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LETTERS
TO THE EDITOR

# Catalytic Properties of Rhodium Organometallic Complexes in the Reaction of 1-Octene Oxidation with Molecular Oxygen

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The use of molecular oxygen, which is ecologically pure and accessible oxidizing agent, for obtaining oxygen-containing compounds by the oxidation of hydrocarbons is a very attractive process from the economic and ecological points of view. The possibility of carrying out reactions of hydrocarbons oxidation in mild conditions with a high rate, and also an increase in selectivity of the reactions and, hence, an increase in the target product yield are reached by the use of catalysts capable of affecting various stages of the complicated oxidation process: the initiation, propagation, and termination of reaction chains [1-4].

With the aim of searching for effective catalysts of hydrocarbons oxidation by molecular oxygen we have studied the effect of some rhodium organometallic complexes on the initial rate ($W_0$) of the oxidation of 1-octene by molecular oxygen. Preliminary experiments have shown that the studied complexes affect the oxidation process only in the presence of hydroperoxides. In this work we used *tert*-butyl hydroperoxide. The reaction was carried out in chlorobenzene, the *tert*-butyl hydroperoxide concentration was 0.05 M, and the catalyst concentration, 0.01 M; $T$ 333 K; Acac, Oxq, and OAc are singly charged residues of acetylacetone, 8-hydroxyquinoline, and acetic acid, respectively, Cod is 1,5-cyclooctadien, and DMSO, dimethyl sulfoxide.

The measured rates of the 1-octene oxidation ($W_0 \times 10^5$, mol l$^{-1}$ s$^{-1}$) with various catalysts are given below.

The results show that the systems (*tert*-butyl hydroperoxide–rhodium organometallic complex) exhibit a high activity in the reaction of 1-octene oxidation at 333 K. Complex [Rh(Acac)(PPh$_3$)(CO)] (**II**) is the most active. Complexes of rhodium in the oxidation states + 2 (**XI**) and +3 (**XII**) appeared much less active that all complexes containing rhodium in the oxidation state +1.

| Catalyst | $W_0 \times 10^5$, mol l$^{-1}$ s$^{-1}$ |
|---|---|
| Without a catalyst | 0.1 |
| [Rh(Acac)(CO)$_2$] (**I**) | 2.0 |
| [Rh(Acac)(PPh$_3$)(CO)] (**II**) | 6.5 |
| [Rh(Oxq)(CO)$_2$] (**III**) | 3.6 |
| [Rh(Oxq)(PPh$_3$)(CO)] (**IV**) | 2.1 |
| [Rh(Oxq)(DMSO)(CO)] (**V**) | 2.9 |
| [Rh(PhC(O)CHC(NH)Ph)(CO)$_2$] (**VI**) | 3.2 |
| [Rh(PhC(O)CHC(NH)Ph)(PPh$_3$)(CO)] (**VII**) | 4.0 |
| [Rh(CF$_3$COO)(PPh$_3$)$_2$(CO)] (**VIII**) | 5.4 |
| [Rh(BPh$_4$)(PPh$_3$)$_2$] (**IX**) | 3.5 |
| [Rh(BPh$_4$)(Cod)] (**X**) | 4.3 |
| [Rh$_2$(OAc)$_4$(H$_2$O)$_2$] (**XI**) | 1.8 |

Compounds **I–IV** and **VIII–XI** were synthesized by the procedures [5–9] and compound **XII**, by the procedure [10]; the synthesis of new compounds **V–VII** is described below.

**[Rh(Oxq)(DMSO)(CO)] (V)**. To a suspension of [Rh(Oxq)(CO)$_2$], 0.628 g in 10 ml of MeCN, a freshly prepared solution Me$_3$NO·2H$_2$O, 0.230 g in 38 ml of MeCN, was added dropwise at 0°C with stirring. The reaction mixture was stirred for 1 h at room temperature. The solvent was distilled off in a vacuum, and the residue was dissolved again in MeCN (15 ml). To thus obtained solution a solution of DMSO, 0.328 g in 5 ml of MeCN, was added. Golden needle-like crystals were filtered off, washed by diethyl ether, and dried in a vacuum. The second fraction was obtained upon evaporation of the filtrate. Total yield 0.50 g (69%). IR spectrum ($CHCl_3$), $cm^{-1}$: ν(CO) 2000. $^1H$ NMR spectrum ($CDCl_3$), δ, ppm: 8.5–6.5 (6H, Oxq), 3.41 (6H, DMSO). $^{13}C$ NMR spectrum, δ, ppm (*J*, Hz): 188.28 (CO, 74.8). Found, %: C 40.58; H 3.47; N 3.93. $C_{12}H_{12}NO_3RhS$. Calculated, %: C 40.79; H 3.40; N 3.96.

**[Rh(PhC(O)CHC(NH)Ph)(CO)₂] (VI).** To a solution of $[Rh(CO)_2Cl]_2$, 0.25 g in 10 ml of $CHCl_3$, $PhC(O)CHC(NH_2)Ph$, 0.29 g, and $Ba(CO)_3$, 0.6 g, were added. The reaction mixture was stirred for 2 h at room temperature, filtered, and the filtrate was evaporated in a vacuum. The residue was dissolved in diethyl ether, the solvent was distilled off, and the residue was left in a freezing chamber at –20°C for 48 h. Yield 0.38 g (79%). Orange fine crystals. IR spectrum ($CHCl_3$), $cm^{-1}$: ν(CO) 2072, 2004. $^{13}C$ NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 186.36 (CO, $^1J_{CRh}$ 71.4, $^2J_{CC}$ 8.9, $^3J_{CH}$ 2.9), 185.35 (CO, $^1J_{CRh}$ 64.5). Found, %: C 53.91; H 3.02; N 3.88; Rh 26.97. $C_{17}H_{12}NO_3Rh$. Calculated, %: C 53.56; H 3.15; N 3.67; Rh 26.99.

**[Rh(PhC(O)CHC(NH)Ph)(PPh3)(CO)] (VII).** To a solution of complex (VI), 0.183 g in 20 ml of benzene, $PPh_3$, 0.13 g, was added. The solution was stirred for 30 min. The solvent was distilled off in a vacuum; the residue was treated by hexane and held in a freezing chamber at –20°C for several days. Yield 0.39 g (81%). Yellow fine crystals. The substance consists of a mixture of isomers. IR spectrum ($CHCl_3$), $cm^{-1}$: ν(CO), 1968. In the prevailing isomer (>90%) $PPh_3$ is in the *trans*-position to the nitrogen atom. $^{13}C$ NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 190.3 (CO, $^1J_{CRh}$ 75.1, $^2J_{CP}$ 22.2, $^3J_{CH}$ 2.0). $^{31}P$ NMR spectrum ($CDCl_3$), δ, ppm (*J*, Hz): 41.5 ($PPh_3$, $^1J_{CRh}$ 149.3). Found, %: C 66.81; H 4.10; N 2.02; Rh 16.59. $C_{34}H_{27}NO_2PRh$. Calculated, %: C 66.35; H 4.39; N 2.27; Rh 16.72.

The IR spectra were measured on a Specord-75IR spectrometer. The $^{13}C$, $^{31}P$, and $^1H$ NMR spectra were measured on a DPX-300 spectrometer for solutions in $CDCl_3$, working frequencies 75, 120, and 300 MHz, respectively. The $^{13}C$ and $^1H$ chemical shifts were measured in relation to the internal standard ($CDCl_3$, δ($^{13}C$) 77.0 ppm, δ($^1H$) of residual protons 7.25 ppm) and reported with respect to TMS. The $^{31}P$ chemical shifts were measured from the external standard (85% aqueous $H_3PO_4$).

Oxidation was carried out on a gasometric installation [11] in a glass reactor with a temperature-controlled jacket and a magnetic stirrer.

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