CATALYTIC HYDROGENATION RATE OF CYCLOPENTENE IN PRESENCE OF PALLADIUM CLUSTER $[Pd_5(PPh)_2]_n$

A. S. Berenblyum, S. L. Mund,
L. G. Danilova, and I. I. Moiseev

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The cluster of composition $(PhP)_2Pd_5$ (I) catalyzes the reduction of dienic hydrocarbons by molecular H_2 to olefins, the subsequent hydrogenation of which in the presence of dienes proceeds much more slowly [1]. In order to ascertain the reasons for the observed selectvity we studied the reduction rate of cyclopentene (CP, S) in DMF solutions of complex (I).

The H_2 absorption rate (W) is a nonlinear function of [S] and $[H_2]$ (Fig. 1). This indicates that the step of hydrogenating CP, like in the case of reducing other unsaturated compounds [1, 2], precedes the reversible complex formation:

$$(I) + S \rightleftarrows (I \cdot S) \tag{1}$$

The (I·S) complex reacts with H_2 to give cyclopentane (P) and the regeneration of (I). Based on the GLC data, the absorption of 1 mole of H_2 is accompanied by the conversion of 1 mole of (S) to 1 mole of (P).

$$(I \cdot S) + H_2 \rightarrow (I) + P \tag{2}$$

The relation between the H_2 absorption rate and the (I) concentration is also nonlinear and, beginning with $[I] > 6 \cdot 10^{-5}$ mole/liter, shows little change with increase in [I] (see Fig. 1b). Such a relation indicates that (I) associates, whose activity is lower than that of (I), are formed with increase in the (I) concentration.

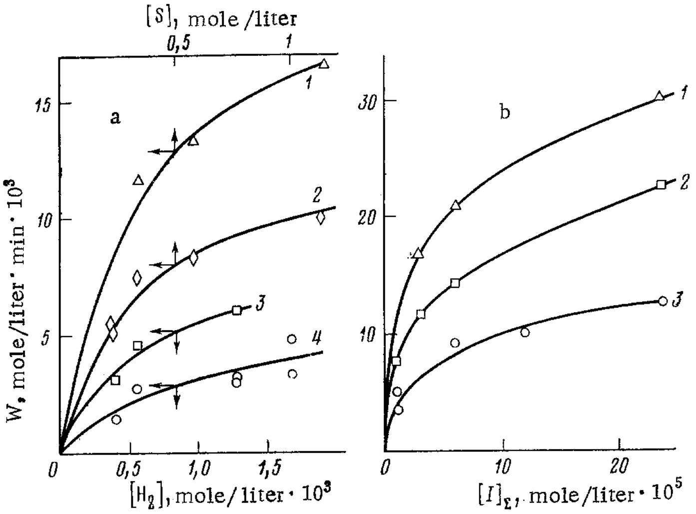

Fig. 1. Hydrogenation rate of cyclopentene: a) as a function of S and H_2 concentrations: 1) $[I]_\Sigma = 3 \cdot 10^{-5}$, $[H_2] = 1.7 \cdot 10^{-3}$; 2) $[I]_\Sigma = 1 \cdot 10^{-5}$, $[H_2] = 1.7 \cdot 10^{-3}$; 3) $[I] = 3 \cdot 10^{-5}$, $[S] = 0.23$; 4) $[I] = 1 \cdot 10^{-5}$, $[S] = 0.23$ mole/liter; b) as a function of (I) concentration when $[H_2] = 1.7 \cdot 10^{-3}$ mole/liter: 1) $[S] = 1.15$; 2) $[S] = 0.34$; 3) $[S] = 0.23$ mole/liter.

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$$n\,(\mathrm{I}) \leftrightarrows (\mathrm{II}) \tag{3}$$

The (II) complex is also probably capable of reversible reaction with S.

$$(\mathrm{II}) + m\mathrm{S} \rightleftarrows (\mathrm{II}\cdot\mathrm{S}_m) \tag{4}$$

The hydrogenation of the $(\mathrm{II}\cdot\mathrm{S_m})$ complex leads to the formation of P and the regeneration of (II).

$$(\mathrm{II}\cdot\mathrm{S}_m) + m\mathrm{H}_2 \rightarrow (\mathrm{II}) + m\mathrm{P} \tag{5}$$

In harmony with Eqs. 3 and 4, an increase in the (I) concentration should lead to an increase in the $(\mathrm{II}\cdot\mathrm{S_m})$ concentration and, consequently, the rate of hydrogenating (S), which is not observed even when $[\mathrm{I}] > 6\cdot10^{-5}$ mole/liter. Hence it follows that the $(\mathrm{II}\cdot\mathrm{S_m})$ complex is less active than the $(\mathrm{I}\cdot\mathrm{S})$ complex in reducing CP and reaction (5) can be neglected.

Taking into account the material balance for the consumption of the (I) complex

$$[\mathrm{I}]_\Sigma = [\mathrm{I}] + [\mathrm{I}\cdot\mathrm{S}] + n[\mathrm{II}] + n[\mathrm{II}\cdot\mathrm{S}_m]$$

and, as an approximation, a steadiness in the $(\mathrm{I}\cdot\mathrm{S})$ concentration, the following equation is valid for schemes (1)-(4).

$$\frac{[\mathrm{I}]_\Sigma}{W} = nK_3(1 + K_4[\mathrm{S}]^m)\left(\frac{k_{-1} + k_2[\mathrm{H}_2]}{k_1k_2[\mathrm{H}_2][\mathrm{S}]}\right)^n W^{n-1} + \frac{k_{-1}}{k_1k_2[\mathrm{H}_2][\mathrm{S}]} + \frac{1}{k_1[\mathrm{S}]} + \frac{1}{k_2[\mathrm{H}_2]} \tag{A}$$

It can be seen that $[\mathrm{I}]_\Sigma/W$ is proportional to W^{n-1}. The obtained experimental data (see Fig. 1a, b) are best linearized when $n = 4$ (Fig. 2a, b). Taking this into account, Eq. (A) can be written as

$$\frac{[I]_\Sigma}{W} = \alpha W^3 + \left(\frac{k_{-1}}{k_1k_2[\mathrm{H}_2]} + \frac{1}{k_1}\right)\frac{1}{[\mathrm{S}]} + \frac{1}{k_2[\mathrm{H}_2]} \tag{B}$$

$$\frac{[I]_\Sigma}{W} = \alpha W^3 + \left(\frac{k_{-1}}{k_1k_2[\mathrm{S}]} + \frac{1}{k_2}\right)\cdot\frac{1}{[\mathrm{H}_2]} + \frac{1}{k_1[\mathrm{S}]} \tag{C}$$

where $\alpha = 4K_3(1 + K_4[\mathrm{S}]^m)\left(\frac{k_{-1} + k_2[\mathrm{H}_2]}{k_1k_2[\mathrm{S}][\mathrm{H}_2]}\right)^4$.

Straight lines in the coordinates $[\mathrm{I}]_\Sigma/W$ vs W^3 intercept sections on the ordinate that are equal to $\left(\frac{k_{-1}}{k_1k_2[\mathrm{H}_2]} + \frac{1}{k_1}\right)\cdot\frac{1}{[\mathrm{S}]} + \frac{1}{k_2[\mathrm{H}_2]}$ (see Fig. 2a) and $\left(\frac{k_{-1}}{k_1k_2[\mathrm{S}]} + \frac{1}{k_2}\right)\frac{1}{[\mathrm{H}_2]} + \frac{1}{k_1[\mathrm{S}]}$ (see Fig. 2b).

The fact that the found values are a linear function of $1/[\mathrm{S}]$ (Fig. 3) and $1/[\mathrm{H}_2]$ (Fig. 4) testifies to an agreement of the proposed scheme with the observed kinetic rules. From Figs. 3 and 4 were found the values: $k_1 = 1.4\cdot10^4$ liter/mole·min, $k_{-1} = 6.1\cdot10^3\ \mathrm{min}^{-1}$, and $k_2 = 1.3\cdot10^6$ liter/mole·min.

In order to verify the values of the constants k_1, k_{-1}, and k_2, which were found for the hydrogenation of CP, we studied the joint hydrogenation of a mixture (1:1 composition) of CP and cyclopentadiene (CPD, S') in DMF in the presence of (I). From the GLC data on the decrease in CPD and accumulation of P we determined the hydrogenation rates (W' and W) of CPD and CP. In this case the overall process for the joint hydrogenation of CPD and CP, besides steps (1)-(4), should include the reactions for the formation of the (I) and (II) complexes with CPD and their reaction with H_2.

$$(\mathrm{I}) + \mathrm{S}' \rightleftarrows (\mathrm{I}\cdot\mathrm{S}') \tag{6}$$

$$(\mathrm{I})\cdot\mathrm{S}' + \mathrm{H}_2 \rightarrow (\mathrm{I}) + \mathrm{S} \tag{7}$$

$$(\mathrm{II}) + m\mathrm{S}' \rightleftarrows (\mathrm{II}\cdot\mathrm{S}_m') \tag{8}$$

$$(\mathrm{II}\cdot\mathrm{S}_m') + \mathrm{H}_2 \rightarrow (\mathrm{II}) + \mathrm{S} \tag{9}$$

The value of K_6 [1] is sufficiently high for practically all of (I) being tied up as the $(\mathrm{I}\cdot\mathrm{S})$ complex. Due to this, the (II) concentration is so small that the contribution of reactions (4), (5), (8), and (9) can be neglected.

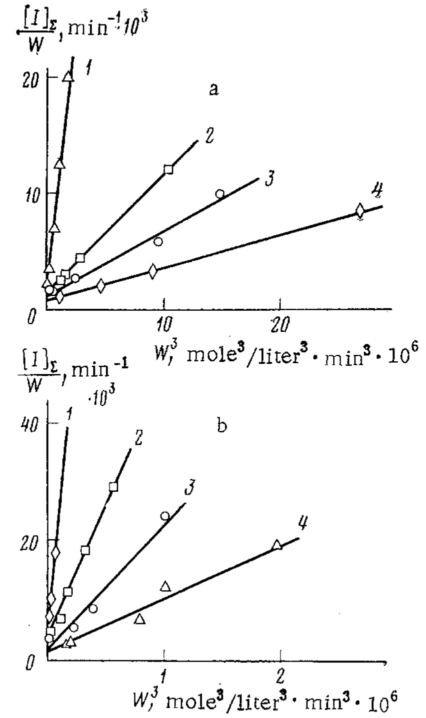

Fig. 2

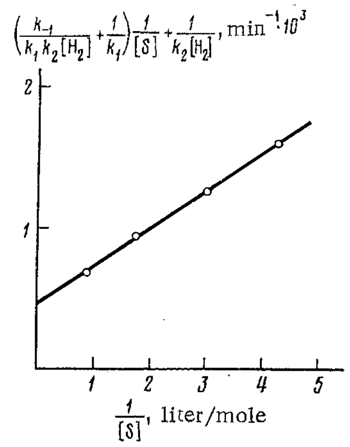

Fig. 3

Fig. 2. $[I]_\Sigma/W$ as a function of W^3: a) $[H_2] = 1.7 \cdot 10^{-3}$ mole/liter: 1) [S] = 0.23; 2) [S] = 0.34; 3) [S] = 0.58; 4) [S] = 1.15 mole/liter; b) [S] = 0.23 mole/liter: 1) $[H_2] = 0.41 \cdot 10^{-3}$; 2) $[H_2] = 0.56 \cdot 10^{-3}$, 3) $[H_2] = 1.30 \cdot 10^{-3}$; 4) $[H_2] = 1.70 \cdot 10^{-3}$ mole/liter.

Fig. 3. $\left(\frac{k_{-1}}{k_1k_2[H_2]} + \frac{1}{k_1}\right) \cdot \frac{1}{[S]} + \frac{1}{k_2[H]}$ as a function of 1/[S] when $[H_2] = 1.7 \cdot 10^{-3}$ mole/liter.

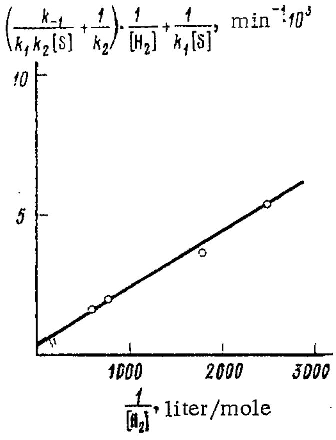

Fig. 4. $\left(\frac{k_{-1}}{k_1k_2[S]} + \frac{1}{k_2}\right)\frac{1}{[H_2]} + \frac{1}{k_1[S]}$ as a function of $1/[H_2]$ when [S] =0.23 mole/liter.

Taking into account the material balance for the consumption of the (I) complex and, as an approximation, a steadiness in the (I·S) concentration, the following equation is valid for schemes (1), (2), (6), and (7):

$$\frac{W'}{W} = \frac{k_7K_6[S'](k_{-1} + k_2[H_2])}{k_2k_1[S]} \tag{D}$$

where W and W' are respectively the hydrogenation rates of CP and CPD. Substituting in Eq. (D) the values of K_6 and k_7 [1], [S] = [S'] = 0.12 mole/liter, and also the values found under these conditions, $W = 7.6 \cdot 10^{-5}$ and $W' = 1.6 \cdot 10^{-2}$ mole/liter·min, we obtained the value $\frac{k_{-1} + k_2[H_2]}{k_1 k_2} = 4.6 \cdot 10^{-7}$, which is in good agreement with that found when studying the reduction rate of CP in the absence of CPD.

The obtained kinetic results permit analyzing the factors that govern the selectivity during the hydrogenation of dienic hydrocarbons to olefins. The constant for the hydrogenation of the CPD—(I) complex [1] is close to the rate constant for the reaction of H_2 with the CP—(I) complex. However, since the equilibrium constants for the formation of the corresponding complexes differ by $\sim 10^2$ times, the observed difference in the reduction rates of the diene and olefin during their joint hydrogenation is due to the predominant tendency of (I) to form the complex with the diene, and not with the olefin. At low diene concentrations, where the monomeric (I) and tetrameric (II) forms of the catalyst can exist in commensurate concentrations, the total catalyst concentration $[I]_\Sigma$ can affect the selectivity of the reaction. Since under these conditions the amount of (II) increases with increase in [I], the CP hydrogenation rate remains practically constant, the same as is shown in Fig. 1. In contrast, the increase in W' will be linear with increase in $[I]_\Sigma$. Due to this a higher selectivity can be achieved at higher values of $[I]_\Sigma$.

The reaction rates of (I) with CP and of (I·S) with H_2 are close. Due to this, as is shown by an analysis of the kinetic data when $P_{H_2} > 10$ atm, the hydrogenation rate is limited by the reaction of (I) with CP [reaction (1)]. Under these conditions the selectivity depends on the ratio of the rate constants for the formation of the (I) complexes with CP and CPD. If the rate constants for the formation of the complexes correlate with the corresponding equilibrium constants, then an increase in the selectivity can be expected with increase in the pressure.

EXPERIMENTAL

DMF was purified as described in [1]. CP was purified by vacuum-distillation after keeping over KOH for a day. The rate was studied volumetrically [2] at 20°C and 1 atm. The error in determining the rate constants did not exceed 10%. The catalyzate was analyzed by GLC as described in [1].

CONCLUSIONS

1. Kinetic data were obtained for the hydrogenation of cyclopentene in the presence of a DMF solution of $(PhP)_2Pd_5$. They were interpreted within the framework of a mechanism that includes the reversible formation of the Pd complex with the substrate, which, reacting with H_2, forms cyclopentane and the starting Pd compound. With increase in the catalyst concentration the $(PhP)_2Pd_5$ complex forms associates, which form equilibrium complexes with the substrate, whose activity in the reaction with H_2 is substantially lower than that of the analogous complex with the monomeric form of the catalyst.

2. A kinetic equation was found that satisfactorily describes the reduction rate of cyclopentene. The rate constants were determined for the steps of forming and decomposing the Pd complex with the substrate and its hydrogenation by H_2. On the basis of the kinetic data an estimate was made of the degree of association of the $(PPh)_2Pd_5$ complex with increase in its concentration.

LITERATURE CITED

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