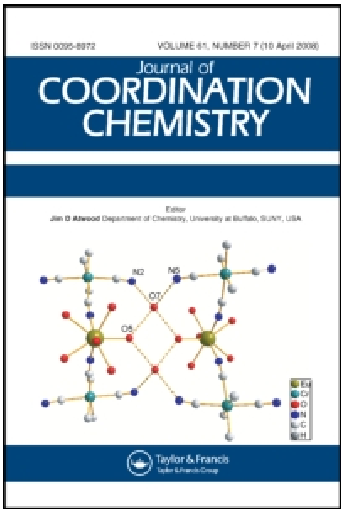

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# EPR STUDY OF THE SYSTEM [DIAQUOCOBALOXIME AMINE] AS A CATALYST FOR THE HYDROGENATION OF NITROBENZENE

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# EPR STUDY OF THE SYSTEM [DIAQUOCOBALOXIME + AMINE] AS A CATALYST FOR THE HYDROGENATION OF NITROBENZENE

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Reaction of cobalt dimethylglyoxime dihydrate with amines gives rise to a catalyst for hydrogenation of nitrobenzene. Solutions of this catalyst in acetone are paramagnetic and EPR spectra of these solutions were measured. The presence of nitrobenzene considerably alters the EPR spectra. It was also observed that electron transfer from cobaloximes to TCNE is only possible in the presence of $PhNO_2$. Changes of the EPR spectra during catalytic process were observed and interpreted.

## INTRODUCTION

Cobalt dimethylglyoxime complexes are known[1] to be catalysts for homogeneous hydrogenation of nitrobenzene. The simplest procedure for the preparation of the catalyst involves interaction of an amine with diaquocobaloxime (I) a well known source of divalent cobalt.[2]

$$Co(dmgH)_2 \cdot 2H_2O + \text{amine} \xrightarrow{\text{acetone}} \text{catalyst} \qquad (1)$$

Products of reaction (1), which are soluble in acetone, catalyze the hydrogenation of $PhNO_2$:

$$PhNO_2 + H_2 \xrightarrow{\text{catalyst}} PhNH_2 \qquad (2)$$

Reaction of pyridine with cobaloxime, probably a methanol solvate $Co(dmgH)_2(CH_3OH)_2$, was studied by EPR.[3] In methanol solution three complexes were observed:

$$Co(dmgH)_2(CH_3OH)_2 + py \xrightarrow{CH_3OH} \underset{(II)}{Co(dmgH)_2py} + \underset{(III)}{Co(dmgH)_2(py)_2} + \underset{(IV)}{pyCo(dmgH)_2 \cdots Co(dmgH)_2py} \qquad (3)$$

and their formation constants measured. Complexes (II) and (III) are paramagnetic; (IV), which is a diamagnetic dimer, results from (II). It was of interest to know whether these same substances are formed in acetone solution.

At present, there is no evidence concerning the mechanism of the catalytic hydrogenation of nitrobenzene and the nature of the catalytically active species. We used EPR as a method of studying the interaction of nitrobenzene with cobaloximes prior to and in the course of the reaction, in order to determine the nature of the catalytically active intermediates.

## EXPERIMENTAL

### *Reagents*

Diaquocobaloxime (I) was prepared according to Schrauzer.[4] Morpholine, pyridine, pyrrolidine, piperidine, aniline, benzylamine, allylamine, t-butylamine, diethylamine as well as nitrobenzene were commercial laboratory reagents and were distilled before use. Acetone, containing 0.5% of $H_2O$, was supplied by POCh Gliwice. Argon, nitrogen and hydrogen were purified by passing successively over BTS catalyst and molecular sieves.

### *Reaction of (I) with Amines in Acetone Solution*

The sample containing 0.2 g (6.1 × $10^{-4}$ M) of (I) was introduced into a 100 ml flask. The flask was flushed several times with nitrogen and 30 ml of acetone was introduced by a hypodermic syringe. (I) is partly soluble in acetone. The appropriate amine in the desired molar ratio was added to the suspension of (I) under vigorous stirring. The complex dissolved completely within several seconds. Concentration of cobalt was 20 mM. Aliquots of acetone solution were transferred to the EPR tubes by applying suction and over-pressure and careful avoiding any contact with air.

### *Standard Catalytic Reaction*

The solutions of cobaloxime amine complexes in acetone were connected to the vacuum system and nitrogen was removed by freeze-pump-thaw cycles at ~170 K. Subsequently hydrogen was introduced and the temperature was raised up to 22–24°C. At this temperature nitrobenzene was added by hypodermic syringe in the molar ratio 1 Co : 60 $PhNO_2$. Absorption of $H_2$ starts without an induction period. Under vigorous stirring 95% conversion to $PhNH_2$ was achieved within about 210–220 min. The same rates and conversions were observed if the preparation of the catalyst was done in an atmosphere of $H_2$, provided that solid cobaloxime was in contact with $H_2$ no longer than 10 min. The kinetics of the reaction were studied at constant pressure, volume and temperature. The hydrogen uptake was monitored automatically. Details of this apparatus will be described in a forthcoming paper.

TABLE I
Conditions for spectra shown in Figures 6 and 7.

| Figure 6 | | | |
|---|---|---|---|
| Spectrum | Field sweep G | Modulation G | Amplification |
| 1 | 3390 ± 50 | 4 | 8.9 · 100 |
| 2 | 3300 ± 1000 | 20 | 4.0 · 100 |
| 3 | 3300 ± 1000 | 20 | 4.0 · 100 |
| 4 | 3390 ± 50 | 0.02 | 1.4 · 100 |
| Figure 7 | | | |
| 1 | 3100 ± 500 | 2 | 32 |
| 2 | 3100 ± 500 | 2 | 50 |
| 3 | 3100 ± 500 | 2 | 100 |
| 1A | 3100 ± 500 | 2 | 63 |
| 2A | 3100 ± 500 | 2 | 63 |
| 3A | 3100 ± 500 | 2 | 63 |

### *EPR Spectra*

The EPR spectra were recorded on the JES-ME-3X type spectrometer in *X* band with a field modulation of 100 kHz. Microwave power was 10 mW. Conditions at which spectra shown in Figures 6 and 7 have been obtained, are given in Table I.

## RESULTS AND DISCUSSION

### *Reaction of Diaquocobaloxime with Amines in Acetone*

A saturated solution of $Co(dmgH)_2 \cdot 2H_2O$ (I) in acetone (~3 × $10^{-4}$ M) at room temperature and under nitrogen does not show any EPR spectrum. However, at liquid nitrogen temperature the spectrum shown in Figure 1 has been obtained. This spectrum is very similar to the spectrum of $Co(dmgH)_2 \cdot (CH_3OH)_2$ in methanol.[3]

Addition of amines considerably increases the solubility of the cobalt complex. As an amine, morpholine (MR) was most commonly used. The EPR spectra of soluble reaction products of $Co(dmgH)_2 \cdot 2H_2O$ with MR in molar ratios 1 : 1, 1 : 2, 1 : 10 are shown in Figure 2. Essentially the same picture was obtained with pyridine, piperidine and pyrrolidine. Reaction with aniline was considerably slower but after appropriate time the spectrum was quite

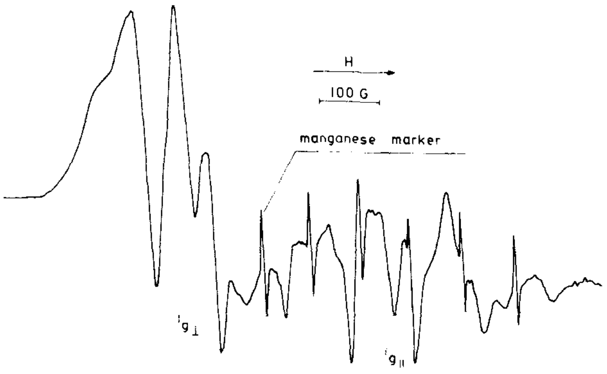

FIGURE 1 EPR spectrum of diaquocobaloxime (I) in frozen acetone solution at 77 K (~3.$10^{-4}$ M).

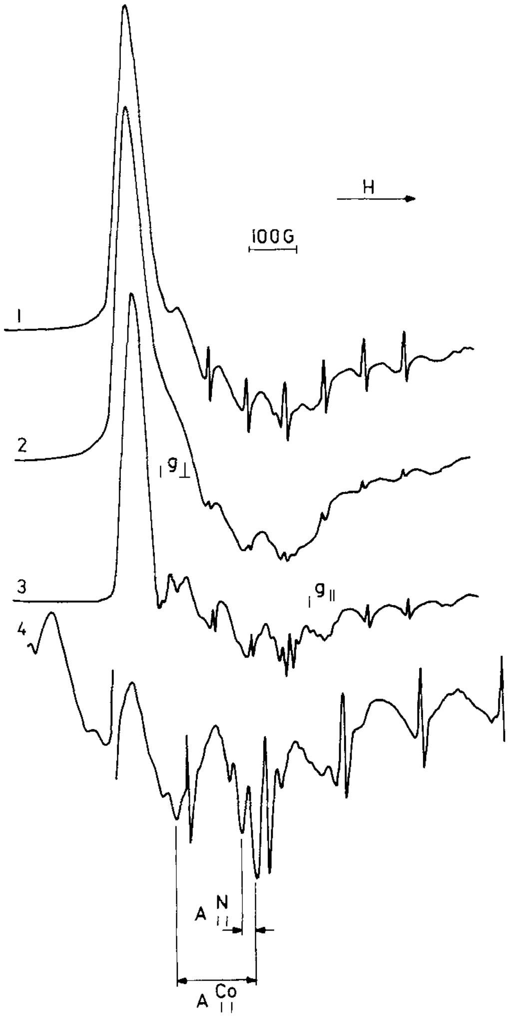

FIGURE 2 EPR spectra of reaction products of (I) with morpholine in molar ratios Co : MR = 1) 1 : 1; 2) 1 : 2; 3) 1 : 10; spectrum 4) – high field part of the spectrum recorded with smaller field sweep. Spectra taken in frozen acetone solution at 77 K with a cobalt concentration of $3.10^{-4}$ M.

analogous to that shown in Figure 2 and very similar to the spectrum obtained for pyridine and picoline complexes in methanol and ethanol.[3,5] For molar ratios 1 : 1 and 1 : 2 there is a superposition of signals of $Co(dmgH)_2 \cdot MR$ (1 : 1 : 1 triplet) and of $Co(dmgH)_2 \cdot (MR)_2$ (1 : 2 : 3 : 2 : 1 quintet). Superhyperfine structure is therefore not well resolved. For a ratio Co : MR = 1 : 10, there is only one strong signal of the dimorpholine complex, and a satisfactorily resolved superhyperfine quintet is visible. Coupling constants and $g$ values are given in Table II. As is evident from Table I, parallel coupling constants diminish as the basicity of the base increases. This regularity is in agreement with the trend observed in ethanol solutions.[5] The same outcome was obtained under hydrogen.

These results indicate that reaction of amines with diaquocobaloxime in acetone solution gives rise to the compounds of the type (II) and (III). The existence of compounds analogous to (IV) seems to be a reasonable suggestion. With an increase of amine concentration predominant compounds are dibase adducts $Co(dmgH)_2B_2$.

### *Catalytic Hydrogenation of Nitrobenzene with Different Amines*

We performed a series of measurements of the rate of reaction (2) using catalysts prepared with different amines and at the variable ratios of Co : B. For three selected amines the dependence of (2) upon Co : B is shown in Figure 3. As follows from Figure 3, the rate of catalytic hydrogenation decreases (after passing a maximum) as the ratio Co : B increases. For every amine studied the maximum rate occurred at a different ratio Co : B. This is given in Table III.

Amines can affect the rate of hydrogenation in two ways:

TABLE II
Coupling constants and $g$ values of cobaloximes with different axial ligands in acetone solution.

| | | | Co–$B_2$ | | | |
|---|---|---|---|---|---|---|
| | | | $A_\perp$ | $A_\parallel$ | $A_N$ | Molar ratio |
| Cobaloxime | $g_\perp$ | $g_\parallel$ | G | G | G | Co : amine |
| $Co(dmgH)_2 \cdot 2H_2O$ in acetone | 2.260 | 2.013 | 35.65 | 114.5 | – | |
| $Co(dmgH)_2(CH_3OH)_2$ in $CH_3OH$ | 2.236 | 2.0106 | 30.3 | 105.0 | – | |
| + aniline | 2.237 | 2.010 | 27.4 | 105.7 | 11.2 | 1 : 60 |
| + py | 2.259 | 2.015 | – | 89.4 | 16.3 | 1 : 60 |
| $Co(dmgH)_2 \cdot 2H_2O$ + MR | 2.250 | 2.014 | – | 89.9 | 15.2 | 1 : 60 |
| + piperidine | 2.244 | 2.011 | – | 93.0 | 14.8 | 1 : 60 |
| + pyrolidine | 2.249 | 2.016 | – | 84.9 | 15.6 | 1 : 60 |

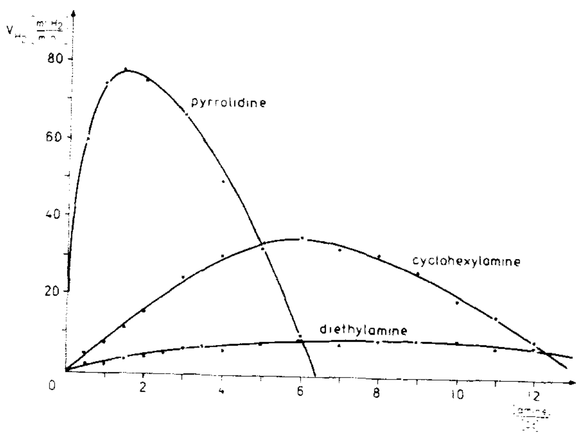

FIGURE 3 Rates of reaction (2) as a function of the ratio amine : Co for three selected amines.

1) Provided that, in the reaction (1) the Co : B ratio was kept constant within the series of different amines, there are different concentrations of amine complexes of the type (II) and (III) because their formation constants vary.[6] Most probably complex (II) is a catalyst precursor and variation in its concentration will cause variation in the concentration of the catalyst and therefore of the reaction rate.

2) The rate of hydrogen transfer to the substrate in the elementary process would depend on the electron distribution within the complex, which is the product of reaction of $H_2$ with hydrogen activating cobaloxime. This electron distribution is, in turn, influenced by the donor properties of amines. Strong $\sigma$ donating amines will build up negative charge on the in-plane $dmgH^-$ moiety,[7] as well as in an axial position of the cobaloxime.[8] This is a complex phenomenon and no clear conclusion can be made at the moment.

*Interaction of Nitrobenzene with Cobaloximes in Acetone Solution*

Addition of nitrobenzene to the solution of the products of reaction (1) brings about the following changes of the EPR spectrum:

1) a considerable decrease in the signal intensity

2) the spectrum with $PhNO_2$ is very similar to the spectrum characteristic for Co-$B_2$ complex, even in the ratio Co : B = 1 : 2.

Additionally there is no more superposition of two superhyperfine structures and a well-resolved quintet 1 : 2 : 3 : 2 : 1 is seen. It is shown in Figure 4. The rationale for these two facts is, that in the presence of nitrobenzene the monoamine complex is no longer present. Possible reasons for disappearance of $Co(dmgH)_2B$ could be as follows:

a) oxidation by nitrobenzene:

$$[Co^{II} - B] + PhNO_2 \longrightarrow [Co^{III} - B]_2 + \text{nitrobenzene reductions products} \qquad (4)$$

b) complex redox process analogous to interaction of pentacyanocobaltate with nitrobenzene.[9]

$$3\,Co(dmgH)_2B + H_2O + C_6H_5NO_2 \longrightarrow B\,Co(dmgH)_2N(C_6H_5)O^{\bullet} + 2\,Co(dmgH)_2OH \qquad (5)$$

c) dimerization:

$$2\,[Co^{II} - B] + PhNO_2 \longrightarrow \underset{(VI)}{[Co^{II} - B]_2 \cdots O_2NPh} \qquad (6)$$

We looked for possible products of nitrobenzene reduction, but none of them was detected by TLC and GC.

TABLE III
Dependence of the maximum turnover numbers (MTN) on molar ratio amine : Co.

| Amine | MTN for reaction (2) mol $H_2$/mol [Co] · 1 min | Molar ratio amine : Co for MTN | $pK_a$ (25°C) |
|---|---|---|---|
| pyrrolidine | 0.070 | 1.5 : 1 | 11.27 |
| piperidine | 0.067 | 1.8 : 1 | 11.12 |
| morpholine | 0.063 | 2.0 : 1 | 8.33 |
| benzylamine | 0.049 | 4.0 : 1 | 9.62 |
| allylamine | 0.039 | 5.5 : 1 | 9.49 |
| cyclohexylamine | 0.031 | 6.0 : 1 | 10.68 |
| pyridine | 0.023 | 7.0 : 1 | 5.21 |
| t-butylamine | 0.018 | 7.5 : 1 | 10.68 |
| diethylamine | 0.009 | 9.0 : 1 | 11.04 |

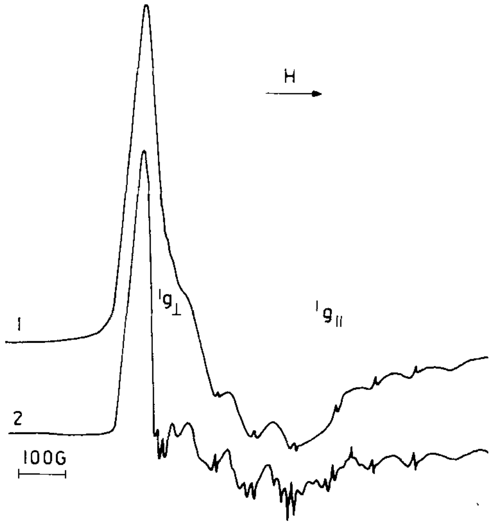

FIGURE 4 Influence of $PhNO_2$ on EPR spectra of the products of reaction (1): 1) (I) + MR in acetone (molar ratio (I) : MR = 1 : 2); 2) The same solution after addition of $PhNO_2$; (I) : $PhNO_2$ = 1 : 20. Both spectra in frozen acetone solution at 77 K.

As a consequence of reaction (5), if that would take place, base complexed cobaloxime-aryl-nitroxide should be formed. Formation of analogous cobaloxime-aryl-nitroxide without coordinated base was reported by Swanwick and Waters,[10] but under very different conditions:

$$CoCl_2 + dmgH_2 + Na_2CO_3 + PhNO \xrightarrow{CH_3OH/aq.} \underset{(VII)}{Co(dmgH)_2N(C_6H_5)O^\bullet} \qquad (7)$$

Although we were able to produce (VII), starting from PhNO:

$$Co(dmgH)_22H_2O + PhNO \xrightarrow{acetone} Co(dmgH)_2N(C_6H_5)O^\bullet \qquad (8)$$

we could not obtain (VII) from $PhNO_2$. The EPR spectrum of this cobaloxime-aryl-nitroxide has been reported by Swanwick and Waters. The EPR spectrum of acetone solution of (VII) is shown in Figure 5. Splitting constants amount to 20.3 G. We have obtained identical spectra under Ar and under $H_2$. This spectrum is analogous to but not identical with that of Swanwick and Waters probably because they measured it in $CH_3OH$/aq. medium at *pH* 8–9, at room temperature.

However, in all varieties of interaction of diaquocobaloxime with nitrobenzene, with and without hydrogen, we never observed formation of (VII). There is also no formation of base complexed cobaloxime-aryl-nitroxide in reaction of base complexed cobaloxime with PhNO.

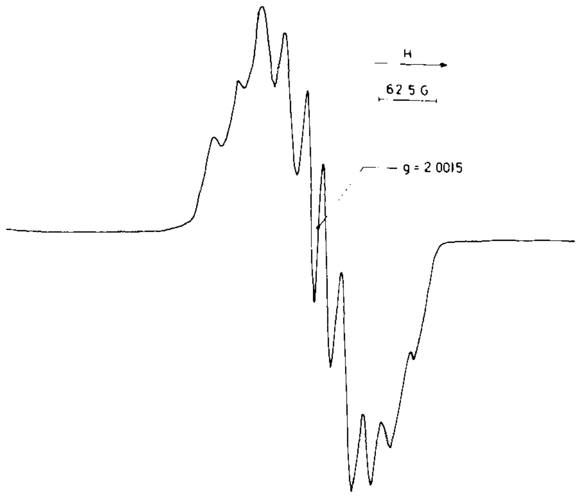

FIGURE 5 EPR spectrum of the cobaloxime-phenyl-nitroxide obtained from the reaction of $Co(dmgH)_22H_2O$ + PhNO in acetone with $c_{Co}$ = 40 mM. Spectrum taken in frozen acetone solution at 110 K.

Formation of a diamagnetic dimer (VI) is the most probable explanation for the observed disappearance of the signal of (II).

The structure of an intermediate (VI) is shown in Figure 6. According to this structure nitrobenzene binds together two monoamine cobaloximes to such an extent that Co—Co interaction takes place and this accounts for the diamagnetism. A free coordination

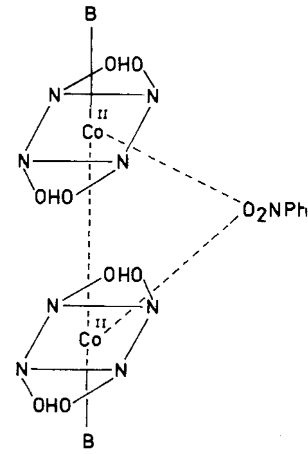

FIGURE 6 Plausible structure of nitrobenzene complexed dimeric cobaloxime.

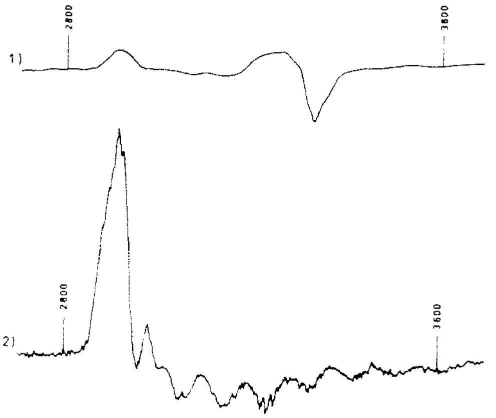

FIGURE 7 Influence of diene on EPR spectra of catalytic solution: 1) 4 methyl 1,3 pentadiene + $PhNO_2$ present together in the standard catalytic solution. Molar ratio Co : diene = 1 : 5; 2) The some solution after diene and $PhNO_2$ have been hydrogenated.

position is not necessary for such kind of an interaction. The mechanism of such bonding consists on charge transfer from $d_{xz}$, $d_{yz}$ cobalt orbitals to LUMO of nitrobenzene.

The confirmation of this concept comes also from series of experiments with conjugated dienes. Dienes strongly influence EPR spectra of cobaloximes giving rise to new signals.[11] These observations will be reported elsewhere. We noticed that when *n*-methyl 1,3 pentadiene was added to the catalytic solution it brings about complete diamagnetization. Such a solution absorbs hydrogen producing aniline and diene hydrogenation products. As soon as the diene has been hydrogenated, the known signal of diamine cobaloxime is again visible in the solution (Figure 7). These observations are rationalized according to eqs. (9) and (10):

$$2Co(dmgH)_2B_2 + PhNO_2 + diene \longrightarrow diene[Co(dmgH)_2B]_2O_2NPh + 2B \quad (9)$$

$$diene[Co(dmgH)_2B]_2O_2NPh + B + H_2 \longrightarrow monoene + PhNH_2 + 2Co(dmgH)_2B_2 \quad (10)$$

Further important information was obtained after measurement of the following EPR spectra: 1) $PhNO_2$ + TCNE in acetone, 2) (I) + TCNE in acetone, 3) (I) + MR + TCNE in acetone, and 4) (I) + MR + $PhNO_2$ + TCNE in acetone. Corresponding spectra are shown in Figure 9.

In the first case, only a very weak signal is observed. Signals shown in 2) and 3) can be tentatively ascribed to the compound formed by complexation of TCNE to the cobaloxime by one of its —CN groups. Signals numbered 1), 2) and 3) are much weaker than $TCNE^{\dot{-}}$ signal shown in 4). In fact, the origins of these signals are of secondary importance to the problem of interaction of $PhNO_2$ with cobaloxime. A strong $TCNE^{\dot{-}}$ signal is observed only when cobaloxime and nitrobenzene are present together in the solution. Although TCNE is a strong acceptor, it is not able to detach an electron from cobaloxime in the absence of $PhNO_2$. This again implies that $PhNO_2$ interacts with the $Co(dmgH)_2$ moiety and forms a charge transfer complex with cobaloxime.

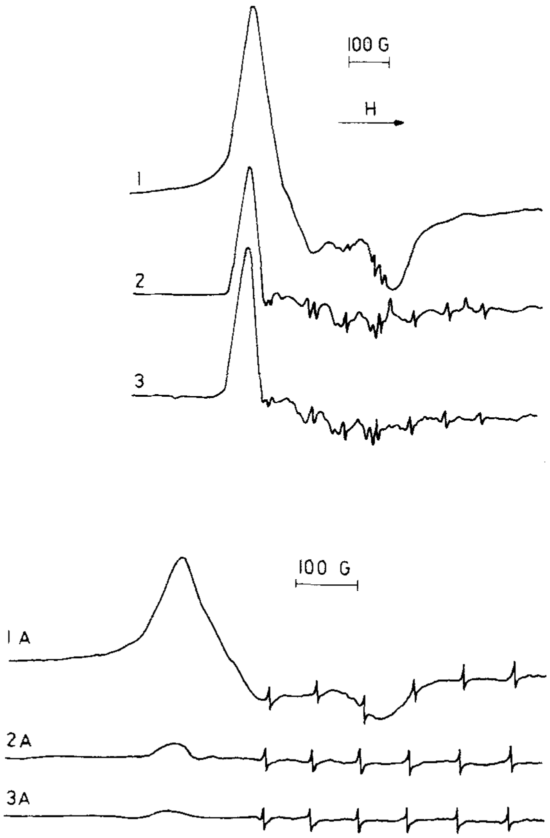

FIGURE 8 Decrease of the intensity of the EPR signal during catalytic hydrogenation. Standard catalytic reaction : spectrum taken after: 1) 30 min; 2) 90 min; 3) 200 min, spectrum taken after $H_2$ admission has been stopped: 1A) 3 min; 2A) 8 min; 3A) 15 min. All spectra in frozen acetone solution at 77 K.

### *Changes of the EPR Spectra During the Catalytic Reaction*

It was observed that the intensity of the EPR signal slowly decreases in the course of the reaction. However, the rate of the hydrogenation does not decrease. A

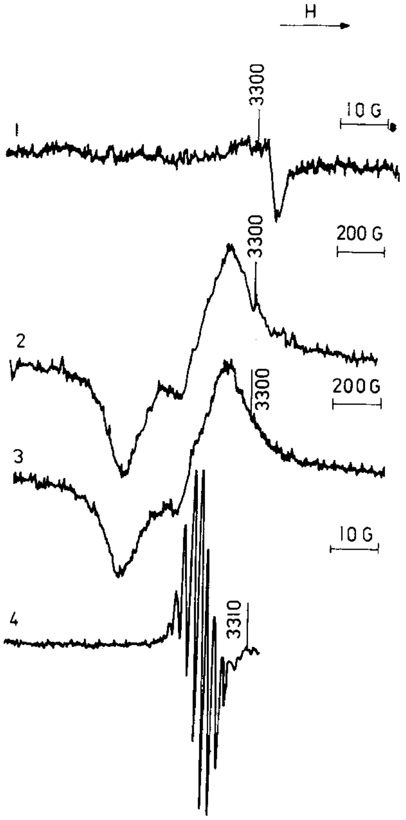

FIGURE 9 Formation of TCNE$^{\cdot-}$ in the system (I) + MR + $PhNO_2$ + TCNE in actone: 1) $PhNO_2$ + TCNE (1 : 1); $c_{PhNO_2} = 0.42$ M; 2) (I) + TCNE (1 : 1); $c_{Co} = 0.188$ M; 3) (I) + MR + TCNE (1 : 2 : 1); $c_{Co} = 0.0188$ M; 4) (I) + MR + $PhNO_2$ + TCNE (1 : 2 : 20 : 1); $c_{Co} = 0.0188$ M.

much faster decrease in the signal intensity was observed if hydrogen admission was stopped for a short period of time. Provided that this period was long enough (~30 min), it was possible to produce catalytic solution that was EPR-inactive. After $H_2$ has been readmitted the reaction starts again without any induction period and proceeds with the same rate as before. Changes of the signal intensity are shown in Figure 8.

Reduction of $PhNO_2$ to $PhNH_2$ is undoubtedly a multistep process, which involves several intermediates:

$$\begin{aligned} PhNO_2 + H_2 &\longrightarrow A \\ A + H_2 &\longrightarrow B \\ B + H_2 &\longrightarrow C \\ C &\longrightarrow PhNH_2 \qquad (11) \end{aligned}$$

Very fast disappearance of the signal after $H_2$ has been stopped indicates that intermediates A, B and C are very reactive species. Provided that $H_2$ is no longer available, A, B and C have no possibility to react with hydrogen and they react with other components of the solution (due to its free radical character[12]). Some paramagnetic solution component is a reasonable candidate for reacting with A, B and C. After readmission of $H_2$, the reaction proceeds with this same rate; concentration of the catalyst, therefore, is not diminished by this reaction.

Among the possible reasons of diamagnetism after $H_2$ addition has been stopped, one should consider reactions (12)–(14):

$$2\,[Co^{II}] \longrightarrow [Co^{I}] + [Co^{III}] \qquad (12)$$

$$[Co^{II}] \xrightarrow{\text{reduction}} [Co^{I}] \qquad (13)$$

$$2\,[Co^{II}] + H_2 \longrightarrow 2\,[Co^{III}] - H \qquad (14)$$

Reaction (12), however, takes place only in strongly alkaline media.[12] The conditions of our reaction are very different in comparison to alkaline water conditions necessary for (12) to take place. Formation of $Co^{I}$ by reduction was observed in the following cases:

$$ClCo^{III}(dmgH)_2P(nBu)_3 + H_2 \xrightarrow[KOH/H_2O]{PtO_2} [Co^{I}] \qquad (15)^{12}$$

$$ClCo^{III}(dmgH)_2PPh_3 + NaBH_4 \longrightarrow [Co^{I}] \qquad (16)^{13,14}$$

$$ClCo^{III}(dmgH)_2HCl + B + NaBH_4 \xrightarrow{CH_3OH/H_2O} [Co^{I}] \qquad (17)^{15}$$

One cannot completely exclude the possibility of hydrogenation of $Co^{II}$ to $Co^{I}$ with hydrogen by the reaction similiar to (15):

$$2Co^{II}(dmgH)_2(MR)_2 + H_2 \longrightarrow 2Co^{I}(dmgH)(dmgH_2) + 2MR \qquad (18)$$
$$\text{(VIII)}$$

However, it was found,[16] that pyridine complex $Co(dmgH)_2(py)_2$ does not interact with $H_2$.

Reaction (18) should occur without participation of $PhNO_2$. Interaction of $H_2$ with acetone solutions of cobaloximes (II), (III) and (IV), in the absence of $PhNO_2$, does not decrease the intensity of the EPR signal in the course of the standard catalytic reaction (3.5 h). This observation also makes formation of (VIII) unlikely.

The following observations are noteworthy:

1) the decrease of the intensity of the EPR signal in the presence of $PhNO_2$;

2) the disappearance of the signal of Co(dmgH)$_2$MR after PhNO$_2$ has been added;

3) the complete diamagnetization of the solution when diene and PhNO$_2$ are present together. Appearance of the signal of Co(dmgH)$_2$B$_2$ after diene has been hydrogenated;

4) the formation of TCNE$^{\dot{-}}$ provided that PhNO$_2$ is in the solution;

5) the impossibility of generating cobaloxime-aryl-nitroxide by reaction of diaquocobaloxime with nitrobenzene.

These indicate, that PhNO$_2$ is very likely complexed with diamagnetic, dimeric cobaloxime (VI). This explanation is supported by observation of Das[17] that nitrobenzene coordinates rather strongly to Co$^{III}$ in salen complexes.

Kinetics and description of the mode of hydrogen transfer will be a subject of the forthcoming paper.

## ACKNOWLEDGEMENT

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