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SELECTIVE HYDROGENATION OF NITROBENZENE IN APROTIC MEDIA

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UDC 541.127:542.941.7:547.546

The kinetics of hydrogenation of nitrobenzene in aprotic media was studied, and a scheme of the mechanism and a kinetic equation, corresponding to it, for the initial reaction rate are proposed. High selectivity with respect to N-phenylhydroxylamine is apparently due to the aprotic nature and donor properties of the solvent and also to the functioning of the catalyst as a unique "hydrogen electrode."

In [1], the hydrogenation of nitrobenzene (NB) catalyzed by the product of reduction of the complex $Pt(DMSO)_2Cl_2$ by sodium borohydride in DMSO (dimethyl sulfoxide) was studied, and conclusions were drawn concerning the reasons for acceleration of the reaction by additions of quinones. In the present paper, data of kinetic investigations are presented, and a possible scheme of the process is proposed.

EXPERIMENTAL

The following complexes were used: $Pt(DMSO)_2Cl_2$ (I), $Pt(DMS)_2Br_4$ (II), $Pt(PQ)_2Cl_2$ (III), $Pt(Ml)_2$ (IV), and $Pt(Al)_2$ (V), where DMS is dimethyl sulfide, PQ is 9,10-phenanthrene quinone, Ml is 3-hydroxy-2-methyl-γ-pyrone (maltol), and Al is 1,2-dihydroxy-9,10-anthraquinone (alizarin). Complexes (III) and (IV) were synthesized according to [2], and (V) was synthesized according to [3]. The synthesis of (I) and (II) and the main experimental procedures are described in [1].

Before use in the reaction, (I) and (II) were reduced by sodium borohydride [$NaBH_4$:Pt = 3:1 (molar ratio)], and (III)-(V) were reduced by H_2 for 15 min.

The catalysts Pt/C, Ir/C, Pd/C, and Os/C containing 1 wt. % metal and Raney nickel were prepared according to [4]. Catalytic poisons were removed from water and heavy water by heating over 5% Pt/C. Kinetic measurements were carried out at 40°C and 0.1 MPa H_2, and the concentration of the complex was $4 \cdot 10^{-3}$ M.

RESULTS AND DISCUSSION

In [2], it was noted that (III) and (IV) in DMA (dimethylaniline), DMSO, pyridine (Py), and HMPA (hexamethylphosphoric triamide) are completely dissociated. A study of the current-voltage characteristics of complex (V) showed that in these solvents it also is dissociated. We could expect that the catalytic properties of (III)-(V), (I), and (II) with additions of appropriate ligands would be close, which was in fact observed (Table 1).

The product of the reduction of (I)-(V) was apparently a colloid of metallic platinum (particle size ≥400 Å), which did not undergo sedimentation during ultracentrifugation

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N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka Branch. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, pp. 45-48, January, 1991. Original article submitted December 4, 1989.

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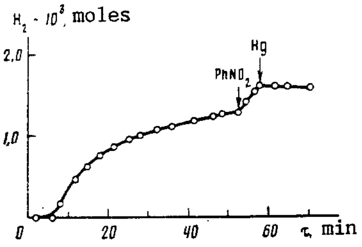

Fig. 1

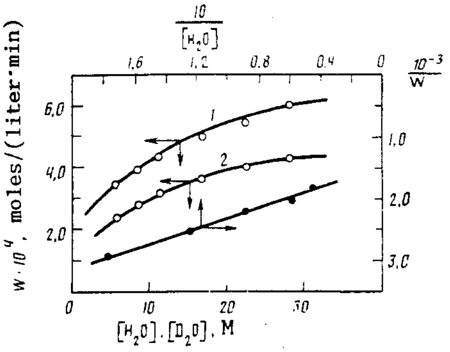

Fig. 2

Fig. 1. Kinetic curve of hydrogen adsorption during hydrogenation of NB (C_0 = 0.066 M) in DMSO (10 ml) catalyzed by product of reduction of (I) ([Pt] = $2 \cdot 10^{-2}$ M). The arrows denote the place of addition of NB and Hg.

Fig. 2. Relation of initial rate of hydrogenation of NB (C_0 = 0.1 M) at [Pt] = $2 \cdot 10^{-2}$ M to initial concentration of H_2O (1) or D_2O (2) in DMSO (10 ml) and anamorphosis 1 in coordinates $1/W_0 \sim 1/[H_2O]_0$.

TABLE 1. Specific Activities of Platinum Catalysts in Hydrogenation of NB (C_0 = 0.1 M) in Aprotic Solvents (volume of liquid phase 10 ml)

No.	Solvent	DN_{SbCl_5}	$A \cdot 10$, moles/mole of Pt·min				
			(I) *	(II) *	(III)	(IV)	(V)
1	DMF	26,6	–	–	21,2	5,0	15,1
2	DMA	27,8	1,9	1,9	27,5	9,1	20,3
3	DMSO	29,8	3,7	3,7	33,8	15,0	25,6
3a	DMSO + PQ**		32.9	32,6	–	–	–
3b	DMSO + Ml**		14,8	14,6	–	–	–
3c	DMSO + Al**		25,7	25,3	–	–	–
4	Py	33,1	8,3	8,2	41,8	20,4	37,5
5	HMPA	38,8	10,0	9,9	150,4	62,6	102,6

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*Initial 1,4-benzoquinone concentration 0.05 M.

**Pt:additive molar ratio = 1:2.

(20,000 g for 2 h), but was decolorized and lost catalytic activity (Fig. 1) after treatment with metallic mercury. Unlike most known ones, the investigated colloids were stabilized by the solvent.

In DMA, DMSO, Py, and HMPA, colloids (I)-(V) catalyzed the hydrogenation of NB with formation of N-phenylhydroxylamine (PHA) (up to 98%) and azoxybenzene. The specific activity of the catalysts increased in parallel to the donor number of the solvent that was used (Table 1).

The hydrogenation of NB was autocatalytic (Fig. 1) and was accelerated by the reaction product (H_2O); additions of D_2O also acted similarly, but the reaction rate in this case was 1.4-fold lower (Fig. 2). Unlike additions of quinones, hydroquinones, and phenols, additions of H_2O can lead to the formation of aniline [1]. These data agree with the hypothesis of [1] and [5] concerning the action of water, phenols, hydroquinones, and their quinone percursors as proton donors.

Considering colloids (I)-(V) as a unique "hydrogen electrode" [5], we can propose the following scheme for description of the NB hydrogenation process in aprotic media:

a) colloid catalyst K activates hydrogen with accumulation of electrons

$$K + H_2 \overset{K_1}{\rightleftharpoons} K^* + 2H^+;$$

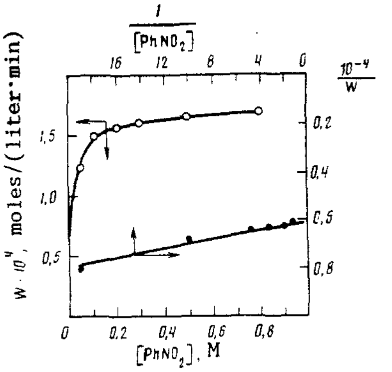

Fig. 3

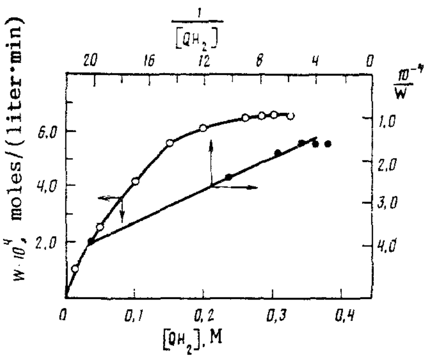

Fig. 4

Fig. 3. Relation of initial rate of hydrogenation of NB in DMSO (10 ml) in presence of 0.1 M 1,4-hydroquinone and [Pt] = $2 \cdot 10^{-2}$ M to initial concentration of NB and anamorphosis in coordinates $1/W_0 \sim 1/[PhNO_2]_0$.

Fig. 4. Relation of initial rate of hydrogenation of NB (C_0 = 0.1 M) at [Pt] = $2 \cdot 10^{-2}$ M to initial 1,4-benzoquinone concentration (QH_2) in DMSO (10 ml) and anamorphosis in coordinates $1/W_0 \sim 1/[QH_2]$.

b) $PhNO_2$ (C) associates with K*, forming in the composition of the associate $PhNO_2^{\cdot-}$:†

$$K^* + C \overset{K_2}{\rightleftharpoons} KC^{**};$$

c) $PhNO_2^{\cdot-}$ is irreversibly protonated by proton donor QH_2 (hydroquinones, water, etc.) with acidity constant K_a with the formation of $PhNO_2H^{\cdot}$(PK) which is the product of limiting steps (taking into account that it is reduced more facilely than $PhNO_2$ [6])

$$KC^{**} + QH_2 \xrightarrow{k_3} PK + QH^-.$$

With the completely probable assumption that [KC**] ≪ [C], such a scheme leads to an expression for the initial reaction rate

$$W_0 = \frac{K_1K_2k_3[K]_0[C]_0[H_2]_0[BH]_0}{K_a \cdot [BH]_0 + K_1[H_2]_0 + K_1K_2[C]_0[H_2]_0},$$

reflecting the actually observed linear anamorphoses in coordinates $1/W_0 \sim 1/[C]_0$, $1/W_0 \sim 1/[BH]_0$ (Figs. 2-4) and the process of W_0 reaching a limit with increasing $[C]_0$ and $[BH]_0$ (Figs. 3 and 4).

The concepts of the studied colloid as a unique "hydrogen electrode" [5] and the analogy between hydrogenation and electrochemical reduction of NB [1, 5] lead to an understanding that in the presence of catalysts similar to the studied ones PhA may be the final product of the hydrogenation process in media with limited proton concentration (aprotic solvents).

On catalyst active centers, the resulting PHA can also undergo other conversions, e.g., disproportionation [7]. Because of its donor properties, an aprotic dipolar solvent can inhibit this process by competing with PHA for catalyst active centers.

Another way of decreasing the rate of disproportionation of PHA may be the creation of systems including a strong base which inhibits adsorption of the weak base (PHA) (e.g., [8]).

The aprotic nature of such solvents may also be useful in inhibition of other processes occurring by a reduction-protonation mechanism, e.g., in hydrogenation of olefins (observed in the case of 1-hexene and 1-octene) or dehydrochlorination of nitrobenzenes [9]. Thus,

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†The radical anion $PhNO_2^{\cdot-}$ observed [1] in solution is apparently a result of dissociation of KC**.

aprotic dipolar solvents inhibit dehydrochlorination during hydrogenation of chloronitrobenzenes.

It is understood that these possibilities of aprotic dipolar solvents can be realized during hydrogenation only for catalysts functioning as "hydrogen electrodes." Thus, not only the studied platinum colloid, but also the catalysts with low (≤1%) Pt, Ir, and Os contents probably function in the same way. Thus, for example, during hydrogenation of NB catalyzed by catalysts containing ≤1% Ir, Os, or Pt on carbon in DMSO, the selectivity with respect to PHA reached 93-95% (only 85% for 5% Pt/C). Apparently, nickel and palladium activated the hydrogen by a different mechanism: The selectivity with respect to PHA during hydrogenation of NB in the presence of 1% Pd/C or Raney nickel in DMSO was ≤40%.

Thus, the catalysts functioning as "hydrogen electrodes" together with the aprotic dipolar solvents are efficient catalytic systems for selective hydrogenation of substrates undergoing conversion by a reduction-protonation mechanism. The action of such systems can be predicted on the basis of analogies between hydrogenation and electrochemical reduction.

The author thanks V. V. Strelets for useful discussion.

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