2. With increasing cobalt content in the catalysts, the yield of liquid products of the synthesis of hydrocarbons from CO and H_2 and the content of n-paraffins in them increased.

LITERATURE CITED

1. A. L. Lapidus, Hoang Trong Diem, and A. Yu. Krylova, Khim. Tverd. Topl., 6, 7 (1983).
2. A. Yu. Krylova, S. M. Salekhuddin, A. G. Gazaryan, et al., Neftekhimiya, 25, No. 4, 498 (1985).
3. R. L. Chin and D. M. Hercules, J. Phys. Chem., 86, 360 (1982).
4. A. L. Lapidus, A. Yu. Krylova, and L. T. Kondrat'ev, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1432 (1980).
5. A. S. Lisitsyn, V. L. Kuznetsov, and Yu. I. Ermakov, Kinet. Katal., 23, No. 4, 926 (1982).
6. Yu. Yu. Lur'e, Handbook of Analytical Chemistry [in Russian], Khimiya, Moscow (1972).
7. Yu. Fal'be (ed.), Chemical Substances from Coal [in Russian], Khimiya, Mosocw (1980).

REDUCTION OF NITROBENZENE IN THE LIQUID PHASE BY CARBON MONOXIDE (II) IN THE PRESENCE OF PALLADIUM COMPLEXES

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It was shown earlier [1] that nitrobenzene can be reduced to p-aminophenol by CO in the presence of palladium complexes in the liquid phase. The goal of the present work was to isolate the catalytically active forms of palladium and to investigate their transformations during the reaction.

RESULTS AND DISCUSSION

The investigated reduction of $Ph\text{-}NO_2$ by carbon monoxide is an oxidation—reduction reaction and the catalyst may be present in its oxidized or reduced form during this process.

In the two-phase system $n\text{-}BuOH/H_2SO_4$ at 40°C, i.e., under the conditions of the investigated catalytic reaction, $Pd(OAc)_2$ is reduced by carbon monoxide to $Pd_2(PPh_3)_4(CO)\cdot H_2SO_4$ (I) [2]. The produced compound could not be isolated, and, therefore, its analog $Pd_2(PPh_3)_4(CO)\cdot HClO_4$ (II), isolated in its solid form, was investigated more closely [3]. The compounds (I) and (II) easily convert the one into the other [3] and have a dimeric structure because the PMR spectrum of complex (II) exhibits a signal from the H atom in the form of a quintuplet [4]. This is caused by the scission of the H atoms on four equivalent phosphorus atoms. The complexes produced in the atmosphere of CO and in the absence of the oxidant $Ph\text{-}NO_2$ apparently represent the reduced form of the catalyst in the respective systems.

To obtain the oxidized forms, these compounds were subjected to the action of nitrobenzene in an inert atmosphere. It was determined that the complex (I) was converted to $Pd(PPh_3)_2SO_4$ (III), and the complex (II) to $Pd(PPh_3)_3(H_2O)(ClO_4)_2$ (IV),

$$Pd_2(PPh_3)_4(CO)\cdot H_2SO_4 + 2C_6H_5NO_2 + H_2SO_4 \rightarrow 2Pd(PPh_3)_2SO_4 + 2C_6H_5NO + CO + 2H_2O \quad (1)$$

$$Pd_2(PPh_3)_4(CO)\cdot HClO_4 + 2C_6H_5NO_2 + 3HClO_4 + 2PPh_3 \rightarrow 2Pd(PPh_3)_3\cdot \cdot(H_2O)(ClO_4)_2 + 2C_6H_5NO + CO + H_2O \quad (2)$$

The formation of the complexes was confirmed by elemental analysis and by IR spectroscopy. The presence of the SO_4^{2-} ion in the complex (III) was demonstrated by the appearance

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TABLE 1. Oxidation of (II) by Nitrobenzene in Ar at 40°C (initial amount of Pd: 1 mmole; 10 ml n-BuOH; 10 ml $HClO_4$ [4.4 N]; 2 ml Ph-NO_2 [19.5 mmoles])

τ, min	Complex (II)		Complex (IV)		ΣPd, %
	g	%	g	%	
0	0.69	100	0	0	100
15	0,35	50,7	0.42	37.4	88.1
30	0,19	27.5	0,56	50.4	77,9
30	0.24	34.7	0,57	51,3	85.0
45	0,11	15,9	0,78	70.2	86,1
60	0.094	13,6	0.87	78.3	91,9
75	Traces	–	0,99	89.1	89,1

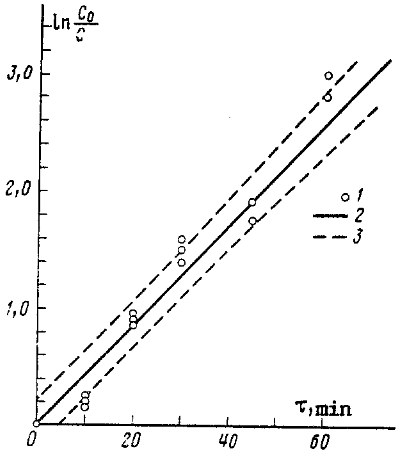

Fig. 1. Variation of the concentration of $Pd(OAc)_2$ as a function of time during the reduction of (II) with carbon monoxide at 40°C ($C_{0Pd(II)}$ = $5 \cdot 10^{-2}$ mole/liter; P/Pd = 3; 10 ml n-BuOH; 10 ml 4.4 N $HClO_4$): 1) experiment; 2) line of regression; 3) range of errors at a reliability probability of 0.95.

in the IR spectrum of three intense bands in the region of 1000-1200 cm^{-1}. The appearance of a wide band in the region of 3500 cm^{-1} testified to the presence of coordinationally bound water in (IV).

It is interesting to note that (III) can be prepared directly from $Pd(OAc)_2$ and PPh_3 in H_2SO_4 by mixing the reagents in an inert atmosphere (yield, 79%),

$$Pd(OAc)_2 + H_2SO_4 + 2PPh_3 \rightarrow Pd(PPh_3)_2SO_4 + 2HOAc \tag{3}$$

The complex (IV) was produced in a similar manner with a yield of 45%.

One more possible reduced form of palladium in such systems can be the hydride complex $Pd(PPh_3)_3 \cdot HClO_4$ (V). The formation of this latter depends on the nature of the solvent used. It was prepared in [3] by reducing $Pd(OAc)_2$ in acetone by carbon monoxide, but it can be more conveniently prepared by reacting $Pd(PPh_3)_4$ with $HClO_4$,

$$Pd(PPh_3)_4 + HClO_4 \rightarrow Pd(PPh_3)_3 \cdot HClO_4 + PPh_3 \tag{4}$$

By reacting the complex (V) with Ph-NO_2 in the presence of $HClO_4$, the complex (IV) was produced,

$$Pd(PPh_3)_3 \cdot HClO_4 + C_6H_5NO_2 + HClO_4 \rightarrow Pd(PPh_3)_3(H_2O)(ClO_4)_2 + C_6H_5NO \tag{5}$$

TABLE 2. Ratio between the Forms of the Catalyst in the Reduction of PH-NO_2 by Carbon Monoxide (II) at Different Times (40°C; v_{CO} = 0.5-1.0 liter/h; initial amount of (II): 695 mg (1 mmole); 10 ml n-BuOH; 10 ml $HClO_4$ (4.4 N); 2 ml Ph-NO_2 (19.5 mmoles))

τ, min	Amount of CO_2, mmole	Complex (II)		Complex (IV)		ΣPd, %
		g	%	g	%	
0	0	0.69	100	0	0	100
15	0,7	0,29	41,7	0,58	52,2	93,9
30	1,5	0,26	37,4	0,62	55,8	93,2
60	2,8	0,33	47,5	0.50	45,0	92,5
90	4.5	0,40	57,6	0.34	30,6	89,2
120	6,0	0,48	69,1	0,28	25,2	94,3

The complexes (III) and (IV) have been described in [5, 6]. They are reduced by CO to the starting compounds (I) and (II),

$$2Pd(PPh_3)_2SO_4 + 3CO + 2H_2O \rightarrow Pd_2(PPh_3)_4(CO)\cdot H_2SO_4 + 2CO_2 + H_2SO_4 \qquad (6)$$

$$2Pd(PPh_3)_3(H_2O)(ClO_4)_2 + 3CO + H_2O \rightarrow Pd_2(PPh_3)_4(CO)\cdot HClO_4 + 2CO_2 + 3HClO_4 \qquad (7)$$

Thus, the data given above demonstrate the existence of the catalyst in at least two forms: reduced [complexes (I), (II), and (V)] and oxidized [complexes (III) and (IV)]. The relative amounts of each form present during the catalytic reaction are determined by the ratio between the oxidation rate constant (k_1) and the reduction rate constant (k_2). In order to determine the values of these constants in the $HClO_4$ medium, the catalytic reduction of nitrobenzene was carried out in stages.

The apparent oxidation rate constant was determined from the oxidation of the complex (II) by nitrobenzene with a significant excess of the latter. This allowed us to process the data using an equation of the first order. Table 1 gives the amounts for both forms: the oxidized (IV) and the reduced (II) at different time instants. By applying the method of least squares, these results gave $k_1 = (2.8 \pm 0.4)\cdot 10^{-2}$ min^{-1}.

The apparent reduction rate constant for the complexes of Pd(II) was determined in a fashion similar to that described for the oxidation. In this case the concentration of the reducing agent (CO) was kept constant. The experimental results were processed using an equation of the first order (Fig. 1). The result was $k_2 = (4.2 \pm 0.7)\cdot 10^{-2}$ min^{-1}.

The values given above for the constants were obtained by carrying out the oxidation and reduction of the palladium complexes in stages. However, we cannot exclude the possibility that the catalyst may be present in the reaction in forms with intermediate degrees of oxidation. Single-electron transitions taking place in the reduction of nitrocompounds by H_2 have been postulated in [6, 7].

We conducted special tests to evaluate the nature of the oxidized and the reduced forms of the catalyst. The conditions of these tests (Table 2) were chosen so as to make the values of k_1 and k_2 of the same order of magnitude. This ensured the presence of sufficient amounts of both forms of the catalyst in the stationary state. The subsequent sudden interruption of the reaction and the isolation of both forms of the catalyst, directly from the contact solution, showed (Table 2) that the oxidized and reduced forms of the catalyst had the composition of complexes (IV) and (II), i.e., they were formed in approximately equal amounts as was to be expected from the values of k_1 and k_2.

These results allowed us to assume that the essential stage of this reaction is a two-electron process which, using the analogy of a heterogeneous catalysis [8], can be represented by the following scheme:

$$Ph - NO_2 + 2H^+ + 2\bar{e} \rightarrow Ph - NO + H_2O \qquad (8)$$

Our combined data show that the reduction of the nitro compound in the investigated system probably follows a different mechanism than that described in [7, 9], where a radical type mechanism was involved.

EXPERIMENTAL

The purification of the starting substances and the analysis of the obtained compounds were described in [3, 10]. (I) and (II) were synthesized following the methods given in [2] and [3], respectively. $Pd(PPh_3)_4$ was prepared according to [11].

Interaction of (I) with $Ph-NO_2$. 0.8 ml of $Ph-NO_2$ (8 mmoles) and 262 mg (1 mmole) of PPh_3 were added to the complex (I) (1 mmole) (prepared according to [2]), dissolved in n-BuOH (20 ml)/H_2SO_4 (5.5 N, 20 ml), in an Ar atmosphere. The reaction mixture was stirred for 1 h. After the reaction was completed, the organic layer was separated and washed twice with water. The residue was taken in a five-fold amount of ether, held for 24 h, filtered, washed with several portions of ether, and dried in vacuum. We obtained 0.58 g of $Pd(PPh_3)_2 \cdot SO_4$. The complex was reprecipitated from dichloroethylene with ether. Found: Pd 14.46; P 8.49; S 4.0%; P/Pd = 2.02; S/Pd = 0.92; IR spectrum (νSO_4, cm^{-1}): 1255, 1182, 1140, 1090; νCO was absent. The yield, based on Pd, was 81%. $C_{36}H_{30}O_4SP_2Pd$. Calculated: Pd 14.63; P 8.52; S 4.4%.

Reduction of $Pd(PPh_3)_2SO_4$(III) by CO. 726 mg of (III) (1 mmole), 20 ml of n-BuOH, 20 ml of H_2SO_4 (5.5 N), and 288 mg PPh_3 (1.1 mmole) were charged into a thermostated reactor. The reduction with CO was conducted for 2 h at 40°C. 1.08 mmole of CO_2 evolved. Complex (I) was produced with some amount of $Pd(PPh_3)_4$. Because the complex (I) exists only in solution, the results of the reduction were additionally evaluated on the basis of the formation of $[Pd_2(PPh_3)_4(CO)]_n$ when (I) was treated with an alkali [2, 3]. After the reduction, the mixture was filtered. The precipitated $Pd(PPh_3)_4$ was washed with EtOH, with two or three drops of HOAc added to it. It was then washed with Et_2O and dried in vacuum. 0.20 g of the precipitate was obtained. The yield, based on Pd, was 17.3%. Found: Pd 9.19; P 10.93%; P/Pd = 4.06. $C_{72}H_{60}P_4Pd$. Calculated: Pd 9.21; P 10.72%. The νCO bands were not present in the IR spectra.

The aqueous phase was separated from the organic phase. This latter was washed with two portions of water and treated with a 1 N aqueous NaOH solution. The precipitated light-brown residue was immediately filtered, washed three times with EtOH and once with hexane, and dried in vacuum. 0.40 g of the precipitate was obtained. The yield, based on Pd, was 62.1%. Found: Pd 16.77; P 9.42%; P/Pd = 1.93. $C_{73}H_{60}OP_4Pd_2$. Calculated: Pd 16.51; P 9.62%. IR spectrum: νCO 1835 cm^{-1}.

Preparation of Complex (III) from $Pd(OAc)_2$, PPh_3, and H_2SO_4. 225 mg of $Pd(OAc)_2$ (1 mmole), 1048 mg PPh_3 (4 mmoles), 40 ml n-BuOH, and 40 ml of 5.5 N H_2SO_4 were charged into a thermostated reactor furnished with a stirrer. N_2 was passed through the mixture which was agitated for 1 h at 40°C. The methods for the isolation and the identification of the complex was described above (see, interaction of (I) with $Ph-NO_2$). 0.57 g of $Pd(PPh_3)_2SO_4$ was obtained with a yield of 79%.

Interaction of (II) with $Ph-NO_2$. 2 ml of $Ph-NO_2$ (19.5 mmoles) and 26.3 mg of PPh_3 (0.1 mmole) were added to 1 mmole of complex (II), obtained *in situ* following the method in [3], in a current of Ar. The reaction mixture was stirred for 75 min at 40°C. The small amount of unreacted complex (II) was filtered out, the aqueous phase was separated, and the organic phase was washed with two portions of water. The organic phase was then treated with a mixture of Et_2O (100 ml) and hexane (50 ml). The cream-colored residue was held refrigerated during 24 h, filtered, washed with six or seven portions of dry Et_2O, and dried in an Ar atmosphere at 20°C. 0.99 g of complex $Pd(PPh_3)_3(H_2O)(ClO_4)_2$ was obtained. The yield based on Pd, was 88.8%. The mp was 212-214°C. Found: Pd 9.54; P 8.23; Cl 6.43%; P/Pd = 2.96; Cl/Pd = 2.02. $C_{54}H_{47}O_9Cl_2P_3Pd$. Calculated: Pd 9.58; P 8.37; Cl 6.39%. IR spectrum (ν, cm^{-1}): 3500 (H_2O), 1080 (ClO_4^-).

The experiments listed in Tables 1 and 2 were carried out using the same methods. In the first case, the reaction was interrupted at different time intervals, the unreacted complex (II) was filtered out, washed, dried, and analyzed. The complex (IV), remaining in solution, was isolated as was described above. All the operations in the tests given in Table 2 were carried out in a current of CO, i.e., under the conditions of the catalytic reaction. The reaction was monitored by the evolutiion of CO_2.

Reduction of Complex (IV) by CO. 407 mg (0.38 mmole) of (IV), 10 ml of n-BuOH, and 10 ml of 4.4 N $HClO_4$ were charged into thermostated reactor. The reaction was carried out at 40°C in a current of CO. The reaction took 2 h. 0.35 mmole of CO_2 evolved during this time. The molar ratio was $CO_2/Pd = 0.92$. The mixture was treated as was described in [3] and the analytical and spectral characteristics of complex (II) were determined also according to [3]. The yield, based on Pd, was 84.0%.

Preparation of Complex (IV) from $Pd(OAc)_2$, PPh_3, and $HClO_4$. 225 mg of $Pd(OAc)_2$, 812 mg PPh_3 (3.1 mmoles), 20 ml n-BuOH, and 20 ml of 4.4 N $HClO_4$ were charged into a thermostated reactor furnished with an agitator. The mixture was stirred for 1 h at 40°C in a N_2 atmosphere. A yellow-cream residue precipitated. It was filtered, washed with ether, and dried in the current of an inert gas. 0.51 g of the residue was isolated and identified as the complex (IV). The yield was 45%. 0.41 g of an unidentified complex was isolated from the filtrate. Its yield, based on Pd, was 39%. Found: Pd 9.91; P 7.81%; P/Pd = 2.70.

Preparation of $Pd(PPh_3)_3 \cdot HClO_4$ (V). 1154 mg of $Pd(PPh_3)_4$ (1 mmole), 10 ml of n-BuOH, and 10 ml of 4.4 N $HClO_4$ were charged into a thermostated reactor. The mixture was swept with Ar and stirred for 1 h at 40°C. After completing the reaction, the precipitate was filtered and washed with two portions of EtOH, with two or three drops of HOAc added to it. It was then washed with Et_2O and dried in vacuum. 0.865 g of a yellow-green precipitate was obtained. The yield, based on Pd, was 87.1%. Found: Pd 10.71; P 9.21; Cl 3.4%; P/Pd = 2.95; Cl/Pd = 0.96. $C_{54}H_{46}O_4ClP_3Pd$. Calculated: Pd 10.72; P 9.37; Cl 3.57%. IR spectrum ν ClO_4^- 1080 cm^{-1}.

Interaction of (V) with $Ph\text{-}NO_2$. It was carried out in the same way as the interaction of complex (II) with $Ph\text{-}NO_2$. 1 g of a yellow precipitate was obtained. It was identified as complex (IV) by elemental analysis and by IR spectra. The yield, based on Pd, was 90%.

CONCLUSIONS

We investigated the transformations of catalysts based on palladium complexes under the conditions of the catalytic reduction of nitrobenzene by carbon monoxide (II). We established that the reduced forms of the catalyst are $Pd_2(PPh_3)_4(CO) \cdot H_2SO_4$ and $Pd_2(PPh_3)_4(CO) \cdot HClO_4$, while the reduced forms are $Pd(PPh_3)_2SO_4$ and $Pd(PPh_3)_3(H_2O)(ClO_4)_2$ in the sulfate and the perchlorate media, respectively.

LITERATURE CITED

1. A. I. Min'kov, N. K. Eremenko, and O. A. Efimov, Dokl. Akad. Nauk SSSR, 283, 160 (1985).
2. A. I. Min'kov, N. K. Eremenko, S. E. Merkur'eva, and O. A. Efimov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1347 (1986).
3. A. I. Min'kov, O. A. Efimov, N. K. Eremenko, and E. B. Klimenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 9, 2075 (1987).
4. V. N. Zudin, V. D. Chinakov, V. M. Nekipelov, et al., J. Organomet. Chem., 289, 425 (1985).
5. F. Cariati, R. Ugo, and F. Bonati, Inorg. Chem., 5, 1128 (1966).
6. P. Zdunneck, A. Häster, and E. Venschun, Z. Chem., 26, No. 8, 302 (1986).
7. A. V. Bulatov, M. V. Klyuev, and M. L. Khidekel', Kinet. Katal., 28, No. 2, 263 (1987).
8. D. V. Sokol'skii, ed., Hydrogenation Catalysts [in Russian], Nauka, Alma-Ata (1975) p. 307.
9. A. V. Bulatov, 7th Coll. French—Soviet Catal., Strasbourg, 1, 81, September 21-26 (1986).
10. V. A. Klimova, The Fundamental Microanalytical Methods for Organic Compounds [in Russian], Khimiya, Moscow (1975), p. 222.
11. V. A. Likholobov, N. K. Eremenko, and V. N. Zudin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk., No. 7, 102 (1976).