

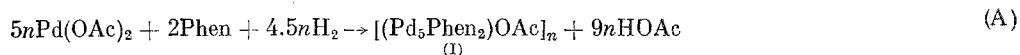
HYDROGENATION CATALYSIS BY PALLADIUM CLUSTER
COMPLEXES WITH PHENANTHROLINE

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UDC 541.128: 542.941

Palladium cluster complexes with phosphorus-containing ligands are used as active catalysts for the hydrogenation of unsaturated compounds [1, 2]. The present paper will describe the catalytic action of a new type of palladium cluster complex which contains o-phenanthroline as a stabilizing ligand [3].

A water-benzene emulsion containing $\text{Pd}(\text{OAc})_2$ and o-phenanthroline (Phen) in 5:2 proportions was found to adsorb ~ 0.9 mole H_2 per g-atom of Pd at 20°C and 1 atm, the fact that the benzene layer lost its coloration while the water layer took on a dark brown hue suggesting that the absorption process had led to the formation of ionic reaction products. The consumption of system components in the absorption could be represented by an equation of the form*



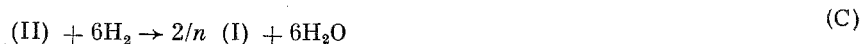
The fact that the OAc groups were located in the external coordination sphere of complex (I) was indicated by the observation that the complex would not react with H_2 as did those complexes of the metal which contained Pd-OAc bonds [5]. The Phen molecule occupies two coordinated positions per metal atom in the palladium complex [6]. It would therefore seem that three of the five Pd atoms present in complex (I) must either be bound to H_2O molecules or are bound to other Pd atoms through Pd_5 groups. Aqueous solutions of (I) took up 0.3 mole of O_2 per 1 g-atom of Pd. Here reaction led to the separation of a complex which was shown by elementary analysis and molecular mass determinations to have the formula $[\text{Pd}_{10}\text{Phen}_4(\text{O}_2)_3](\text{OAc})_2$ (II) [2]. The PMR spectra of complex (II) showed bands at 1.82 ppm (OAc), and at 6.97, 7.82, and 8.86 ppm (Phen), the ratio of proton signal intensities being such that Phen/OAc = 5.3. The IR spectrum of complex (I) showed a band for C=O band absorption in OAc in 1580 cm^{-1} . The oxygenyl complex (II) was therefore formed through a reaction of the type



This same complex could be prepared by reacting the $[(\text{RP})_2\text{Pd}_5]_n$ cluster [2] with Phen and HOAc in C_6H_6 , and then bringing the solution into contact with O_2 .

The fact that H_2O_2 was formed through the interaction of (II) with acids [3] was taken as an indication that the coordinated oxygen existed as O_2^{2-} in the complex. On this basis it was considered that reaction (B) was an instance of the oxidative addition of O_2 to a low-valence palladium complex.

Although aqueous solutions of (I) did not react with H_2 under gentle treatment, aqueous solutions of (II) took up H_2 in quantities corresponding to the formation of (I) and H_2O , but without the appearance of HOAc, if one could judge from the GLC data



Catalytic hydrogenation of O_2 [sum of reactions (B) and (C)] led to the formation of H_2O when an aqueous solution of (I) was brought into contact with a 2:1 H_2 - O_2 mixture.

* The H_2O molecules occupying the vacant position in the coordination sphere of the palladium cluster have been omitted in writing this equation. It seems likely that n is an even number here since the complex (I) would otherwise be of the paramagnetic type rarely met in the chemistry of palladium [4].

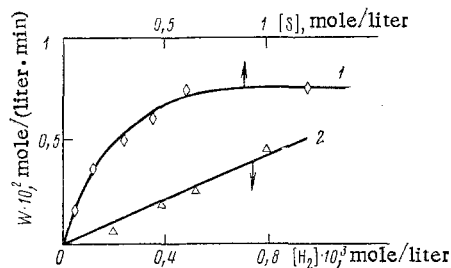


Fig. 1. Variation of the rate of hydrogenation of allyl alcohol with $[S]$ and $[H_2]$ (30°C , $[I] = 0.5 \cdot 10^{-4}$ mole/liter): 1) $[H_2] = 0.8 \cdot 10^{-3}$ mole/liter; 2) $[S] = 0.3$ mole/liter.

The hydrogenation of unsaturated hydrocarbons proceeded in a similar fashion. Thus, aqueous solutions of (I) were found to absorb H_2 only after they had been treated with either 1,3-pentadiene or allyl alcohol (S). The rate of H_2 uptake by a solution containing (I) at 10^{-4} mole/liter concentration was found to be only slightly dependent on S concentration at $[S] > 0.6$ mole/liter (Fig. 1). These facts suggested that substrate hydrogenation precedes (I · S) complex formation, here just as in the case of other palladium cluster complexes [7], possibly proceeding through oxidative addition of the hydrogenating substrate to Pd according to the reaction



The (I · S) complex reacted with H_2 more readily than complex (I), reaction proceeding through a heterolytic mechanism of hydrogenation and the regeneration of (I)



The kinetics of unsaturated hydrocarbon hydrogenation were studied through the reduction of allyl alcohol.

On the basis of GLC data it would seem that the hydrogenation of allyl alcohol leads to the formation of propyl alcohol with yields in excess of 90%.* The catalyst for the reaction did not decompose and was not poisoned by the alcohol formed on it. Thus, the kinetic curve for H_2 absorption could be completely reproduced by introducing a second portion of substrate into the solution left from the S hydrogenation.

For a steady-state (I · S) concentration in reactions (1)-(2), the reaction rate W is given by an expression of the form

$$W = \frac{k_1 k_2 [H_2] [I]_{\Sigma} [S]_{\Sigma}}{k_{-1} + k_2 [H_2] + k_1 [S]_{\Sigma}} \quad (3)$$

in which the k_i are the rate constants for steps (1) and (2), and $[I]_{\Sigma}$ and $[S]_{\Sigma}$ are the respective total concentrations of free and complexed (I) and S in the system.

By drawing on the procedure of [7], Eq. (3) could be rewritten as

$$\frac{1}{W} = \frac{k_{-1} + k_2 [H_2]}{k_1 k_2 [I]_{\Sigma} [H_2]} \cdot \frac{1}{[S]_{\Sigma}} + \frac{1}{k_2 [I]_{\Sigma} [H_2]} \quad (4)$$

The rate of reaction proved to be linearly dependent on the H_2 pressure over the interval from 0.25 to 1.0 atm (see Fig. 1), thus indicating that $k_{-1} \gg k_2 [H_2]$, and suggesting that Eq. (4) itself be rewritten as

$$\frac{1}{W} = \frac{k_{-1}}{k_1 k_2 [I]_{\Sigma} [H_2] [S]_{\Sigma}} + \frac{1}{k_2 [I]_{\Sigma} [H_2]} \quad (5)$$

* Hydrogenation was accompanied by substrate isomerization to propanal.

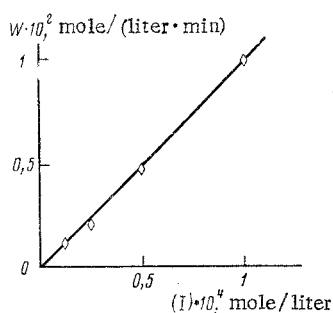


Fig. 2

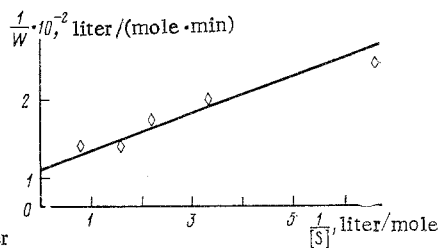


Fig. 3

Fig. 2. Variation of the rate of H₂ absorption with [I] ([S] = 0.3; [H₂] = 0.8 · 10⁻³ mole/liter, 30°C).

Fig. 3. Variation of 1/W with 1/[S] ([H₂] = 0.8 · 10⁻³, [I] = 0.5 · 10⁻⁴ mole/liter, 30°C).

The fact that the experimental data of Figs. 1 and 2 could be linearized by plotting in 1/W vs 1/S coordinates (Fig. 3) was an indication of the adequacy of the kinetic equations. The quantities

$$\frac{1}{k_2 [I]_{\Sigma} [H_2]}, \quad \frac{k_{-1}}{k_1 k_2 [I]_{\Sigma} [H_2]}$$

were estimated graphically, and the results used to calculate the constants k_2 [2.4 · 10⁵ liters/(mole · min)] and $K = k_1/k_{-1}$ [4.7 liters/mole].*

EXPERIMENTAL

The hydrogenation experiments were carried out by first degassing the DMFA solution of complex (II) and then introducing the allyl alcohol in a stream of gaseous H₂.

The hydrogenation kinetics were studied volumetrically, working at 30°C and 1 atm pressure. The long-necked hydrogenation flask-type reactor was shaken at a rate of 500–700 min⁻¹ in order to assure that reaction would take place in the kinetic region.

The procedure followed in preparing [Pd₁₀(Phen)₄(O₂)₃](OAc)₂ from Pd(OAc)₂ and Phen has been described in [3].

Preparation of [Pd₁₀(Phen)₄(O₂)₃](OAc)₂ from Pd(OAc)₂, PBu₃, and Phen. To a solution containing 0.12 g (5.3 · 10⁻⁴ mole) of Pd(OAc)₂ dissolved in 5 ml of benzene there was added, under constant agitation, 0.14 ml (5.3 · 10⁻⁴ mole) of PBu₃ dissolved in 1 ml of benzene; the resulting mixture was degassed and then treated with H₂, again under constant agitation, for 1 h. The color of the solution changed from yellowish orange to brown during this treatment. At the end of this period, a solution containing 0.18 g (8 · 10⁻⁴ mole) of Pd(OAc)₂ dissolved in 15 ml of benzene was introduced by pipette under the liquid layer in the system, introduction being in the form of three separate 5-ml batches over a 15-min interval, with the entire operation carried out in a stream of H₂.

After introduction of the Pd(OAc)₂ had been completed, a solution containing 0.14 g (7.8 · 10⁻⁴ mole) of phenanthroline dissolved in 15 ml of benzene was run into the system. Addition of water, and exposure of the reaction mixture to the action of air, caused the aqueous layer to take on a brownish coloration, while the benzene layer became light yellow. The aqueous layer was separated off, filtered, and the water eliminated from it by evaporation to a volume of 3–5 ml. Addition of acetone brought down a black powder which was filtered off, washed with acetone, and dried. Found: C 39.9; H 2.3; N 5.5%. C₅₂H₃₈N₈O₁₀Pd₁₀. Calculated: C 31.3; H 1.9; N 5.6%.

Analysis of the reaction mixture was carried out by GLC (LKhM SMD, flame-ionization detector, 15% Carbowax-200 on Chromaton, He carrier gas, 40 ml/min, 3 × 0.002 m column). The allyl alcohol was a cp grade which had been purified by distillation. Distilled water was used as the solvent.

* The n of (I) was set equal to 2 for these calculations.

CONCLUSIONS

1. The $[(Pd_5Phen_2)OAc]_n$ (I) cluster complex is formed through the reaction of palladium diacetal with molecular hydrogen in the presence of *o*-phenanthroline. A product of composition $[Pd_{10}Phen_4(O_2)_3](OAc)_2$ separates out when this complex is treated with oxygen.

2. The hydrogenation of O_2 , 1,3-pentadiene, and allyl alcohol are catalyzed by aqueous solutions of (I).

3. The kinetic data on the hydrogenation of allyl alcohol by (I) in aqueous solution can be described by a mechanism involving complexing between cluster and substrate, reaction with hydrogen leading to the formation of the alcohol and regeneration of the original palladium compound. Rate constants have been determined for the various steps in this mechanism.

LITERATURE CITED

1. A. S. Berenblyum, G. V. Turkova, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 514 (1981).
2. A. S. Berenblyum, A. G. Knizhnik, S. L. Mund, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2175 (1979).
3. A. S. Berenblyum, S. L. Mund, T. P. Goranskaya, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1948 (1980).
4. M. N. Vargaftik, T. A. Stromnova, and I. I. Moiseev, *Zh. Neorg. Khim.*, **25**, 242 (1980).
5. A. S. Berenblyum, A. G. Knizhnik, S. L. Mund, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2711 (1978).
6. M. N. Vargaftik, T. A. Stromnova, T. S. Khodasheva, M. A. Porai-Koshits, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1690 (1980).
7. A. S. Berenblyum, S. L. Mund, L. C. Danilova, and I. I. Moiseev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1761 (1980).

ACID-CATALYZED HYDROLYSIS OF BENZOYLHYDRAZINE IN SULFURIC ACID

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UDC 541.128:542.938:547.556.8

Many heterochain polymeric materials are synthesized and restructured in H_2SO_4 solution. There is the possibility that hydrolytically unstable bonds would be hydrolyzed in the course of such processes. Estimation of the effect of this factor calls for a study of the hydrolysis mechanism. We have, therefore, investigated the acid-catalyzed hydrolysis of benzoylhydrazine, a compound used to model the hydrolytically unstable fragments in polyhydrazines and polyoxadiazoles.

EXPERIMENTAL

The kinetics of the benzoylhydrazine hydrolysis in aqueous H_2SO_4 solution were studied at 50–90°C, working at concentrations ranging from 0.01 to 0.1 M, and in solutions containing from 20 to 76% H_2SO_4 . Measurement was made of the alteration of the optical density at λ 210 nm, where the spectroscopic difference between the reactants and products was most pronounced. Under our working conditions, the hydrolysis of benzoylhydrazine was an irreversible process, the spectrum of the reaction products being a superpositioning of the spectra for hydrazine and benzoic acid. Hydrolysis rate constants were calculated from a first-order equation (Table 1), and the results obtained extrapolated to 25°C (Table 2).

* Deceased.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 11, pp. 2476–2478, November, 1981. Original article submitted March 23, 1981.