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Oxygenation of aromatic hydrocarbons with hydrogen peroxide catalyzed by rhodium carbonyl complexes

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Hexanuclear rhodium carbonyl cluster, $Rh_6(CO)_{16}$, catalyzes benzene hydroxylation with hydrogen peroxide in acetonitrile solution. Phenol and (at lower concentration) quinone are formed with the maximum attained total yield and turnover number 17% and 683, respectively. Certain other rhodium carbonyl complexes, containing cyclopentadienyl ligands, $Rh_2Cp_2(CO)_3$ and $Rh_3(CpMe)_3(CO)_3$, are less efficient catalysts. Cyclopentadienyl derivatives of rhodium which do not contain the carbonyl ligands, $Rh(CpMe_5)(CH_2{=}CH_2)_2$, RhCp(cyclooctatetraene) and Rh_2Cp_2(cyclooctatetraene) turned out to be absolutely inactive in the benzene hydroxylation. Styrene is transformed into benzaldehyde and (at lower concentration) acetophenone and 1-phenylethanol.

Keywords: benzene; homogeneous catalysis; hydrogen peroxide; hydroxylation; rhodium complexes; phenol

Introduction

Transformation of aromatic and saturated hydrocarbons into valuable oxygen-containing compounds under mild conditions is an important goal of contemporary organic chemistry. One of the approaches is oxygenation of benzene and its derivatives with hydrogen peroxide catalyzed by various transition metal complexes.[1] Organometallic derivatives of transition metals relatively rarely exhibit high activity in alkane oxygenations.[2] A well-known example is methyltrioxorhenium (MTO),[3] which catalyzes hydroxylation of aromatic and saturated hydrocarbons in the presence of pyrazin-2-carboxylic acid.[4] Rhodium derivatives[5] have been used in various catalytic processes, for example, in hydroformylation and hydroaminomethylation,[6] hydrosilylation,[7] hydrogenation and isomerization,[8] transfer hydrogenation with formic acid,[9] C–C bond cleavage reactions,[10] addition of aldehydes to olefins,[11] carboxylation of arenes,[12] C–H activation[13] and asymmetric addition to olefins.[14] Rhodium carbonyls are efficient promoters in some catalytic processes.[15] Less is known about activity of rhodium compounds in oxidations with peroxides.[16] Earlier we have demonstrated that hydrocarbons can be oxygenated with peroxides in the dark or molecular oxygen under light irradiation if organometallic derivatives of the following metals are used as catalysts: iron,[17] molybdenum and tungsten,[18] osmium[19] and iridium.[20] Continuing our studies on peroxide oxidation of saturated and aromatic hydrocarbons catalyzed by organometallic complexes, we decided to check the possibility of hydrocarbon oxidation with H_2O_2 in the presence of organometallic derivatives of rhodium.

Results and Discussion

In this work, we have found that hexanuclear rhodium carbonyl cluster, $Rh_6(CO)_{16}$ (compound **1**), catalyzes the transformation of benzene to phenol as well as quinone by hydrogen peroxide in acetonitrile solution. Some results are summarized in Table 1. Kinetic curves of the product accumulation at two temperatures (70 and 40 °C) are shown in Fig. 1. It can be seen that the best results were obtained when an excess of benzene over hydrogen peroxide was used. Thus, the total yield of phenol and quinone reached 14.7% after 6 h at 70 °C (entry 9) and 11.6% after 12 h at 40 °C (entry 16). Turnover numbers were 533 and 467, respectively. The phenol/quinone ratio was higher (5.6; entry 9) at 70 °C in comparison with this value (1.75) measured at 40 °C (entry 16). Some non-productive decomposition of hydrogen peroxide to molecular oxygen and water occurred during the hydroxylation. This side-reaction was depressed when the process began at room temperature and then temperature was slowly (during 15 min) raised to 70 °C. When after this the reaction mixture was stirred at 70 °C for an additional 1 h, the yield of products and turnover number (TON) attained 17% and 683, respectively (entry 12). It should be noted that compound **1** is insoluble in the reaction mixture in the initial period of the reaction. However within the first few minutes at temperature 70 or 40 °C solid, almost black complex **1** gradually transfers to the homogeneous solution and the solution instead of being colourless becomes light yellow. The benzene hydroxylation in the initial period occurs with autoacceleration, as is testified by the kinetic curves in Fig. 1. Then in the course of the benzene hydroxylation the colour of the solution

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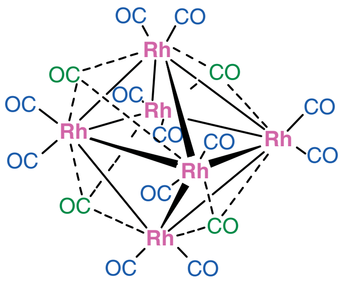
Table 1. Oxidation of benzene catalyzed by $Rh_6(CO)_{16}$ (**1**)[a]

Entry	Catalyst (mmol)	Temperature (°C)	Benzene (mmol)	H_2O_2 (mmol)	MeCN (ml)	Time (h)	Products: Phenol (mmol)	Products: Quinone (mmol)	Total yield (%)	TON
1	0.001	70	4.0	4.0	0.5	1	0.042	0.022	1.6	64
2	0.001	70	4.0	4.0	0.5	3	0.12	0.020	3.5	140
3	0.001	70	4.0	4.0	0.5	18	0.30	0.010	7.4	310
4	0.001	70	2.0	4.0	0.5	48	0.20	0.030	11.5	230
5[b]	0.001	70	4.0	4.0	0.5	1	0.15	0.010	4.1	170
6	0.003	70	12.0	12.0	2.0	0.33	0.17	0.05	1.8	73
7	0.003	70	12.0	12.0	2.0	0.67	0.61	0.23	7.0	280
8	0.003	70	12.0	12.0	2.0	1	1.22	0.34	13.3	520
9	0.003	70	12.0	12.0	2.0	6	1.57	0.28	14.7	533
10[c]	0.003	20–70	12.0	12.0	2.0	0.33	0.50	0.18	5.8	227
11[c]	0.003	20–70	12.0	12.0	2.0	0.67	0.96	0.29	10.4	417
12[c]	0.003	20–70	12.0	12.0	2.0	1	1.65	0.40	17.2	683
13	0.001	40	4.0	4.0	0.5	3	0.12	0.07	4.7	190
14	0.003	40	12.0	12.0	2.0	1	0.16	0.14	2.4	100
15	0.003	40	12.0	12.0	2.0	3	0.63	0.48	9.2	370
16	0.003	40	12.0	12.0	2.0	12	0.89	0.51	11.6	467
17	0.003	70	12.0	12.0	0	1	0.16	0.14	0.5	20
18	0	70	4.0	4.0	0.5	1	0.0	0.0	0.0	–
19	0	70	4.0	4.0	0.5	3	0.05	0.0	1.2	–
20	0	70	4.0	4.0	0.5	6	0.05	0.0	1.2	–
21	0	70	4.0	4.0	0.5	18	0.11	0.003	2.8	–
22	0	70	4.0	4.0	0.5	48	0.18	0.0	4.5	–

[a] Conditions: H_2O_2 (35% aqueous). Total yield of the two products was calculated based on the initial amount of benzene. Turnover number (TON) is number of moles of the formed phenol and quinone per one mol of the catalyst.

[b] Trifluoroacetic acid (0.06 mmol) was added.

[c] The reaction components were mixed at 20 °C, then the temperature was raised to 70 °C and the reaction was carried out for an additional 20, 40 and 60 min.



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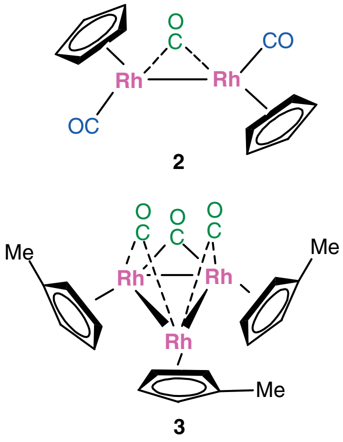
Scheme 1. Formula of catalyst $Rh_6(CO)_{16}$ (**1**) .



Scheme 2. Formulae of catalysts $Rh_2Cp_2(CO)_3$ (**2**) and $Rh_3(CpMe)_3(CO)_3$ (**3**).

is changed from light yellow to orange and rufous. It is noteworthy that in the absence of either benzene or hydrogen peroxide compound **1** does not produce homogeneous solution. Thus, one can assume that a soluble rhodium derivative simultaneously containing π-coordinated benzene and peroxo ligands is formed in the initial period.

Addition of acids is known to accelerate some oxidations (see, for example, catalysis by complexes of vanadium,[21] manganese,[22] copper,[23] rhenium,[24] rhodium[25a,b] and platinum[25c–e]). In our case, when trifluoroacetic acid was added to the reaction catalyzed by cluster **1**, the initial reaction rate was approximately 3 times higher (compare entries 5 and 1 in Table 1).

Styrene (1.9 mmol) was oxidized by hydrogen peroxide (2.0 mmol) in acetonitrile (0.6 ml) in the presence of complex **1** (0.001 mmol) to produce after 2 h at 70 °C benzaldehyde (0.37 mmol), acetophenone (0.045 mmol) and 1-phenylethanol (0.033 mmol); the total yield of the oxygenates was 24%. We were unable to detect any oxygenated products when alkanes were used as substrates in **1**-catalyzed oxidations. Ethyl groups in ethylbenzene were also not oxygenated.

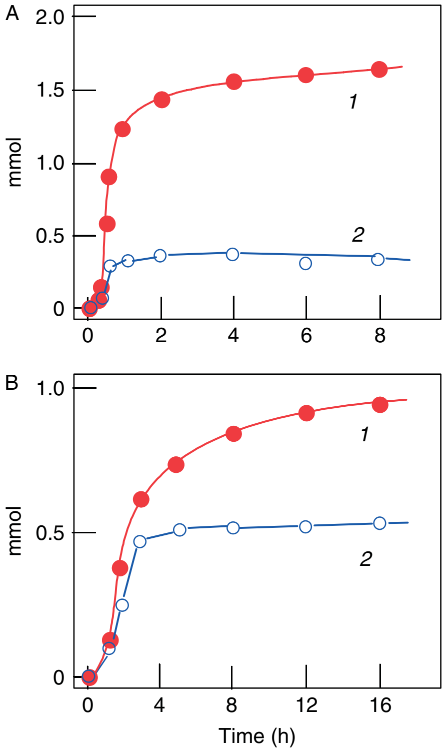
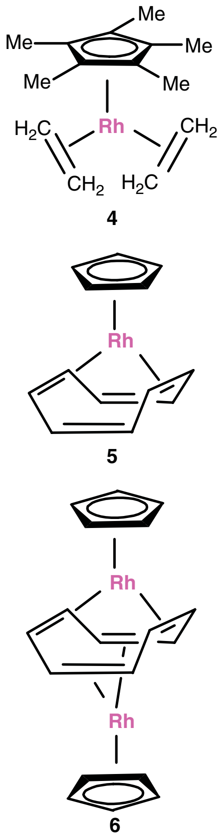


Figure 1. Accumulation of oxygenates (amounts, mmol, of phenol, curve *1* and quinone, curve *2*, are given) in the benzene (initial amount 12 mmol) oxidation with H_2O_2 (4 mmol) catalyzed by **1** (0.003 mmol). Conditions: solvent MeCN; total volume of the reaction solution was 5.0 ml; temperature was 70 °C (A) and 40 °C (B).



Scheme 3. Formula of compounds RhCp*(η^2-$CH_2{=}CH_2$)$_2$ (**4**), RhCp (η^4-COT) (**5**) and $Rh_2Cp_2(\eta^4:\eta^4$-COT) (**6**).

Two other tested carbonyl derivatives of rhodium also containing cyclopentadienyl ligands, $Rh_2Cp_2(CO)_3$ (**2**) and $Rh_3(CpMe)_3(CO)_3$ (**3**), exhibited some activity in the benzene hydroxylation, although their efficiency was lower in comparison with $Rh_6(CO)_{16}$. Indeed, the yields and TONs (Table 2, entries 1–5) did not exceed in all these cases 4% and 147, respectively.

Surprisingly, cyclopentadienyl derivatives of rhodium that do not contain the carbonyl ligands (compounds **4, 5** and **6**) turned out to be absolutely inactive in the benzene hydroxylation (Table 2, entries 6–8). Compounds **4, 5** and **6** (unlike complexes **1, 2** and **3**) do not contain Rh–Rh and Rh–CO bonds. The most active catalyst precursor **1** contains the highest number of these bonds. One can assume that the interaction of cluster **1** with hydrogen peroxide leads to splitting of Rh–Rh and Rh–CO bonds with formation of vacant sites which coordinate benzene molecules. Possibly, the {Rh}–CO fragment is oxidized in the initial period of the reaction to afford {Rh}–C(O)OH and {Rh}–C(O)OOH species.

On the basis of the obtained data, the catalytic cycle depicted in Fig. 2 can be proposed for the oxidation reaction. In the

Table 2. Oxidation of benzene catalyzed by some rhodium complexes[a]

							Products			
Entry	Catalyst	Catalyst amount (mmol)	Benzene (mmol)	H_2O_2 (mmol)	MeCN (ml)	Time (h)	Phenol (mmol)	Quinone (mmol)	Total yield (%)	TON
1	$Rh_2Cp_2(CO)_3$ (**2**)	0.001	4.0	4.0	0.5	6	0.13	0.005	3.3	135
2	$Rh_2Cp_2(CO)_3$ (**2**)	0.003	12.0	12.0	2.0	6	0.37	0.0	3.0	123
3	$Rh_3(CpMe)_3(CO)_3$ (**3**)	0.001	4.0	4.0	0.5	3	0.06	0.010	1.7	70
4	$Rh_3(CpMe)_3(CO)_3$ (**3**)	0.003	12.0	12.0	2.0	3	0.39	0.0	3.3	130
5	$Rh_3(CpMe)_3(CO)_3$ (**3**)	0.003	12.0	12.0	2.0	6	0.44	0.0	3.7	147
6	RhCp*(η^2-$CH_2{=}CH_2$)$_2$ (**4**)	0.001	4.0	4.0	0.5	6	0.0	0.0	0	0
7	RhCp(η^4-COT) (**5**)	0.001	4.0	4.0	0.5	6	0.0	0.0	0	0
8	$Rh_2Cp_2(\eta^4:\eta^4$-COT) (**6**)	0.001	4.0	4.0	0.5	6	0.0	0.0	0	0

[a] Conditions: H_2O_2 (35% aqueous), 70 °C. Total yield of the two products was calculated based on the initial amount of benzene. Turnover number (TON) is number of moles of the formed phenol and quinone per one mole of the catalyst. Cp, cyclopentadienyl; CpMe, ethylcyclopentadienyl; Cp* pentamethylcyclopentadienyl; COT cyclooctatetraene.

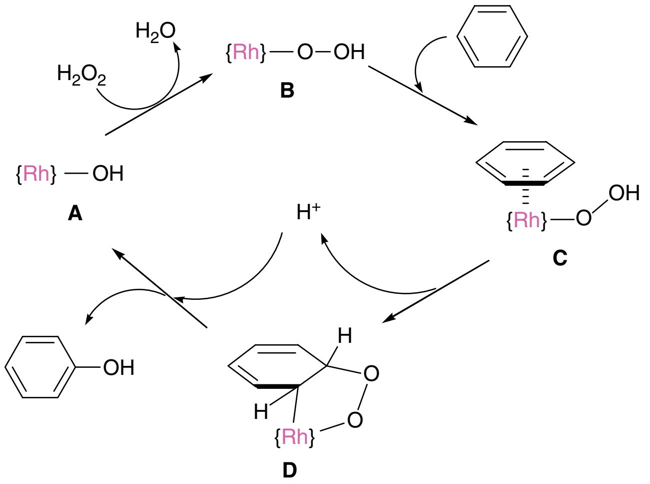


Figure 2. A proposed cycle for the Rh-catalyzed benzene hydroxylation to phenol by hydrogen peroxide.

initial period, a rhodium complex under the action of hydrogen peroxide and water is transformed into a hydroxy derivative **A**. The interaction of species **A** with hydrogen peroxide affords a hydroperoxo derivative **B**, which forms a π-arene complex **C**. The participation of peroxo derivatives [26a–c] and π-olefin complexes of rhodium has been proposed in the literature for olefin oxygenations with dioxygen and hydrogen peroxide [16c, 26d–f]. Species **C** can be converted into rhodadioxolane **D** [16c], which is decomposed further to produce phenol and initial catalytically active species **A**.

Conclusions

Rhodium complexes catalyze benzene hydroxylation with H_2O_2 only if they contain carbonyl ligands, and the process apparently occurs via the formation of arene π-complexes containing also peroxo ligands.

Experimental

Synthesis and characterization of used rhodium complexes **1**,[27a,b] **2**,[27c] **3**,[27d] **4**,[27e] **5**[27f] and **6**[27g] were described in the literature previously.

The oxidations of hydrocarbons were carried out in acetonitrile solution in air using thermostated Pyrex cylindrical vessels with vigorous stirring. In various experiments, the total volume of the reaction solution was 1–5 ml. Initially, a portion of H_2O_2 (35% aqueous) was added to the mixture of the catalyst and substrate in acetonitrile. After a few minutes the solution became homogeneous. Concentrations of products obtained in the oxidation of benzene after certain time intervals were measured using ^{1}H NMR method (solutions in acetone-d_6; Bruker AMX-400 instrument, 400 MHz). For the determination of concentrations of phenol and quinone, signals in aromatic region were integrated using added 1,4-dinitrobenzene as a standard. Areas of methyl group signals were measured to quantify oxygenates formed in oxidations of styrene.

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