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Rhodium-catalyzed oxidation of organic compounds with t-butyl hydroperoxide

Paul Müller and Hamid Idmoumaz

Département de Chimie Organique, Université de Genève, CH-1211 Genève 4 (Switzerland)

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Abstract

The metal-catalyzed oxidation of organic compounds with t-butyl hydroperoxide (TBHP) and $RhCl(PPh_3)_3$ and Rh^+(diphos) has been investigated. Under appropriate conditions both catalysts give identical results: anthracene is converted into anthraquinone, 1-octene into 2-octanone, and 1-phenylethanol into acetophenone, with 95 to 100% isolated yields. The phosphine ligands of the catalysts are rapidly attacked during the oxidations, but this does not decrease the activity of the catalytic system. The formation of 2-octanone from 1-octene is believed to be due to a metal-centered mechanism rather than to a free radical pathway. The same mechanism should apply to the oxidation of anthracene and 1-phenylethanol.

Introduction

Transition metal catalyzed oxidations proceeding via free radical mechanisms usually exhibit poor product specificity and are therefore of limited practical interest. Accordingly, much work in the field of oxidations is oriented towards the search for novel catalytic non-radical oxidative pathways, where reaction occurs in the coordination sphere of the metal. The discovery of metal-catalyzed epoxidation of allylic alcohols by t-butyl hydroperoxide (TBHP) [2], which in the presence of chiral catalysts results in high asymmetric inductions [3], is the principal advance in this field in recent years. Among the various catalytic systems of current interest, those based on Rh are prominent. The first catalytic oxidations involving Rh were radical reactions [4,5], but mechanisms involving oxygen transfer from Rh-coordinated O_2 [6–9] or TBHP [5] to coordinated substrate have been suggested since 1971. Recent investigations carried out by Mimoun [10] and Drago [11] confirm this mechanistic hypothesis for the $RhCl_3$-catalyzed oxidation of terminal alkenes to ketones with O_2 or TBHP, although the nature of the catalytically active species remains unknown.

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The oxidation of anthracene to anthraquinone by $O_2/RhCl(PPh_3)_3$, first reported by Fusi et al. [12], was the starting point for our own investigation. It was found that the reaction proceeds via solvent derived hydroperoxides [13]. On the basis of this observation a catalytic system for oxidation of anthracene with $TBHP/RhCl(PPh_3)_3$ was developed [14]. The reaction did not show characteristic free radical behavior, but the nature of the oxygen transfer step could not be established [15,16].

1 2

The objectives of the present work were to improve the efficiency of the catalytic system and to extend it to other functional groups. It was further expected that comparison with other Rh-catalyst/oxidant combinations recently described in the literature [11,17,18] would shed some light on the reaction mechanisms and possibly provide some evidence for a common reactive species.

Results

Oxidation of anthracene

The oxidation of anthracene (**1**) proceeds in the presence of 1% $RhCl(PPh_3)_3$ and 4 equivalents of TBHP during 48 h to give 96% of anthraquinone (**2**) with consumption of 3.4 equivalents of oxidant (Table 1) [13]. Under slightly different but comparable conditions, the cationic complex $[Rh^+(diphos)]$ [17] shows about the same efficiency, while $[(COD)Rh(diphos)]BF_4$ is almost totally unreactive. A somewhat lower activity is also observed with $RhCl(CO)(PPh_3)_2$, while Rh^{II} complexes ($Rh(OAc)_2$, $Rh_2(OAc)_4$)) [19] are inferior to Rh^I. Unsatisfactory results were obtained with $RhCl_3$, although this complex reportedly catalyzes oxidation of octene with O_2 and TBHP [11,18], and the results are no better in the presence of LiCl, which is beneficial in the oxidation of octene with $RhCl_3$ [18]. The efficiency of the $RhCl(PPh_3)_3$ catalyst shows a marked dependence upon the solvent. Nitrobenzene gives the best results followed by benzene, chlorobenzene, toluene and tetrachloroethylene [13]. Nitrobenzene is also the solvent of choice for $[Rh^+(diphos)(MeOH)_2]$.

All the other transition metals tried were less effective: $IrCl(CO)(PPh_3)_3$ brings about only 15% conversion under the conditions used for $RhCl(PPh_3)_3$. Similarly, TBHP in conjunction with $Cr(CO)_6$, VO(acac), $Mo(CO)_6$ and $Pd(OAc)_2$ [20] produces anthraquinone, but the reactions are sluggish and require either long reaction times or high catalyst concentrations. Slow oxidation also occurs with $RuCl_2(PPh_3)_3$, which has been used for several functional group oxidations by TBHP [21] and other oxygen sources [22].

The results shown in Table 1 allow only qualitative comparisons, since the conditions used for the various runs are not identical. Modifications were made

Table 1

TBHP-oxidation of anthracene (1) [a]

Catalyst [f]	Solvent	TBHP (eq.)	T (°C)	t (h)	Anthraquinone (2) [b] (%) [f]
1% $RhCl(PPh_3)_3$	C_6H_6	4	70	48	96 [e]
2% $Rh^+(diphos)(MeOH)_2]$	$C_6H_6/MeOH$ [d]	4	70	48	98
$[(COD)Rh(diphos)]BF_4$	$C_6H_6/MeOH$ [d]	4	70	48	3 [c]
1% $RhCl(CO)(PPh_3)_2$	C_6H_6	3	70	48	40
1% $Rh(OAc)_2$aq	$CHCl_3$	3	80	3 d	32
0.5% $Rh_2(OAc)_4$	CH_3CN	3.5	65	24	52
1% $RhCl_3 \cdot 3H_2O$	$C_6H_6/EtOH$	4	70	4 d	37
1% $RhCl_3 \cdot 3H_2O/3LiCl$	$C_6H_6/EtOH$	4	70	3 d	70
1% $RhCl_3 \cdot 3H_2O/10LiCl$	C_6H_6	4	70	48	50 [c]
1% $RhCl_3/Cu(NO_3)_2$	$C_6H_6/EtOH$	4	70	48	53 [c]
1% $RhCl(PPh_3)_3$	$C_6H_5NO_2$	4	70	22	100 [c]
1% $RhCl(PPh_3)_3$	C_6H_5Cl	4	70	48	66 [e]
1% $RhCl(PPh_3)_3$	$C_6H_5CH_3$	4	70	48	32 [e]
1% $RhCl(PPh_3)_3$	Cl_2CCCl_2	4	70	48	0 [e]
2% $Rh^+(diphos)(MeOH)_2]$	$C_6H_5NO_2$	4	70	15	100 [c]
2% $RhCl(PPh_3)_3$	$C_6H_5NO_2$	4	70	22	100 [c]
1% $IrCl(CO)(PPh_3)_3$	C_6H_6	3	70	48	15 [e]
0.5 eq. $Cr(CO)_6$	C_6H_6	4	70	4 d	88
2.5% VO(acac)	C_6H_6	3	70	48	37 [e]
2.5% $Mo(CO)_6$	C_6H_6	3	70	48	37 [e]
$Pd(OAc)_2/Et_3N$	C_6H_6	2	70	7 d	15
1% $RuCl_2(PPh_3)_3$	acetone	4	50	50	63

[a] Conditions: see Experimental. [b] Isolated yield. [c] By GLC. [d] Ratio benzene/co-solvent = 11/1. [e] See Ref. 13. [f] With respect to substrate.

mainly to take account of catalyst solubility and TBHP stability, and to provide consistency with procedures reported in the literature. This qualification applies equally to the subsequent tables.

The reactions summarized in Table 1 were not carried out under turnover conditions, because the emphasis in these experiments was on 100% conversion of substrate, but the turnover can be estimated to be in the order of ca. 4 cycles/h at 70 °C (in $PhNO_2$) for formation of anthraquinone. Since 3 equivalents of TBHP are required for each equivalent of quinone produced, this represents a TBHP turnover of 12. This result is appreciable in the light of the maximum turnover of 4.8 for octanone production from octene with TBHP/$RhCl_3$ at 40 °C [11].

Oxidation of alkenes

The combination of Rh^I/TBHP may be used for conversion of terminal olefins into methyl ketones, as exemplified by the transformation of 1-octene (3) to 2-octanone (4) (Table 2).

3 4

Table 2

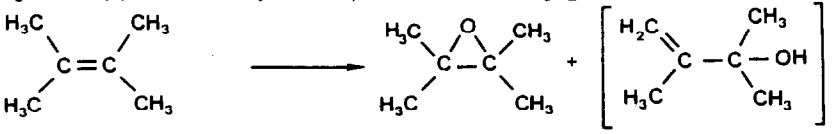
Oxidation of alkenes with Rh^I/TBHP [a]

Alkene	Catalyst	TBHP (eq.)	t (h)	Solvent	Product	Yield (%) [g]	Ref.
Octene (**3**)	$RhCl(PPh_3)_3$	4	42	C_6H_6/MeOH (10/1)	2-Octanone (**4**)	1.5	
3	$RhCl(PPh_3)_3$	4	42	MeOH	**4**	98	
3	$RhCl(PPh_3)_3$	1.5	24	$PhNO_2$	–		
3	Rh^+(diphos)$(MeOH)_2$	1.5	86	MeOH	**4**	36	
3	Rh^+(diphos)$(MeOH)_2$	4	42	MeOH	**4**	83	
3	Rh^+(diphos)$(MeOH)_2$	4	18	MeOH/CH_3SO_3H [b]	**4**	6	
trans-4-Octene (**5**)	Rh^+(diphos)$(MeOH)_2$	3	24	MeOH	–		
Cyclooctene (**6**)	Rh^+(diphos)$(MeOH)_2$	4	24	MeOH	–		
Tetramethylethylene (**7**)	$RhCl(PPh_3)_3$ [c]	1	24	neat, 50 °C	epoxide (**8**)	71 [d]	[16]
7	$RhCl(CO)(PPh_3)_2$ [c]	1	24	neat, 50 °C	epoxide (**8**)	58 [d,e]	[16]
7	$RhCl(CO)(PPh_3)_2$ [c]		1	neat, 25 °C	epoxide (**8**)	100 [f]	[6]

[a] Conditions: T 70 °C; 1.5 mmol of substrate, 2 mol-% [g] of catalyst. Yields determined by GLC. [b] 0.02 mmol of CH_3SO_3H. [c] 0.5 mol-% of catalyst. [d] Based on **7** consumed. Side product: 2,3-dimethylbuten-3-ol (**9**), 29%. [e] Other product: 2,3-dimethylbuten-3-ol (**9**), 42%. [f] Based on TBHP consumed. [g] With respect to substrate.

Oxidation proceeds with both of the catalysts $RhCl(PPh_3)_3$ and Rh^+-(diphos)$(MeOH)_2$ with comparable results. Methanol is the best solvent used so far for these reactions, although an excess oxidant is required to compensate for concomitant solvent oxidation (see below). Benzene, when used as co-solvent reduces the activity of the system, presumably by blocking reactive sites of the Rh. No ketone is produced when the reaction is carried out in nitrobenzene; in this solvent, TBHP simply decomposes without attacking the substrate. This contrasts markedly with the situation for anthracene oxidation, where nitrobenzene is the most efficient solvent; apparently anthracene can compete with the TBHP for the active sites of the catalyst and suppress TBHP decomposition, but the alkene is incapable of doing so. In methanol the TBHP decomposition must be inhibited owing to preferred coordination of the solvent to the Rh.

Apparently ketone formation is restricted to terminal olefins; thus *trans*-4-octene (**5**) and cyclooctene (**6**) are unreactive. Although this observation can be accounted for in terms of steric hindrance, it is still surprising in the light of the clean conversion (100%, based on consumed TBHP) of tetramethylethylene (**7**) into the epoxide (**8**) at 25 °C by TBHP/$RhCl(CO)(PPh_3)_2$ [5]:



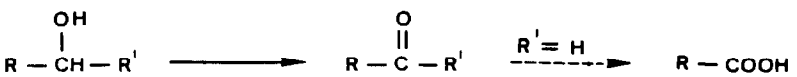
7 **8** **9**

It is noteworthy that the reaction involving $RhCl(CO)(PPh_3)_2$/TBHP with 1-hexene was examined some 25 years ago by Lyons and Turner [5], but under the conditions they used (25 °C, 1 h) none of the expected epoxide was obtained. This result is understandable in the light of our observation that ketone formation from 1-octene in our system requires ca. 42 h at 70 °C for completion. The higher reactivity of tetramethylethylene (**7**) than of terminal alkenes towards Rh^I/TBHP indicates that steric crowding is only one factor among others that determine the reactivity of the alkene. In the case of **7** the steric effect exerted by the methyl groups is apparently outweighed by their electron release.

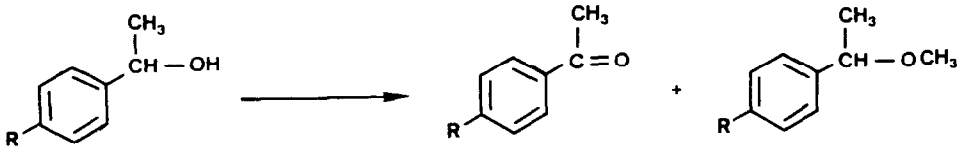
Several catalytic systems capable of converting terminal alkenes to methyl ketones based on Rh and involving non-radical pathways have been reported. Originally $RhCl(PPh_3)_3/O_2$ was used as catalyst [8,9], but more recent versions are based on $RhCl_3/O_2$ with $Cu(NO_3)_2$ as co-catalyst [10,11]. Rh^+(diphos)$(MeOH)_2$ is also efficient [17]. Further, Drago [11] and Faraj [18] recently reported that methyl ketones are obtained from terminal alkenes with $RhCl_3$/TBHP. This latter system is very similar to ours, and there are reasons to believe that the same catalytically active species may be involved (see below).

Oxidation of alcohols

The oxidation of alcohols to aldehydes or ketones with cationic Rh^I complexes or $RhCl_3$ combined with O_2 [11,17] or TBHP [18] has been described repeatedly in the literature, but there have been no studies involving structural variations. This oxidation also occurs with Rh^I/TBHP (Table 3).



Initially reactions were carried out in MeOH, but this solvent was unsatisfactory because it undergoes oxidation by TBHP. Better results were obtained with mixtures of benzene/MeOH. We reasoned that further improvement would be possible with a less strongly coordinating solvent, and we found that with nitrobenzene the reaction time is significantly reduced (97% conversion of 1-phenylethanol in 4 h at 70 °C). Addition of CH_3SO_3H or $BF_3(OEt_2)$ to MeOH or $MeOH/C_6H_6$ has no positive effect. $RhCl(PPh_3)_3$ used under comparable conditions to those used for Rh^+(diphos) exhibits about the same reactivity. The system shows significant structural effects: α-tetralol (**11**) is about half as reactive as 1-phenylethanol, while 2-octanol (**12**) reacts ca. 10 times more slowly. Benzyl alcohol (**13**) is oxidized slowly to benzaldehyde (**14**). The latter can be converted into benzoic acid. The presence of unsaturated sites other than α-phenyl substituents is detrimental. 1-Phenyl-2-propanol (**15**) or 1-phenyl-3-propanol (**16**) react very sluggishly, while geraniol (**17**) and *trans*-nonen-2-ol (**18**) give no carbonyl product at all. When the reaction of 1-phenylethanol (**10**) is carried out in the presence of methanesulfonic acid in CH_3OH or with BF_3OEt_2 in CH_3OH/C_6H_6, the ether (**20**) is formed in 48 and 18% yield respectively together with the ketone **19**. In the absence of oxidant **20** is produced in 97% yield.



10 R = H
10a R = OCH_3

19 R = H
19a R = OCH_3

20 R = H
20a R = OCH_3

In these experiments ether formation is due to the presence of the acid catalyst. However, with (4-methoxy)-1-phenylethanol (**10a**) the ether (**20a**) is formed in quantitative yield in the absence of TBHP or acid catalyst. It was hoped that this exchange reaction, which does not occur in the absence of catalyst, would be potentially useful for asymmetric induction, and so the chiral Rh^+((+)DIOP) complex [23] was prepared and used for exchange, but no optical activity was found in the ether product. Similarly, no optical activity was found in the recovered unchanged alcohol when racemic 1-phenylethanol (**10**) was partially oxidized in the presence of the chiral catalyst.

Stability of Rh-phosphine catalysts and of TBHP under oxidation conditions

The stability of metal-phosphine complexes under oxidating conditions is limited. $RhCl(PPh_3)_3$ both in presence or absence of alkenes [9,24] reacts with oxygen to give Ph_3PO. Rh^+(diphos) on the other hand reportedly is more stable and is believed to survive oxidation of alkenes by O_2 [17]. The reaction of *trans*-$[IrX(CO)(PPh_3)_2]$ (X = Cl, Br) with TBHP has been investigated in some detail [25]; bis(alkenylperoxy)iridium complexes $[IrX(OO^tBu)_2CO(PPh_3)_3]$ were isolated in ca. 30% yield, but $Ph_3P{=}O$ was also formed. Phosphine oxide is also obtained upon reaction of $[RhH(CO)(PPh_3)_2]$, but $RhCl(CO)(PPh_3)_2$ affords a dimer $[\{RhCl(PPh_3)_2\}_2]$ and no phosphine oxide [26]. Interestingly, the Ir-peroxy complex $(IrCl(OO^tBu)_2)(CO)(PPh_3)_2)$ does not itself catalyze TBHP decomposition. It

Table 3

Rh^{I}-catalyzed oxidation of alcohols [a]

Alcohol	TBHP (eq.)	Catalyst	Solvent	t (h)	Yield of carbonyl compound (%) [f]
1-Phenylethanol (**10**)	1.5	$RhCl(PPh_3)_3$	MeOH	17	65 [b]
10	1.5	$RhCl(PPh_3)_3$	C_6H_6/MeOH(9/1)	8	94.5 [b]
10	1.5	$RhCl(PPh_3)_3$	$C_6H_5NO_2$	5	98 [c]
10	1.5	Rh^+(diphos)	MeOH	72	75 [c]
10	1.5	Rh^+(diphos)	MeOH/CH_3SO_3H	24	20 [d]
10	1.5	Rh^+(diphos)	C_6H_6/MeOH(2.4/1)	93	85 [c]
10	1.5	Rh^+(diphos)	C_6H_6/MeOH/$BF_3 \cdot Et_2O$	24	24 [e]
10	1.5	Rh^+(diphos)	C_6H_6/MeOH(9/1)	38	99 [c]
10	1.5	Rh^+(diphos)	$C_6H_5NO_2$	4	97 [c]
α-Tetralol (**11**)	1.5	Rh^+(diphos)	$C_6H_5NO_2$	3.5	49
2-Octanol (**12**)	3	Rh^+(diphos)	$C_6H_5NO_2$	24	71
12	4	Rh^+(diphos)	MeOH	24	33
Benzyl alcohol (**13**)	1	Rh^+(diphos)	C_6H_6/MeOH(1.7/1)	50	51
Benzaldehyde (**13**)	2	Rh^+(diphos)	MeOH	19	60 (acid)
3-Phenyl-1-propanol (**16**)	1.5	Rh^+(diphos)	$C_6H_5NO_2$	37	trace
1-Phenyl-2-propanol (**15**)	1.5	Rh^+(diphos)	$C_6H_5NO_2$	37	trace
15	2	Rh^+(diphos)	MeOH	24	14 [c]
Geraniol (**17**)	1.5	Rh^+(diphos)	MeOH	23	–
trans-Nonen-2-ol (**18**)	1.5	Rh^+(diphos)	MeOH	24	–

[a] Conditions: see Experimental. [b] Isolated. [c] GLC analysis. [d] Other product: ether **20** (48%). [e] Other product: **20** (18%). [f] With respect to substrate.

is also inefficient for catalysis of oxidation of octene with TBHP at 25 °C, while a mixture of at least 11 alcohol and carbonyl products is obtained upon reaction of octene with TBHP in the presence of $[IrCl(CO)(PPh_3)_2]$ (25 °C, 6 d) [25].

The stability of $RhCl(PPh_3)_3$ in C_6D_6 and of Rh^+(diphos) in CD_3OD towards TBHP at 70 °C was investigated. $RhCl(PPh_3)_3$ displays a complex ^{31}P NMR with signals at 47.3 (dxt, J(Rh–P) 187.3 Hz) and 51.9 (d, J(Rh–P) 193.2 Hz) ppm relative to H_3PO_4 (in THF/C_6D_6) [27]. When this complex is treated with an excess of TBHP at 70 °C for 2 h, these signals disappear, and only the resonance corresponding to triphenylphosphine oxide is found, at 27.53 ppm. Similarly, the doublet of Rh^+(diphos) at 81.7 ppm (J(Rh–P) 205.7 Hz) (Lit. δ 80, J(Rh–P) 203 Hz [28]) disappears after exposure to TBHP (2 h, 70 °C) and is replaced by a singlet at 37.7 that we attribute to the fully oxidized ligand [29]. The instability of the diphos complex is unaffected by the presence or absence of 1-phenylethanol (**10**). On the other hand, (COD)Rh(diphos)BF_4 is significantly more stable towards TBHP, but it is also much less efficient as an oxidation catalyst.

Since oxidations of organic substrates require significantly longer reaction times for completion, it follows that the presence of the phosphine ligand is not required for the oxidation to occur. This observation leads us to suggest that the catalytically active species in our system might be similar, although probably not identical to that obtained from $RhCl_3$ [10,11]. It is noteworthy in this context that Rh^+(diphos) also reacts rapidly with dioxygen to form an isolate adduct [30], whereas oxidation of the ligand proceeds much more slowly [17].

In addition to the stability of Rh-phosphine complexes in presence of TBHP, the decomposition of TBHP in the presence of Rh^I provides a major point for discussion. The reaction was reported as early as 1968 [31], and related papers have appeared regularly in recent years. Decomposition occurs at 25 °C in toluene [6] and probably proceeds via the classical Haber–Weiss mechanism [25,32] to give t-BuOH and O_2.

In benzene $t_{1/2}$ at 40 °C is 9 min in presence of 0.55% of $RhCl(PPh_3)_3$ [31], and ^tBuOH and O_2 are formed in 93 and 88% yield, respectively. Reaction in toluene is some 100 times slower and no O_2 is formed, but low yields of benzyl alcohol (9%), benzaldehyde (15%), and benzoic acid (26%) are obtained [29]. Methanol inhibits the TBHP decomposition. Decomposition is also retarded by cycloalkenes [27] and tetramethylethylene [6]. The effect of a radical scavenger, *N*-phenyl-β-naphthylamine, on the decomposition of TBHP catalyzed by $Rh(PPh_3)_2(CO)Cl$ and $Rh(diphos)_2Cl$ has been investigated [33]; the decomposition rate was significantly lower in the presence of the scavenger, but only a small fraction of the latter was consumed. Complementary results were obtained from the $Rh(PPh_3)_3Cl$-catalyzed decomposition of cyclohexenyl peroxide [32,35]. Evidence was presented that there was no radical chain process taking place in this case, but rather that each hydroperoxide molecule was catalytically decomposed to give a free radical.

We have previously reported similar observations for the Rh^I-catalyzed oxidation of anthracene with TBHP in benzene (70 °C) [13,16]. Under the conditions used (0.3% of $RhCl(PPh_3)_3$ the TBHP decomposed within ca. 2 h in the absence of the substrate, but in presence of anthracene decomposition was suppressed; the TBHP was consumed within ca. 24 h, and practically all of it was used for anthracene oxidation. However, the TBHP decomposition was not inhibited by the presence of 2,3-dimethylnaphthalene even though no oxidation of the substrate took place.

The stability of TBHP was examined in MeOH, C_6H_6/MeOH, and nitrobenzene under standard conditions (1% of catalyst, 50 °C) by iodometric titration of unchanged TBHP. The decomposition curves are shown in the figure. The kinetics are clearly not first-order, but approximate half-lives can be estimated by first-order treatment of the TBHP decomposition curves, and are ca. 150 h in MeOH and C_6H_6/MeOH but only 3 h in nitrobenzene. Upon addition of 1-phenylethanol (**10**) as substrate (1 equivalent with respect to TBHP) the decomposition rate in MeOH increases significantly but that in nitrobenzene decreases. From this and our experiments at 70 °C it can be seen that the oxidations are fastest in the solvent in which TBHP is the least stable, namely nitrobenzene), provided that the substrate interacts sufficiently with the catalyst so as to suppress nonproductive TBHP decomposition. This latter condition is not fulfilled with octene in nitrobenzene, where TBHP decomposes without oxidizing the substrate. MeOH used neat or as co-solvent with C_6H_6 blocks TBHP decomposition efficiently. However oxidations in MeOH are slow in comparison to those in nitrobenzene; apparently the substrate has to compete with the solvent for the coordination site or sites of the catalyst. The use of benzene as co-solvent in the alcohol oxidations presumably facilitates complexation of the substrate compared with that in neat MeOH. However, benzene alone is unsuitable for alkene oxidation, because in the absence of a strongly coordinating substrate (anthracene) the TBHP decomposes rapidly [13,15].

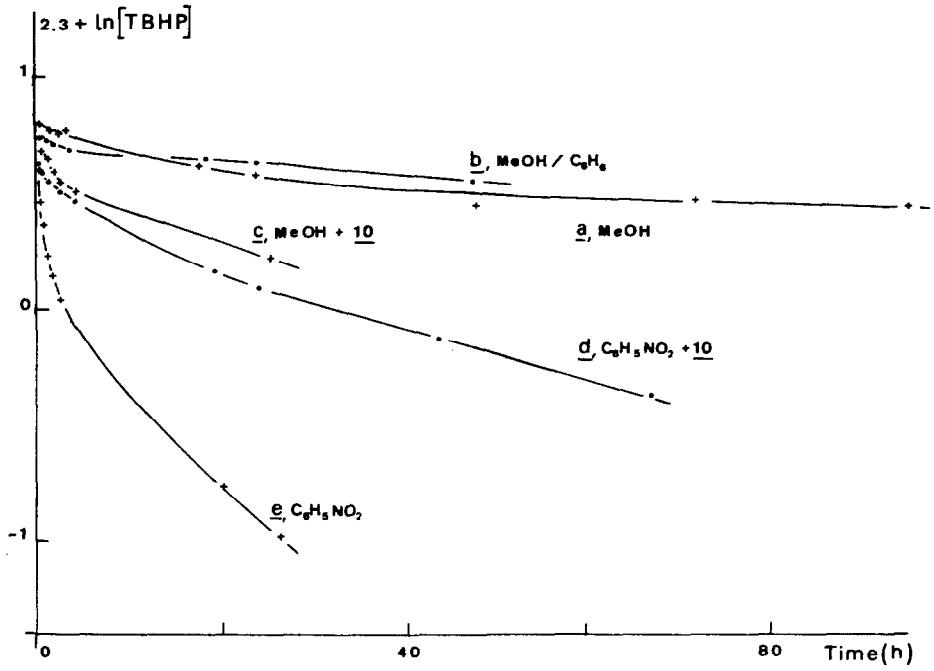


Fig. 1. Decomposition of TBHP in the presence of 1.0% of Rh^+(diphos), 50 °C. (a) in MeOH; (b) in MeOH/benzene (1/9); (c) in MeOH in the presence of 1 equivalent of 1-phenylethanol (**10**); (d) in nitrobenzene in the presence of 1 equivalent of **10**; or (e) in nitrobenzene.

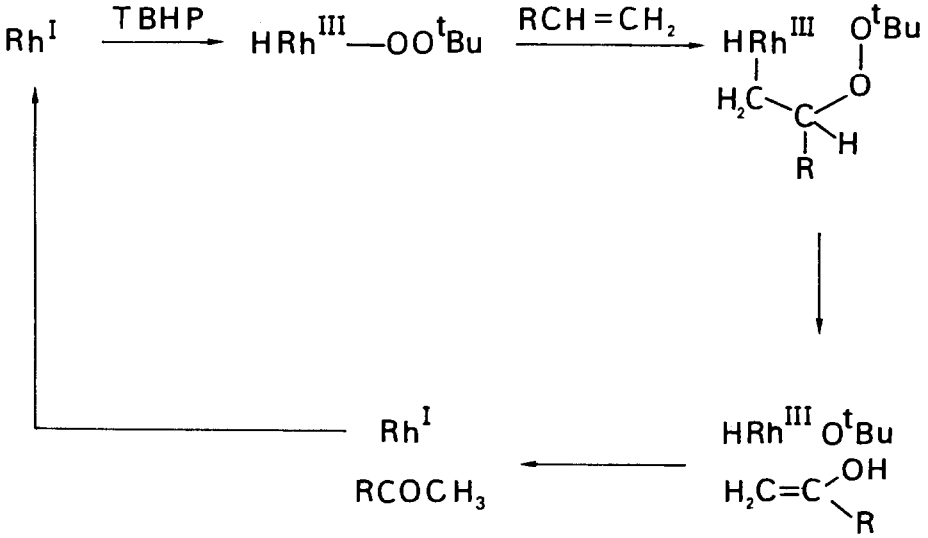
Reaction mechanism

The behaviour of the oxidation system upon solvent change is relevant to the reaction mechanism. The decrease in the rate of the TBHP decomposition in benzene [13,15] or nitrobenzene upon addition of substrate can be ascribed to a blocking of the radical chain decomposition of TBHP. In this case the role of the substrate consists in occupation of coordination sites of the Rh species, thereby reducing the amount of free Rh available for TBHP decomposition to oxygen and t-butanol [31]. However substrate oxidation may still proceed by a radical chain mechanism provided that the intermediate t-butoxy or t-butylperoxy radicals are efficiently trapped by the substrate and the intermediate organic radicals are capable of generating a self-sustaining radical chain. Whatever is the mechanism, substrate oxidation is clearly slower than the free-radical decomposition of TBHP. On the other hand, the fact that in MeOH the TBHP decomposition is faster in the presence of substrate than in its absence, is inconsistent with a radial chain mechanism. If the substrate competes with the solvent and with TBHP for the coordination sites of the catalyst, this cannot lead to a displacement of the equilibria in favor of TBHP and increase its rate of decomposition. It could be argued that the free radical chain based on organic substrate should be faster than that based on TBHP alone, but this seems unlikely because in benzene and nitrobenzene substrate oxidation is clearly slower than TBHP decomposition in its absence. Since in the presence of substrate most of the TBHP is consumed in formation of organic oxidation products rather than oxygen, a pathway other than free radical decomposition of TBHP must be available for oxidation of the substrate.

The hypothesis of a non-radical pathway is supported by the formation of 2-octanone (**4**) upon reaction of 1-octene (**3**) with Rh^I/TBHP. Methyl ketones are considered untypical products for radical oxidation of terminal alkenes [8] since radical attack would lead by hydrogen abstraction to an allylic radical, which would be further oxidized to an alkene substituted in positions 1 or 3, but not in position 2; the production of the allylic alcohol **9** from tetramethylethylene (**7**) is an example of such a process. On the other hand, radical addition to the double bond would be expected to lead to 1,2-disubstituted alkenes, such as epoxides or diols or higher oxidation products, but not methyl ketones. This argument does not apply to the other oxidation products observed in these reactions; the formation of anthraquinone (**2**) from anthracene (**1**), of ketones from alcohols, and epoxide **8** from tetramethylethylene (**7**) can all occur by radical or non-radical pathways.

The oxidation of terminal alkenes to methyl ketones constitutes also an argument against a mechanism in which a Rh-oxo species attacks uncoordinated alkene, since metal-oxo complexes react with alkenes to give epoxides or 1,2-diols but not ketones [36].

The precise nature of the oxidation step in these reactions remains unknown, but the analogy with Mimoun's [10] and Drago's [11] $RhCl_3/O_2$ and TBHP alkene oxidations suggest, that similar species might be involved. Oxidative addition of TBHP to the Rh^I will lead to a Rh^{III} species, the structure of which is unknown. Oxygen transfer can then occur in a Wacker-type process to free or coordinated alkene (Scheme 1), and the catalytic cycle is completed by reductive elimination of t-butanol. An analogous mechanism can be written for the 9,10-positions of anthracene, while alcohol oxidation should proceed via hydride elimination in a Rh^{III} alkoxide [11]. However, it is not possible to rule out mechanisms for alkene or anthracene oxidation, involving nucleophilic attack by TBHP on the Rh^{III}-coordinated substrate, or where reactions proceed via an intermediate Rh=O species.



Scheme 1

Experimental

General

All oxidations were carried out under an inert atmosphere. *Rh^I complexes:* $Rh(PPh_3)_3Cl$ was purchased from Fluka. The Rh^+(diphos) complex was synthesized from $RhCl_3 \cdot 3H_2O$ via $[Rh(COD)Cl]_2$ [37] and (COD)Rh(acac) [38], followed by treatment with diphos in HBF_4 [23,39]. The resulting (COD)Rh^+(diphos) complex was then hydrogenated in CH_3OH. When oxidations were carried out in nitrobenzene the latter was added to the methanolic solution and the CH_3OH was evaporated off under reduced pressure. Alternatively, CH_3OH was evaporated on a vacuum line and the dry orange complex was dissolved in nitrobenzene.

Oxidation of anthracene (sample run)

The complex [(COD)]Rh(diphos)]BF_4 (27.8 mg, 0.04 mmol) was dissolved in MeOH (2.0 ml) and hydrogenated. After reduction MeOH was added (6.0 ml) and the solution was mixed with one of anthracene (**1**) (360 mg, 2.0 mmol) in C_6H_6 (35 ml). After dropwise addition of TBHP (80%, 0.90 g, 8 mmol) the solution was kept at 70 °C and the progress of the reaction was monitored by GLC, and found to be 98% complete in 43 h. A similar procedure was used for oxidations in nitrobenzene but the anthracene (**1**) (2 mmol) had to be heated with nitrobenzene (17 ml) to 50 °C to ensure complete its dissolution before the addition of TBHP. GLC analysis showed total transformation of **1** to **2** after 15 h at 70 °C.

Oxidation of alkenes (sample run)

To a solution of octene (**3**) (168 mg, 1.5 mmol) and $Rh(PPh_3)_3Cl$ (27.7 mg, 0.03 mmol) in MeOH (5.5 ml) was added TBHP (80%; 0.68 g, 4 eq.) dropwise at RT. The mixture was kept at 70 °C for 42 h and GLC analysis revealed that 98% of **3** had been converted into 2-octanone (**4**). After evaporation of the solvent crude **4** was purified by column chromatography (isolated yield 72.5%) and identified by IR and NMR spectroscopy.

Oxidation of alcohols

General procedure: To a solution of $Rh(PPh_3)_3Cl$ (19.4 mg, 0.02 mmol) and 1-phenylethanol (126 mg, 1 mmol) in MeOH (5.0 ml) at 40 °C was added TBHP (80%, 169 mg, 1.5 mmol). The mixture was kept at 70 °C for 17 h. After evaporation of the solvent the product was purified by chromatography to give acetophenone (79 mg, 0.65 mmol) in 65% yield. Analogous procedures were used for the reactions summarized in Table 3.

Stability of Rh-phosphine complexes in the presence of TBHP

$RhCl(PPh_3)_3$ and TBHP. A suspension of the complex (50 mg, 0.054 mmol) in C_6H_6 (0.8 ml) containing TBHP (80%, 24 mg, 0.22 mmol) was kept at 70 °C for 2 h. The ^{31}P NMR spectra recorded immediately afterwards showed a singlet at + 27.53 ppm corresponding to $PO(Ph)_3$.

Rh^+(diphos) and TBHP. The COD-complex (33 mg, 0.047 mmol) in CD_3OD (0.7 ml) was hydrogenated at room temperature. After addition of TBHP (21.5 mg, 0.19 mmol) the solution was kept at 70 °C for 2 h, after which the ^{31}P NMR was recorded immediately, and showed a singlet at + 37.65 ppm corresponding to diphos-dioxide.

The same result was obtained when the reaction was carried out in the presence of **10** (ca. 10 equivalents with respect to Rh^+). With [(COD)Rh(diphos)]BF_4 after 23 h at 70 °C only partial oxidation of the ligand had occurred, either in the presence or absence of **10**.

Decomposition of TBHP in the presence of Rh complexes [13]

[(COD)Rh(diphos)]BF_4 (83.4 mg, 0.12 mmol) in MeOH was hydrogenated and added to a solution of **10** (1.46 g, 12 mmol) in MeOH (45 ml). TBHP (80%, 1.35 g, 12 mmol) was added at 50 °C. Samples (1.0 ml) were withdrawn and added to 20 ml of 2-propanol/AcOH (18/2), an excess of NaI (1.0 g) was added and the mixture was heated under reflux for 5 min. After addition of 50 ml of distilled H_2O and 15 ml of $CHCl_3$ the solution was titrated immediately with 0.1 *N* $Na_2S_2O_3$. The infinity value after 52.5 h was 1.0×10^{-5} *M*. This value was also used for the reaction in the absence of **10**, for which the infinity value could not be obtained, the TBHP being too stable under these conditions. For the reactions in nitrobenzene the COD complex was hydrogenated in MeOH. The solvent was removed on a vacuum line and replaced by nitrobenzene (50 ml).

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References

1 R.A. Sheldon and J.K. Kochi, Metal Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
2 K.B. Sharpless and T.R. Verhoeven, Aldrichim. Acta, 12 (1979) 63.
3 Y. Gao, R.M. Hanson, J.M. Klunder, S.Y. Koo, H. Masamune and K.B. Sharpless, J. Am. Chem. Soc., 109 (1987) 5765.
4 V.P. Kurkov, J.Z. Pasky and J.B. Lavigne, J. Am. Chem. Soc., 90 (1968) 4743; J.P. Collman, M. Kubota and J.W. Hosking, J. Am. Chem. Soc., 89 (1967) 4809.
5 J.E. Lyons and J.O. Turner, J. Org. Chem., 37 (1972) 2881.
6 K. Takao, Y. Fujiwara, T. Imanaka and S. Teranishi, Bull. Chem. Soc. Jap., 43 (1970) 1153; K. Takao, M. Wayaku, Y. Fujiwara, T. Imanaka and S. Teranishi, ibid., 43 (1970) 3898.
7 B.R. James and E. Ochiai, Can. J. Chem., 49 (1971) 975.
8 C. Dudley and G. Read, Tetrahedron Lett., (1972) 5273.
9 G. Read and P.J.C. Walker, J. Chem. Soc., Dalton Trans., (1977) 883; C.W. Dudley, G. Read and P.J.C. Walker, J. Chem. Soc., Dalton Trans., (1974) 1926.
10 H. Mimoun, M.M. Perez Machirant and I. Sérée de Roch, J. Am. Chem. Soc., 100 (1978) 5437; F. Igersheim and H. Mimoun, J. Chem. Soc., Chem. Commun., (1978) 559; F. Igersheim and H. Mimoun, Nouv. J. Chim., 4 (1980) 161.
11 R.S. Drago, A. Zuzich and E.D. Nyberg, J. Am. Chem. Soc., 107 (1985) 2898; E.D. Nyberg, D.C. Pribich and R.S. Drago, ibid., 105 (1983) 3538.
12 A. Fusi, R. Ugo, F. Fox, A. Pasini and S. Cenini, J. Organomet. Chem., 26 (1971) 417.
13 P. Müller and C. Bobillier, Tetrahedron Lett., 22 (1981) 5157.
14 P. Müller and C. Bobillier, Tetrahedron Lett., 24 (1983) 5499.
15 P. Müller and C. Bobillier, Helv. Chim. Acta, 68 (1985) 450.
16 C. Bobillier, Ph.D. Thesis, University of Geneva, No 2109, 1983.
17 M. Bressan, F. Morandini, A. Morvillo and P. Rigo, J. Organomet. Chem., 280 (1985) 139; M. Bressan, F. Morandini and P. Rigo, ibid., 247 (1983) C8.
18 M. Faraj, J.M. Brégeault, J. Martin and C. Martin, J. Organomet. Chem. 276 (1984) C23.

19 S. Uemura and S.R. Patil, Tetrahedron Lett., 23 (1982) 4353; S. Uemura and S.R. Patil, Chem. Lett., (1982) 1743.
20 T. Hosokawa, S. Inui and S.I. Murahashi, Chem. Lett., (1983) 1081. A.J. Pearson, Y.S. Chen, S.Y. Hsu and T. Ray, Tetrahedron Lett., 25 (1984) 1235.
21 Y. Tsuji, T. Ohta, T. Ido, H. Minbu and Y. Watanabe, J. Organomet. Chem., 270 (1984) 333.
22 P. Müller and D.M. Gilabert, Chimia, 40 (1986) 127; P. Müller and J. Godoy, Tetrahedron Lett., 22 (1981) 2361; 23 (1982) 3661; Helv. Chim. Acta, 64 (1981) 2531; 66 (1983) 1790.
23 D. Sinou and H.B. Kagan, J. Organomet. Chem., 114 (1976) 325.
24 R. Tang, F. Mares, N. Neary and D.E. Smith, J. Chem. Soc., Chem. Commun., (1979) 274.
25 B.L. Booth, R.N. Haszeldine and G.R.H. Neuss, J. Chem. Soc., Dalton Trans., (1982) 37; J. Chem. Soc., Chem. Commun., (1972) 1074; J. Chem. Soc., Perkin Trans. I, (1975) 209.
26 I.J. Harvie and F.J. McQuillin, J. Chem. Soc., Chem. Commun., (1976) 369; (1977) 241.
27 A.J. Naaktgeboren, R.J.M. Nolte and W. Drenth, J. Am. Chem. Soc., 102 (1980) 3350; T.H. Brown and P.J. Green, J. Am. Chem. Soc., 92 (1970) 2359.
28 P.A.W. Dean and M.K. Hughes, Can. J. Chem., 58 (1980) 180.
29 J. Halpern, D.P. Riley, A.S.C. Chan and J.J. Pluth, J. Am. Chem. Soc., 99 (1977) 8057.
30 A. Morvillo and M. Bressan, Inorg. Chim. Acta, 121 (1986) 219.
31 B. Bierling, K. Kirschke, H. Oberender and M. Schulz, Z. Chem., 9 (1969) 105.
32 R. Hiatt, K.C. Irwin and C.W. Gould, J. Org. Chem., 33 (1968) 1430.
33 S.K. Ivanov, J. Kateva, J. Dahlmann and E. Höft, J. Prakt. Chem., 322 (1980) 529.
34 H. Arzoumanian, A.A. Blanc, J. Metzger and J.E. Vincent, J. Organomet. Chem., 82 (1974) 261.
35 K. Kaneda, T. Itoh, Y. Fujiwara and S. Teranishi, Bull. Chem. Soc. Jap., 46 (1973) 3810.
36 H. Mimoun, in J.L. Portefaix and F. Figueras (Eds.), Chemical and Physical Aspects of Catalytic Oxidation, Editions du CNRS, 1979, p. 17.
37 J. Chatt and L.M. Venanzi, J. Chem. Soc. A, (1952) 4735.
38 R. Cramer, Inorg. Synth., 15 (1974) 16.
39 R.R. Schrock and J.A. Osborn, J. Am. Chem. Soc., 93 (1971) 2397.