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ACTIVATION OF THE CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I) HYDROGENATION CATALYST BY OXYGEN OR HYDROGEN PEROXIDE

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Wilkinson et al. (1,2,3) found chlorotris(triphenylphosphine)rhodium(I) to be an active catalyst in the hydrogenation of olefinic and acetylenic bonds. A mechanism was advanced which involved successively displacement of one triphenylphosphine ligand by a solvent molecule, formation of a rhodium(III) dihydrido complex, co-ordination of olefin, rearrangement, and elimination of alkane. It was stated that oxygen inhibited the reaction (1).

We now report that small quantities of oxygen (0.2-1.0 molar on rhodium) increase the activity of the Wilkinson catalyst. Thus, in the hydrogenation of cyclohexene, acceleration by a factor of 1.3 was observed for an oxygen-rhodium molar ratio of 0.7. Activation was also observed upon addition of hydrogen peroxide. Table I gives some results.

Table I

Effect of hydrogen peroxide on the rate of hydrogenation of cyclohexene[a]

Molar ratio H_2O_2: Rh	-	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Initial rate, ml H_2 min^{-1}	7.4	10.1	11.2	12.2	12.5	12.9	12.7	10.8
Half-life time, min	17.4	12.5	10.9	9.8	9.5	9.1	9.25	11.6

a. In benzene (25 ml) at 25°; 0.1 mmole of $RhCl(PPh_3)_3$; 10 mmoles of cyclohexene.

Acceleration by factors varying from 1.5 to 4 was observed in the hydrogenation of various other olefinic substrates.

We accept that activation of the catalyst by oxidizing substances is effected through oxidation of triphenylphosphine to triphenylphosphine oxide. This implicates elimination of a ligand which competes with the substrate for co-ordination with the rhodium complex. The following observations support this suggestion:

(i) The infrared spectra of catalyst solutions treated with hydrogen peroxide or with oxygen show very prominent absorption at 1120 and 1175 cm^{-1}. These bands are also present in the infrared spectrum of triphenylphosphine oxide, but are weak in infrared spectra of the unactivated catalyst (4).

(ii) The activity of the hydrogen peroxide treated catalyst is about equal to the activity of catalyst solutions prepared in situ from di-μ-chloro-tetrakis(cyclooctene)dirhodium(I) anc triphenylphosphine in the ratio of 1:2.

Regarding the mechanism of oxidation of triphenylphosphine, we suggest that the rhodium complex catalyzes the oxidation by oxygen (5), and probably also by hydrogen peroxide.

In the hydrogenation of cyclohexene we obtained, with good reproducibility, the following values of the rate constant k_1 for the co-ordination step: 0.28 (unactivated catalyst), 0.42 (0.1 mmole of H_2O_2 added). Values for cyclohexene presented by Wilkinson et al. do rather diverge: $k_1 = 0.15$ (1), 0.32 (2), 0.25 (3). It may be noted that Chandlin and Oldham (6) also reported poor reproducibility of some of the experiments.

Finally, it may be mentioned that James and Memon (7) reported activation by oxygen of the trans-carbonylchlorobis(triphenylphosphine)iridium(I) hydrogenation catalyst. This observation might also be explained by oxidation of triphenylphosphine to triphenylphosphine oxide.

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