KINETICS AND MECHANISM OF HYDROGENATION OF NITROBENZENE BY [DIAQUOCOBALOXIME + AMINE] SYSTEM

Stanislaw TYRLIK[a], Michal KWIECIŃSKI[a] and Lech KAWCZYŃSKI

[a] *Institute of Organic Chemistry, Polish Academy of Sciences, 00—961 Warsaw, Poland and*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, 00—961 Warsaw, Poland*

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The initial rate of nitrobenzene hydrogenation catalyzed homogeneously by cobaloximes is second order in cobalt and is inhibited by an excess of nitrobenzene. It also strongly depends upon cobaloxime: amino ratio. These observations were rationalized in terms of binuclear nitrobenzene--complexed intermediate as crucial in the catalytic cycle. This assumption was further supported by the unusual selectivity of cobaloxime system, which does not catalyze hydrogenation of *ortho*--substituted nitrobenzenes.

Cobaloximes are known to catalyze hydrogenation of variety of substances. Kinetics of some of these reactions, such as hydrogenation of styrene[1] (Eq. (*A*)), hydrogenation of dimethylglyoxime ligand (dmgH) in cobaloxime[2] (Eq. (*B*)), reaction of hydrogen with hydroxide ions in the presence of cobaloxime[3] (Eq. (*CC*)) and hydrogenation of benzil[4] (Eq. (*D*)), has been studied.

$$Co(dmgH)_2{\cdot}B + C_6H_5CH{=}CH_2 + H_2 \rightarrow C_6H_5CH_2CH_2Co(dmgH)_2{\cdot}B \qquad (A)$$

$$Co(dmgH)_2 + H_2 \rightarrow Co(dmgH)(C_4H_9N_2O_2) \rightarrow$$
$$\rightarrow Co(dmgH)(C_4H_9N_2O) \rightarrow \text{3-aminobutanone oxime} \qquad (B)$$

$$OH^- + H_2 \xrightarrow{\text{cobaloxime}} H_2O \qquad (C)$$

$$C_6H_5COCOC_6H_5 + H_2 \xrightarrow{\text{cobaloxime}} C_6H_5CH(OH)COC_6H_5 \qquad (D)$$

Reactions (*A*)—(*C*) were found to be second order in cobalt but the reaction (*D*) is first order in cobalt. Hydrogenation of styrene and 1,3-cyclohexadiene[2] proceeds by mechanism involving no interaction of the organic molecule to be hydrogenated with cobaloxime. To date, kinetics of the known[5] hydrogenation of nitrobenzene has not been studied.

This paper describes kinetics and mechanism of catalytic hydrogenation of nitrobenzene (Eq. (*E*)).

$$C_6H_5NO_2 + H_2 \xrightarrow{\text{cobaloxime}} C_6H_5NH_2 \qquad (E)$$

Reaction (*E*) is a multistep process; aniline synthesis involves several hydrogen molecules and proceeds through several intermediates. However, it is very likely that reaction of the first hydrogen molecule with $C_6H_5NO_2$ is the rate limiting process: the first intermediate, once formed, will react much faster with hydrogen giving rise eventually to aniline. The mechanism proposed in this paper describes this very first step of the reaction; this step involves the interaction of nitrobenzene with cobaloxime.

EXPERIMENTAL

Chemicals. Acetone used as a solvent was distilled, degassed and stored under hydrogen. Diaquocobaloxime *I* was prepared according to Schrauzer[6]. Nitrobenzene and morpholine were distilled and degassed before use. All other aromatic nitro-compounds were reagent grade chemicals and were used without further purification. Hydrogen was purified by passing through BTS catalyst and A4 molecular sieves.

Apparatus and procedure. Kinetic measurements were carried out on a hydrogenation apparatus provided with an automatic registration of pressure drop in hydrogen reservoir. This reservoir was connected to an isothermal bath reactor by means of a valve assuring constant pressure to be maintained in the reactor. The H_2 uptake was followed for about 25 min. Uptakes amounted to 20 : 250 ml of hydrogen.

Standard kinetic experiment. Compound *I* (0·2 g, 0·6 mmol) was introduced under hydrogen to the reaction flask. Acetone (12 ml) was siphoned to the flask. Then, 0·097 ml (1·14 mmol) of morpholine was added and the mixture stirred for 10 min, 1·25 ml (12 mmol) of nitrobenzene were injected by hypodermic syringe. Absorption of hydrogen started without any induction period.

RESULTS AND DISCUSSION

Preparation of Catalyst — Reaction of Diaquocobaloxime with Morpholine

Preparation of the catalyst consists of the reaction of amines with diaquocobaloxime (Eq. (*F*)). Among variety of amines morpholine gives rise to rather efficient catalyst. Standard catalytic reaction goes to completion with approx. 4 hours. This was the reason why morpholine was selected for preparing the catalyst. The reaction of morpholine with *I* in acetone proceeds according to Eqs (*G*) and (*H*).

$$Co(II)(dmgH)_2.2\,H_2O + \text{amine} \rightarrow \text{cat.} \qquad (F)$$

$$\underset{I}{Co(dmgH)_2.2\,H_2O} + MR \overset{K_1}{\rightleftharpoons} \underset{II}{Co(dmgH)_2MR\cdot solv} + H_2O \qquad (G)$$

$$\underset{II}{Co(dmgH)_2MR\cdot solv} + MR \overset{K_2}{\rightleftharpoons} \underset{III}{Co(dmgH)_2(MR)_2} \qquad (H)$$

Mono- and dimorpholine mononuclear complexes *II* and *III* were detected[7] in solution by EPR. This observation is in agreement with general coordination chemistry of this system[8]. Formation of diamagnetic dimer $[Co(dmgH)_2MR]$ according to Eq. (*I*) is a reasonable assumption[7].

$$2\,\underset{II}{Co(dmgH)_2MR\cdot solv} \overset{K_3}{\rightleftharpoons} \underset{IV}{[Co(dmgH)_2MR]_2} \qquad (I)$$

Kinetics of H_2 Uptake

Initial reaction rate has been measured as function of the concentration of morpholine, *I* and $C_6H_5NO_2$·Morpholine : cobalt ratio has a very pronounced influence on the rate of reaction (*E*), as illustrated in Fig. 1. For the amine : Co ratio > 8 there is no catalysis. In this range only the dimorpholine complex is present in solution, as proved[9] by EPR. $Co(dmgH)_2(MR)_2$ is not, therefore, a catalyst for this hydrogenation. This is in agreement with the earlier results concerning the lack of any reaction between $Co(dmgH)_2(py)_2$ and hydrogen[2]. There is no catalysis with $Co(dmgH)_2$·2 H_2O either.

Accordingly, we selected morpholine : Co ratio = 1·9 for all the subsequent kinetic experiments. Fig. 2 shows the dependence of the initial hydrogenation rate upon cobalt concentration. Reaction is second order in cobalt.

Rate dependence upon $[C_6H_5NO_2]$ is shown in Fig. 3. Here, the maximum in the rate is observed, and for the higher $C_6H_5NO_2$ concentrations the rate decreases. In neat nitrobenzene there is practically no catalysis. Such a drastic change in the rate cannot be attributed to differences in H_2 solubility. Kinetics of H_2 uptake in dependence on hydrogen pressure has not been studied.

Complexes Formed in Catalyst Solution

Complexes formed during preparation of the catalyst were mentioned in previous section. Hereunder we discuss the intermediates formed: *a*) in the reaction of nitrobenzene with the morpholine-complexed cobaloxime and *b*) in the reaction of hydrogen with the morpholine and nitrobenzene-complexed cobaloxime.

The reaction of $C_6H_5NO_2$ with *II* and *IV* can proceed according to equations (*J*)–(*N*). EPR investigations revealed that neither $Co(dmhH)_2.2\,H_2O$-*I* nor $Co(dmgH)_2(morpholine)_2$-*III* interact with nitrobenzene.

$$II + C_6H_5NO_2 \overset{K_4}{\rightleftharpoons} [II\cdot C_6H_5NO_2] \qquad (J)$$

$$IV + C_6H_5NO_2 \overset{K_5}{\rightleftharpoons} [IV\cdot C_6H_5NO_2] \qquad (K)$$

$$II + [II\cdot C_6H_5NO_2] \overset{K_6}{\rightleftharpoons} [IV\cdot C_6H_5NO_2] \qquad (L)$$

$$[IV\cdot C_6H_5NO_2] + C_6H_5NO_2 \overset{K_7}{\rightleftharpoons} [IV\cdot C_6H_5NO_2]_2 \qquad (M)$$

$$[IV\cdot H_2] + C_6H_5NO_2 \overset{K_8}{\rightleftharpoons} [IV\cdot C_6H_5NO_2\cdot H_2] \qquad (N)$$

$[II\cdot C_6H_5NO_2]$ is a product of the reaction of the monoamine cobaloxime with nitrobenzene of the stoichiometry $Co(dmgH)_2(morpholine)C_6H_5NO_2$ which should be

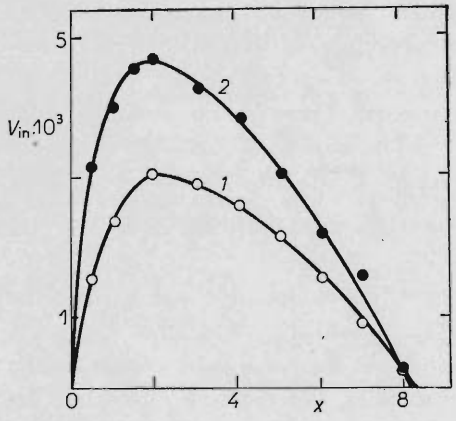

FIG. 1

Initial rate (V_{in}, mol dm^{-3} s^{-1}) of nitrobenzene hydrogenation) *versus* morpholine: Co molar ratio. Solvent acetone; [Co] = = 5 . 10^{-2} mol/l; [$C_6H_5NO_2$] = 0·75 mol/l (curve *1*), 1·00 mol/l (curve **2**); 20 ± 0·1°C; p_{H_2} = 0·1 MPa; x = [morpholine : Co].

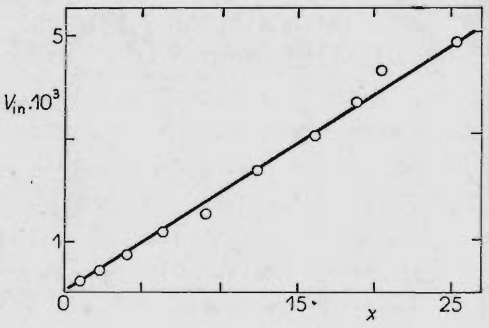

FIG. 2

Initial rate (V_{in}, mol dm^{-3} s^{-1}) of nitrobenzene hydrogenation *versus* square of cobaloxime concentration. Solvent acetone; [$C_6H_5NO_2$] = 1·25 mol/l; morpholine : Co molar ratio = 1·9; 20 ± 0·1°C; p_{H_2} = = 0·1 MPa; x = $[Co(dmhH)_2(H_2O)_2]^2$ . . (10^4 mol^2 dm^6).

paramagnetic. $[IV{\cdot}C_6H_5NO_2]$ – is a diamagnetic dimer $[Co(dmgH)_2(morpholine]. .C_6H_5NO_2$ in which one molecule of nitrobenzene interacts with dimeric cobaloxime. Formation of this dimer has been already suggested[9]. In $[IV(C_6H_5NO_2)_2]$ two molecules of nitrobenzene interact with the cobaloxime dimer. Postulated structures of $[II{\cdot}C_6H_5NO_2]$, $[IV{\cdot}C_6H_5NO_2]$ and $[IV{\cdot}2\ C_6H_5NO_2]$ are shown in Fig. 4.

Interaction of nitrobenzene with Co(II) center in Shiff base complexes was recently described[10]. Bonding is achieved by means of donating electrons from the oxygen atom of the nitro group and by the interaction of nitrobenzene phenyl ring with the phenyl ring of salen ligand. Our proposal is quite analogous to the bonding picture described by Das[10]. However, because of the lack of phenyl–phenyl interaction in cobaloxime complexes the stability of $[II{\cdot}C_6H_5NO_2]$ should be inferior to the stability of $[IV{\cdot}C_6H_5NO_2]$, where the nitro group is connected to two cobalt centers.

Compounds mentioned in Eqs $(J)-(N)$ are considered as well reasonable products of the interaction of $C_6H_5NO_2$ with cobaloxime. Not all of them are very likely to be formed. They are postulated in order to get a picture of nitrobenzene interaction with cobaloximes as complete as possible.

Hydrogen can interact with cobaloximes according to Eqs $(O)-(R)$.

$$II + H_2 \overset{K_9}{\rightleftharpoons} [II{\cdot}H_2] \qquad (O)$$

$$IV + H_2 \overset{K_{10}}{\rightleftharpoons} [IV{\cdot}H_2] \qquad (P)$$

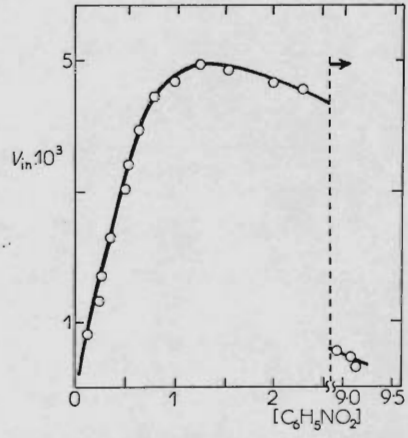

FIG. 3

Initial rate (V_{in}, mol dm^{-3} s^{-1}) of nitrobenzene hydrogenation *versus* nitrobenze concentration (mol dm^{-3}). Solvent acetone; [Co] = 5 . 10^{-2} mol/l; morpholine : Co molar ratio = 1·9; 20 ± 0·1°C; p_{H_2} = 0·1 MPa

$$[II{\cdot}C_6H_5NO_2] + H_2 \overset{K_{11}}{\rightleftharpoons} [II{\cdot}C_6H_5NO_2{\cdot}H_2] \qquad (Q)$$

$$[IV{\cdot}C_6H_5NO_2] + H_2 \overset{K_{12}}{\rightleftharpoons} [IV{\cdot}C_6H_5NO_2{\cdot}H_2] \qquad (R)$$

$[II{\cdot}H_2]$ was considered by Simándi[2] as short-lived "collision" complex. We already proposed[11] very likely bonding picture for $[II{\cdot}H_2]$. In $[IV{\cdot}C_6H_5NO_2{\cdot}H_2]$ bonding of H_2 can be strictly analogous to $[II{\cdot}H_2]$. This is shown in Fig. 5.

Hydrogen Transfer Reactions

The most complete picture of reasonable modes of hydrogen transfer is given below: *a*) reactions of the cobaloxime activated nitrobenzene with nonactivated hydrogen

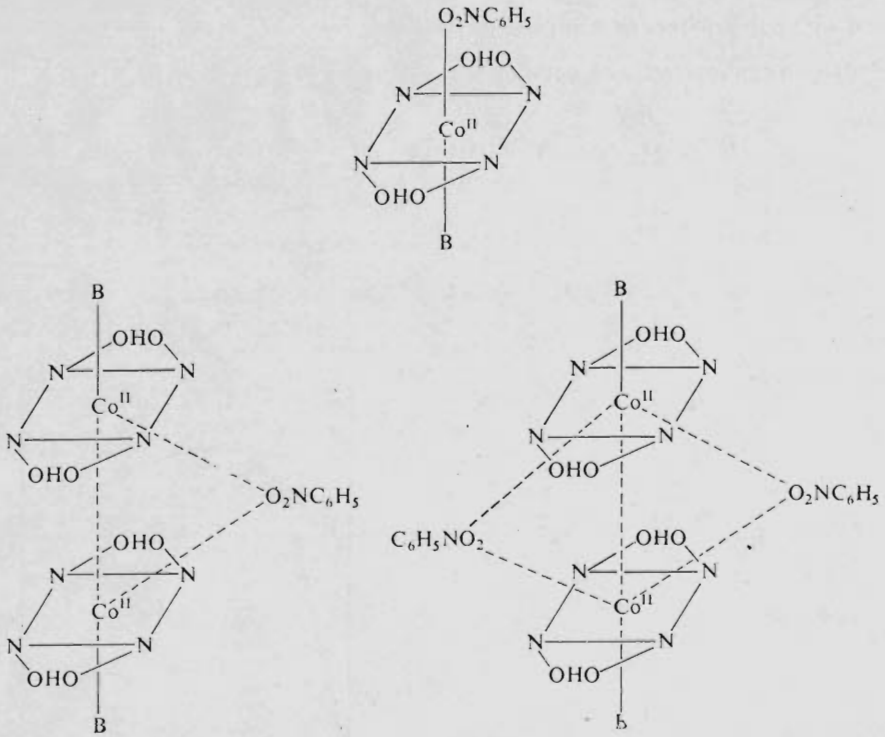

FIG. 4

Postulated structures of nitrobenzene complexed intermediates

(Eqs (*S*) and (*T*)), *b*) reactions of cobaloxime activated hydrogen with nonactivated nitrobenzene (Eq. (*U*)), *c*) reactions of cobaloxime activated hydrogen with cobaloxime activated nitrobenzene (Eqs (*V*)–(*Z*)).

$$[II{\cdot}C_6H_5NO_2] + H_2 \xrightarrow{k_a} II + \text{products} \qquad (S)$$

$$[IV{\cdot}C_6H_5NO_2] + H_2 \xrightarrow{k_b} 2\,II + \text{products} \qquad (T)$$

$$[II{\cdot}H_2] + C_6H_5NO_2 \xrightarrow{k_c} II + \text{products} \qquad (U)$$

$$[II{\cdot}C_6H_5NO_2] + [II{\cdot}H_2] \xrightarrow{k_d} 2\,II + \text{products} \qquad (V)$$

$$[IV{\cdot}C_6H_5NO_2] + [II{\cdot}H_2] \xrightarrow{k_e} 3\,II + \text{products} \qquad (X)$$

$$[II{\cdot}C_6H_5NO_2{\cdot}H_2] \xrightarrow{k_f} II + \text{products} \qquad (Y)$$

$$[IV{\cdot}C_6H_5NO_2{\cdot}H_2] \xrightarrow{k_g} 2\,II + \text{products} \qquad (Z)$$

Rate Equations and Their Analysis

Although there are no precise kinetic data concerning the rates of reactions (*G*)–(*I*) it is quite likely that they are much faster compared to any hydrogen transfer process.

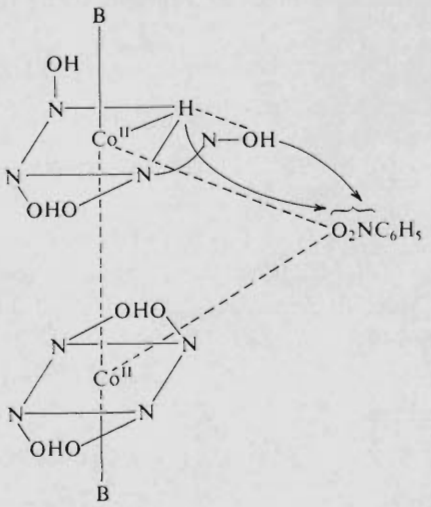

FIG. 5

Mode of hydrogen activation and transfer in nitrobenzene complexed dimeric cobaloxime

In order to assure completeness of $(G)-(I)$ one can wait long enough after morpholine has been added during the catalyst preparation. Reactions with nitrobenzene are probably also very fast: the addition of nitrobenzene to the solution of the catalyst brings about instantaneous change of EPR spectrum[9]. Hydrogen involved preequilibria $(O)-(R)$ were considered[2] as fast reactions. We therefore assume that hydrogen transfer is the rate determining process. Kinetic analysis has been performed based on this assumption.

For different types of hydrogen transfer one can write Eqs $(1a)-(7a)$ – square brackets denote concentrations.

$$v_a = k_a[II\cdot C_6H_5NO_2][H_2] \qquad (1a)$$

$$v_b = k_b[II\cdot C_6H_5NO_2][H_2] \qquad (2a)$$

$$v_c = k_c[II\cdot H_2][C_6H_5NO_2] \qquad (3a)$$

$$v_d = k_d[II\cdot C_6H_5NO_2][II\cdot H_2] \qquad (4a)$$

$$v_e = k_e[IV\cdot C_6H_5NO_2][II\cdot H_2] \qquad (5a)$$

$$v_f = k_f[II\cdot C_6H_5NO_2\cdot H_2] \qquad (6a)$$

$$v_g = k_g[IV\cdot C_6H_5NO_2\cdot H_2] \qquad (7a)$$

Concentration of the cobalt introduced initially as diaquocobaloxime I_0 is equal to the sum of concentrations of all the cobalt-containing intermediates (Eq. $(8a)$).

$$[I_0] = [I] + [II] + [III] + [II\cdot C_6H_5NO_2] + [II\cdot H_2] + 2[IV] + 2[IV\cdot C_6H_5\cdot H_2] + 2[IV\cdot H_2] + 2[IV\cdot H_2] + [II\cdot C_6H_5NO_2\cdot H_2] + 2[IV\cdot (C_6H_5NO_2)_2] \qquad (8a)$$

On the basis of Eqs $(G)-(R)$ we can express concentrations of all the intermediates by $[II]$, $[C_6H_5NO_2]$, $[H_2]$ and by relevant equilibrium constants.

Introducing concentrations of all the respective intermediates into Eq. $(8a)$ we get Eq. (9)

$$a\cdot[II]^2 + b\cdot[II] - c\cdot[I_0] = 0 \qquad (9)$$

where

$$a = 2K_3(1 + K_5\cdot[C_6H_5NO_2] + K_5\cdot K_{12}\cdot[C_6H_5NO_2]\cdot[H_2] + K_5\cdot K_7\cdot[C_6H_5NO_2]^2 + K_{10}\cdot[H_2] \qquad (10)$$

$$b = 1 + \frac{1}{K_1[\mathrm{MR}]} + K_2 \cdot [\mathrm{MR}] + K_4 \cdot [\mathrm{C_6H_5NO_2}] + K_9 \cdot [\mathrm{H_2}] + \\ + K_{11} \cdot K_4 \cdot [\mathrm{C_6H_5NO_2}] \cdot [\mathrm{H_2}] \qquad (11)$$

if one puts:

$$A_1 = \frac{1}{K_1 \cdot [\mathrm{MR}]}\,; \quad A_2 = K_2 \cdot [\mathrm{MR}]$$

$$b = 1 + A_1 + A_2 + K_4 \cdot [\mathrm{C_6H_5NO_2}] + K_9 \cdot [\mathrm{H_2}] + \\ + K_{11} \cdot K_4 \cdot [\mathrm{C_6H_5NO_2}] \cdot [\mathrm{H_2}] \qquad (11a)$$

Root of square equations (*9*) is given by Eq. (*12*), which can be approximated by the first order term in Taylor series as Eq. (*13a*). [*II*] is therefore equal to Eq. (*13b*).

$$[II] = \frac{-b + \sqrt{\{b^2 + 4a[I_0]\}}}{2a} \qquad (12)$$

TABLE I

Rate of hydrogenation (v in mol dm^{-3} s^{-1}) of substituted nitrobenzenes of the type *o*-(*m*,*p*)-$\mathrm{RC_6H_4NO_2}$, [Co] = 5 . 10^{-2} mol/l; morpholine: Co mol. ratio = 1·9; $\mathrm{RC_6H_4NO_2}$: Co mol. ratio = 30; $p_{\mathrm{H_2}}$ = 0·1 MPa; t = 20 ± 0·1°C

No	R[a]	v . 10^3 [b]	
		meta	*para*
1	—$\mathrm{NH_2}$	4·56	3·55
2	—$\mathrm{NHNH_2}$	4·97	3·95
3	—$\mathrm{CH_3}$	5·32	4·82
4	—$\mathrm{OCH_3}$	5·18	4·97
5	—$\mathrm{OC_2H_5}$	5·11	5·32
6	—$\mathrm{COCH_3}$	5·32	5·41
7	—$\mathrm{COOCH_3}$	4·97	5·62
8	—CHO	4·62	5·74
9	—Cl	4·82	6·30
10	—Br	4·96	6·30

[a] v For nitrobenzene = 5·68 . 10^{-3} mol dm^{-3} s^{-1}; [b] all the *ortho*-substituted nitrobenzenes were unreactive.

$$[II] \approx \frac{-b + b\left(1 + \frac{2a[I_0]}{b^2}\right)}{2a} \approx \frac{[I_0]}{b} \qquad (13a)$$

$$[II] = \frac{[I_0]}{1 + A_1 + A_2 + K_9[H_2] + K_4(1 + K_{11}[H_2]\,[C_6H_5NO_2]} \qquad (13b)$$

Concentrations of all remaining intermediates *III*, *IV etc.* are therefore also functions of $[I_0]$, $[C_6H_5NO_2]$, $[H_2]$ and relevant equilibrium constants.

Equations (S)–(Z) take the following forms $(1b)$–$(7b)$, where const_1 and const_2 are the corresponding polynomials and the products of polynomials containing constant components.

$$v_a = k_a K_4 \frac{[I_0]\,[C_6H_5NO]\,[H_2]}{\text{const}_1 + \text{const}_2[C_6H_5NO_2]} \qquad (1b)$$

$$v_b = k_b K_3 K_5 \frac{[I_0]^2\,[C_6H_5NO_2]\,[H_2]}{(\text{const}_1 + \text{const}_2[C_6H_5NO_2])^2} \qquad (2b)$$

$$v_c = k_c K_9 \frac{[I_0]\,[C_6H_5NO_2]\,[H_2]}{\text{const}_1 + \text{const}_2[C_6H_5NO_2]} \qquad (3b)$$

$$v_d = k_d K_9 \frac{[I_0]\,[C_6H_5NO_2]\,[H_2]}{(\text{const}_1 + \text{const}_2[C_6H_5NO_2])^2} \qquad (4b)$$

$$v_e = k_e K_3 K_5 K_9 \frac{[I_0]^3\,[C_6H_5NO_2]\,[H_2]}{(\text{const}_1 + \text{const}_2[C_6H_5NO_2])^3} \qquad (5b)$$

$$v_f = k_f K_4 K_1 \frac{[I_0]\,[C_6H_5NO_2]\,[H_2]}{\text{const}_1 + \text{const}_2[C_6H_5NO_2]} \qquad (6b)$$

$$v_g = k_g K_3 K_8 K_{10} \frac{[I_0]^2\,[C_6H_5NO_2]\,[H_2]}{(\text{const}_1 + \text{const}_2[C_6H_5NO_2])^2} \qquad (7b)$$

Equations $(1b)$, $(3b)$ and $(6b)$ show linear dependence of the rate on $[I_0]$. The rate increases monotonously with $[C_6H_5NO_2]$ and approaches a constant value. No decrease in the rate should be observed. Both these dependencies are not in agreement with experiment and mechanisms giving rise to Eqs (S), (U) and (Y) should be excluded. This is also the case of Eq. (X) which implies the inhibition by an excess of $C_6H_5NO_2$ but shows third order dependence on cobalt.

There are three possible reaction paths in agreement with observed kinetic behaviour: reactions (*T*), (*V*) and (*Z*). Mechanism (*T*) is rather unlikely because it does not imply hydrogen activation. Mechanism (*V*) involves the activation of nitrobenzene on mononuclear cobaloxime and hydrogen on another mononuclear cobaloxime. Both these intermediates should be paramagnetic and should be seen in EPR. Attempts to detect these intermediates have failed. Concentrations of $[II \cdot H_2]$ complex could well be beyond the limit of EPR detection[12] but $[II \cdot C_6H_5NO_2]$ complex, if present, should be detectable by EPR. We already observed[9] that catalysis takes place in solutions showing no EPR absorption, which is an observation against Eq. (*V*), conforming (*Z*), however. Mechanism described by Eq. (*V*) is a bimolecular process in which only collisions of "hydrogen" end of $[II \cdot H_2]$ complex with "nitrobenzene end" of $[II \cdot C_6H_5NO_2]$ complex can give rise to the products. In the light of quite large dimensions of cobaloxime molecule this steric requirement makes Eq. (*V*) unlikely. Only the mechanism (*Z*) is in agreement with the above described experiments.

Attempts to hydrogenate substituted nitrobenzenes gave interesting results. They are shown in Table I.

ortho-Substituted nitrobenzenes, whatever substituent, are not hydrogenated by this system. This observation is also in favour of mechanism (*Z*). In *ortho*-substituted nitrobenzenes steric hindrance prevents the complex $[IV \cdot ortho\text{-}RC_6H_4NO_2]$ to be formed. As a consequence, the most probable reaction path is intermolecular hydrogen transfer within binuclear cobaloxime as the rate determining step. This is shown in Fig. 5.

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REFERENCES

1. Simándi L. J., Budó-Záhonyi E., Szeverenyi Z.: Inorg. Nucl. Chem. Lett. *11*, 773 (1975).
2. Simándi L. J., Budó-Záhonyi E., Szeverenyi Z.: J. Chem. Soc., Dalton *1980*, 276.
3. Simándi L. J., Budó-Záhonyi E., Szeverenyi Z.: Inorg. Nucl. Chem. Lett. *12*, 273 (1976).
4. Tyrlik S., Kucharska M. M., Pietrzycki W., Moskal J.: Abstr. of VII^{ème} Colloque Franco-Polonais sur la Catalyse, Kraków, 4 (1979).
5. Ohgo Y., Takeuchi S., Yoshimura J.: Bull. Chem. Soc. Jap. *44*, 283 (1971).
6. Schrauzer G. N.: Inorg. Syn. *XI*, 64 (1968).
7. Rockenbauer A., Budó-Záhonyi E., Simándi L. J.: J. Chem. Soc., Dalton Trans. *1975*, 1729.
8. Schrauzer G. N.: Accounts Chem. Res. *1*, 97 (1968).
9. Rockenbauer A., Györ M., Tyrlik S., Kwieciński M.: Abstr. of VII^{ème} Colloque Franco-Polonais sur la Catalyse, Kraków, 61 (1979).
10. Das P. K., Das D., De A. K.: J. Indian Chem. Soc. *56*, 651 (1979).
11. Tyrlik S., Kucharska M. M., Wolochowicz I.: J. Mol. Cat. *6*, 393 (1979).
12. Schrauzer G. N., Windgassen R. J.: J. Chem. Soc. *89*, 1842 (1966).