

CATALYTIC PROPERTIES OF PHOSPHORUS-CONTAINING RHENIUM COMPLEXES
IN THE HYDROGENATION OF HEXENE-1

V.M. Belousov, T.A. Palchevskaya, O.M. Negomedzyanova and K.V.
Kotegov

Institute of Physical Chemistry, Kiev 252028, USSR

Received March 19, 1984

Accepted July 26, 1984

ABSTRACT

Rhenium (V,VI) complexes with organophosphorus ligands proved to be catalytically active in hexene-1 hydrogenation. The kinetics of this process catalyzed by $\text{ReOCl}_3(\text{PPh}_3)_2$ has been examined. The organic ligand in the coordination sphere of rhenium complexes was found to affect selectivity to olefin bonds or nitro groups in the hydrogenation of hydrocarbons.

Комплексы рения (V,VI) с фосфорорганическими лигандами обладают каталитической активностью в реакции гидрирования гексена-1. Изучена кинетика этого процесса, катализируемого $\text{ReOCl}_3(\text{PPh}_3)_2$. Показано, что природа органического лиганда в координационной сфере рениевых комплексов влияет на избирательность их действия в реакциях гидрирования олефиновой связи или нитрогруппы углеводородов.

Rhenium (V, VI) complexes with various organic and inorganic ligands have not been examined as homogeneous catalysts. There is only a short communication [1] on the hydrogenation of the end group of aliphatic hydrocarbons in the presence of $\text{ReCl}_2\text{SnCl}_2$. We have shown previously [2] that rhenium thio-complexes hydrogenate selectively the nitro groups of aromatic hydrocarbons not affecting the double bonds. Donor-acceptor properties of the coordinated SnCl_3^- anion are identical to those

of PPh_3 [3]. Hence the introduction of phosphorus-containing ligands into the coordination sphere of rhenium complexes is likely to facilitate the hydrogenation of olefin bonds. This assumption has been confirmed by the catalytic action of rhenium complexes with organophosphorus ligands (Table 1) obtained like in Refs. [4,5], in the hydrogenation of hexene-1 in dimethylformamide.

Table 1

Rhenium (III-IV) complexes with organophosphorus ligands examined in hexene-1 hydrogenation

($P_{\text{H}_2} = 5.06 \times 10^3$ kPa, $T = 338$ K, $[\text{Re}] = 5 \times 10^{-3}$ M, $\tau = 3-4$ h, $[\text{C}_6\text{H}_{12}] = 0.8$ M)

| Formula | X | L |
|----------------------------------|-----------------|--|
| $\text{ReX}_2\text{L}_2\text{X}$ | Cl^- | $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2$ |
| ReX_4L_2 | Cl^- | PPh_3 ; PPhEt_2 ; PPh_2Et |
| $\text{ReOX}_3\text{L}_{1-2}$ | Cl^- | $2(\text{PPh}_2\text{H})$, $\text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_4(\text{O})\text{PPh}_2^*$, $2(\text{PPh}_3)^*$, $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2^*$ |
| | Br^- | $2(\text{PPh}_2\text{H})$, $2(\text{PPh}_3)^*$, $\text{Ph}_2\text{PC}_2\text{H}_2\text{PPh}_2^*$, $\text{Ph}_2\text{P}(\text{O})\text{C}_2\text{H}_4(\text{O})\text{PPh}_2^*$, $\text{Ph}_2\text{PC}_2\text{H}_4\text{PPh}_2^*$ |
| ReO_2XL_4 | NO_3^- | PPh_3 |
| ReX_6L_2^* | Cl^- | PPh_2H^* |

* Reduced during hydrogenation

In the hydrogenation of hexene-1 to hexane (no hexene-1 isomers have been revealed) catalytically active were rhenium complexes containing ligands marked with asterisks. The highest catalytic activity was observed for the rhenium (V, VI) complexes $\text{ReOBr}_3(\text{PPh}_3)_2$ (30%) > $\text{ReOCl}_3(\text{PPh}_3)_2$ (20%) > $\text{ReOBr}_3(\text{Ph}_2\text{PC}_2\text{H}_2\text{PPh}_2)$ (13%) > $\text{ReCl}_6(\text{PPh}_2\text{H})_2$ (6%). The yield of

hexane is shown in parentheses. The other complexes with asterisks are less active and the complexes of rhenium (III) and (IV) are inactive.

Studies of the kinetic peculiarities of olefin hydrogenation in the presence of $\text{ReOCl}_3(\text{PPh}_3)_2$ indicate that an excess of triphenylphosphine stabilizes active forms of the complex. Time dependence of the hexene-1 conversion at different ligand to rhenium concentration ratios is illustrated in Fig. 1. It is

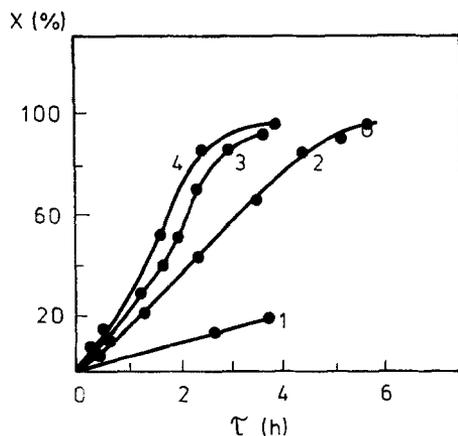
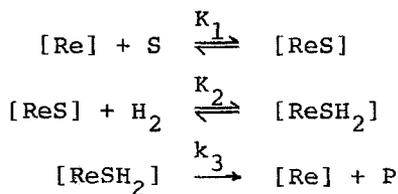


Fig.1. Hexene-1 conversion vs. the hydrogenation time at various triphenylphosphine - rhenium concentration ratios: $[\text{PPh}_3]:[\text{Re}] = 0:1$ (1), $3:1$ (2), $8:1$ (3), $17:1$ (4). 1.6×10^{-2} M, $P_{\text{H}_2} = 5.06 \times 10^3$ kPa, $T = 338$ K

seen that the optimum ratio is 8:1, therefore, the kinetics of olefin hydrogenation was examined at this ratio. The concentration of rhenium oxocomplex and hexene-1 were varied within $(1.2 - 4.8) \times 10^{-2}$ and $(0.16 - 3.2)$ M, respectively, at $P_{\text{H}_2} = (1 - 8.1) \times 10^3$ kPa, $T = 313 - 353$ K and a total reaction mixture² volume of 5 cm^3 .

Reaction orders with respect to substrate, hydrogen and catalyst were 0.5, 0 and 1, respectively.

Like in Ref. [6], the suggested mechanism for hexene-1 hydrogenation involves the three main steps



where [Re] is the catalyst, S is hexene-1 and P is hexane.

Rate-determining step of this process is the redox decomposition of the dihydrido olefin-rhenium complex. Kinetic equation for hexene-1 hydrogenation has the form

$$W = \frac{k_3 K_1 K_2 [\text{S}][\text{Re}][\text{H}_2]}{1 + K_1 [\text{S}] + K_1 K_2 [\text{S}][\text{H}_2]} \quad \text{or} \quad W = \frac{A [\text{Re}][\text{S}]}{B + [\text{S}]}$$

where

$$A = \frac{k_3 K_1 K_2 [\text{H}_2]}{K_1 + K_1 K_2 [\text{H}_2]} \quad \text{and} \quad B = \frac{1}{K_1 + K_1 K_2 [\text{H}_2]}$$

as the reaction is zero order with respect to hydrogen.

Plots of [Re][S]/W against the substrate concentration at various rhenium concentrations permit to determine the constants A and B used to calculate Curves 1-3 in Fig. 2 according to the above equation. Assuming B to be constant ($B = 0.89 \text{ M}$) at all temperatures studied, A can be expressed as:

$$A = 4 \times 10^{11} \exp(-87909/RT) \text{s}^{-1} \quad (E \text{ is in kJ/mol}).$$

Catalytic activity of $\text{ReOCl}_3(\text{PPh}_3)_2$ was examined under similar conditions ($P_{\text{H}_2} = 5.06 \times 10^3 \text{ kPa}$, $T = 338 \text{ K}$, $[\text{Re}] = 1.6 \times 10^{-2} \text{ M}$). After 7 h reaction only 0.1 - 0.3% of aniline was present in the reaction mixture, i.e. the rate of nitro group hydrogenation is $8.5 \times 10^{-8} \text{ M/s}$, which is three orders of magnitude lower than that for the hexene-1 double bond ($8.7 \times 10^{-5} \text{ M/s}$).

It should be noted that the hydrogenation rate of nitrobenzene to aniline catalyzed by rhenium oxocomplexes with sulfur-containing ligands, e.g. 1-methyl-2-mercaptoimidazole, is much higher. Thus, at $[\text{Re}] = 5 \times 10^{-3} \text{ M}$, $P_{\text{H}_2} = 4.05 \times 10^3 \text{ kPa}$ and $T = 368 \text{ K}$, the aniline yield after 4 h reaction is more than 70%, whereas under the same conditions, hexene-1 is not hydrogenated at all.

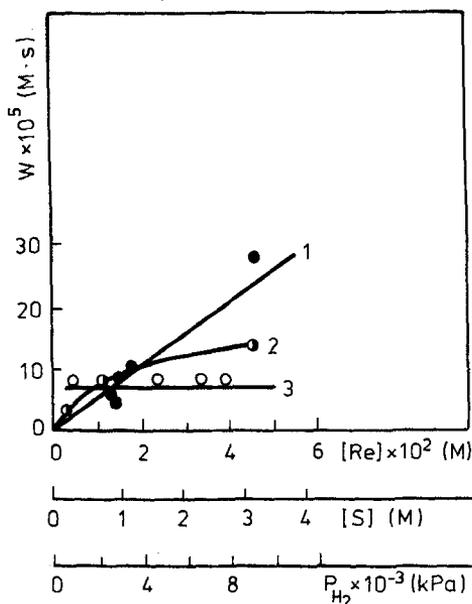


Fig.2. Rate of hexene-1 hydrogenation vs. hydrogen pressure (1), hexene-1 concentration (2) and rhenium concentration (3) at $T = 338 \text{ K}$. All curves were calculated according to the suggested kinetic equation; experimental data are shown as dots

Thus the results indicate that either the nitro group or olefin bond is involved in the hydrogenation reactions of hydrocarbons depending on the ligand in the coordination sphere of rhenium complexes.

REFERENCES

1. A.P. Khrushch, A.E. Shilov: *Kinet.Katal.*, 10, 466 (1966)
2. V.M. Belousov, G.I. Korenyako, Yu.N. Kukushkin, K.V. Kotegov, N.V. Fadeeva: *Dokl.Akad.Nauk Ukr.SSR*, 12, 1011 (1979)
3. R. Mason, P.O. Whimp: *J.Chem.Soc. A*, 18, 2709 (1969)
4. K.V. Kotegov, Yu.N. Kukushkin, N.K. Kobilov, L.V. Konovalova: *Zh.Neorg.Khim.*, 22, 1008 (1977)

BELOUSOV et al.: RHENIUM COMPLEXES

5. K.V. Kotegov, G.N. Sedova, N.N. Kobilov, Yu.N. Kukushkin:
Koord.Khim., 6, 897 (1980)
6. F.J. McQuillin: Homogeneous Hydrogenation in Organic Chem-
istry. Khimiya, Moskva 1980