pure by iodometric titration, main impurity 2-cyclohexen-1-ol), to the action of various "mixed

SCHEME 2

TABLE 4

DECOMPOSITION OF CYCLOHEXENYL HYDROPEROXIDE
0.5 ml of peroxide in 3 ml of cyclohexene and 3 ml of benzene [a]

Catalyst	Relative yields (%)		
	I	(III + IV)	II
$VO(Acac)_2$ alone	22	39	39
$VO(Acac)_2$ + C	22	38	39
$VO(Acac)_2$ + B	12	66	23
$VO(Acac)_2$ + D	24	36	37
$MoO_2(Acac)_2$ alone	36	51	7
$MoO_2(Acac)_2$ + C	39	55	6
$MoO_2(Acac)_2$ + D	40	52	8

[a] 1.1×10^{-3} mol l^{-1} in each catalyst.

catalysts" (equimolecular amounts of each metal) at room temperature and at 55°C. The results are summarized in Table 4.

It is clear that the selectivity for the formation of I and II versus that of (III + IV), including ca. 20% of IV originally present in the hydroperoxide, is overall that observed with dioxygen (Table 4): systems B/vanadium favour the formation of III and IV, while those of C/vanadium give results identical to those obtained with $VO(Acac)_2$ alone (no rhodium carboxylate present). Careful analysis did not reveal any influence of C on the rate or product distribution of vanadium/C-catalyzed decompositions of cyclohexenyl hydroperoxide at room temperature. Moreover, C or D alone decomposes the hydroperoxide only very slowly at 25°C, and it remains largely unchanged after 24 h. At 55°C, the decomposition becomes appreciable and yields III + IV exclusively.

It is known that complexes which have low tendency to undergo oxidative addition or which are poor oxidants, as it is the case for electron deficient rhodium(II) complexes, do not or weakly catalyze the hydroperoxide decomposition [10]. Thus the oxidation with molecular oxygen and combinations of rhodium(II) and of epoxidation catalysts can be accounted for by assuming competitive decompositions of cyclohexenyl hydroperoxide. Rhodium derivatives which are least efficient for promoting the decomposition are also the most selective, since it is then essentially governed by the Mo or V catalyst. The rhodium compounds which effectively compete with the latter for decomposing the hydroperoxide lower the selectivity of the reaction.

These findings are in agreement with the proposals of Ugo et al. for similar mixed catalytic systems [10]. While it is not essential in interpreting the observed results, a direct interaction of the metallic species or the formation of new bimetallic complexes cannot be excluded a priori, since the use of a preoxidized catalyst (i.e. of a catalytic mixture prepared by refluxing for 2 h under oxygen bubbling equimolecular quantities of rhodium trifluoroacetate and of vanadium acetylacetonate) led to the same overall yields and selectivities but with a much shorter induction time.

The preferential formation of II with vanadium catalysts can be understood in terms of the well-known preferential coordination of allylic alcohols to a vanadium center.

In contrast with the autooxidation process, the epoxidation step of the reaction is not homolytic in nature since radical traps such as 4-t-butylcatechol have no effect upon the C/vanadium catalyzed decompositions of cyclohexenyl hydroperoxide listed in Table 4.

Finally, that the formation of II is not the result of an intramolecular rearrangement of the hydroperoxide was shown by the fact that oxidations performed in the presence of 2-cycloocten-1-ol contained appreciable amounts of both II and of cyclooctenol epoxide. These findings are also in agreement with recent work by Sharpless and Chong which has produced good evidence that the intact hydroperoxide is involved in the epoxidation step, and transfers an oxygen to a coordinated allylic alcohol [11].

As for the formation of hydroperoxides, a typical autooxidation process is most likely. The decrease in the percentage of conversion upon addition of an epoxidation catalyst is probably due to the fact that the rate of formation of hydroperoxide is dependent on the concentration of free radicals, which is in turn influenced by the total concentration of hydroperoxide [2]. Thus the consumption of hydroperoxide by Mo or V catalysts in reactions not involving radicals would diminish the rate of oxygen absorption.

We conclude that in the oxidation of cyclohexene by dioxygen no direct activation of oxygen occurs with our catalytic system. The two complexes act separately to give rise to a stepwise mechanism of oxidation. Each step corresponds to a particular catalyst: the rhodium catalyst promotes the formation of cyclohexenyl hydroperoxide (autooxidation), and the latter is used by the epoxidation catalyst to react with the olefin.

Experimental

The catalysts $VO(acac)_2$ and $MoO(acac)_2$ were generously supplied by the Climax Molybdenum Company. Hydrated rhodium(III) chloride was purchased from Johnson Matthey Chemicals Ltd., and the rhodium carboxylates were prepared by reported procedures [2].

Cyclohexene (Aldrich) was distilled under nitrogen, and the fraction boiling above 82° C was chromatographed through neutral alumina under an inert atmosphere and kept in the cold under argon. Benzene was similarly purified, and stored under argon.

The reaction mixtures were analyzed by GLC using a Varian 2800 apparatus equipped with 1.50 m columns packed with 15% FFAP on 60—80 mesh Chromosorb W DMCS. The quantitative calibrations were made with a Varian CDS III instrument.

Cyclohexene oxidations

The weighed amount of catalyst was placed in a 500 ml double-walled flask, equipped with a Vibor-Mischer E 1 (Chemab AG, Switzerland) and thermostated at 55 ± 2° C by oil circulation. The flask was filled with oxygen and purged three times, and the benzene and olefin introduced via a Sovirel screwed-in rubber septum. The pressure was balanced and the apparatus connected to a 2.5 l burette filled with oxygen and equipped with a leveling gauge. The total oxygen absorbed was measured at atmospheric pressure and room temperature.

The reaction time varied from 7 to 50 h, according to the oxidation rates and the desired degree of conversion. The reaction mixture was analyzed by GLC. For quantitative analysis an internal standard, ordinarily trichloroethane, was used, the relative responses of the standard and authentic samples of I, II + III, and IV having been determined. In some cases, the reaction mixture was weighed after the vacuum distillation.

Oxidations with cyclohexenyl hydroperoxide

Purified benzene (3 ml) and purified cyclohexene (3 ml) were introduced into a flask containing the catalyst under argon (catalyst concentration ca. 3×10^{-3} mol l^{-1}). Then, 0.5 ml of cyclohexenyl hydroperoxide was added and the mixture magnetically stirred at room temperature or at 55° C. When the mixture contained no residual hydroperoxide (KI test), the mixture was analyzed by GLC.

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