

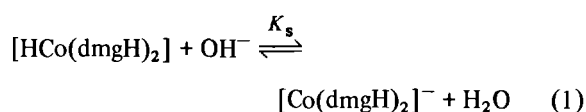
Cobalt Chelates as Hydrogenation Catalysts.
IV.* The pH Dependence of the Benzil
Hydrogenation with [Co(dpnH)]⁺ as Catalyst**

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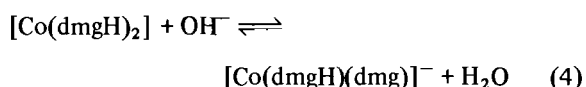
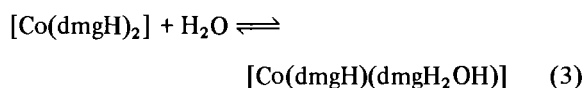
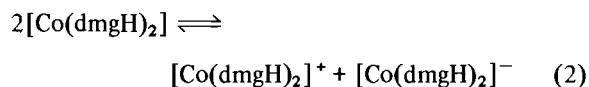
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The spin-paired d⁷-complexes [Co(dmgH)₂] and [Co(dpnH)]⁺ react with hydrogen by forming the monohydrides [HCo(dmgH)₂] and [HCo(dpnH)]⁺ which can dissociate in alkaline solution according to eqn. (1) [2, 3].



In alkaline solution, however, some other reactions such as the disproportionation of the cobalt(II) complex (eqn. (2)) [4, 5], the addition of water to the C=N double bond of the dmgH-ligand (eqn. (3)) [6, 7], and the dissociation of a proton from the -O-H-O-bridge of the ligand (eqn. (4)) [8] have been discussed in the literature.



Whereas the formation of the cobalt(I) complex can be followed very easily by its typical spectrum with strong absorption bands in the range of 14 000–20 000 cm⁻¹, the characterization of the other products is more difficult and therefore it is still not

*For Part III see ref. 1.

**dpnH = DO(DOH)pn = 2,3,9,10-tetramethyl-1,4,8,11-tetraazaundeca-1,3,8,10-tetraen-11-ol-1-olate.

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completely understood under which pH conditions the different products are formed. All these reactions, however, should have an influence on the hydrogenation activity of these complexes because the H₂ activation proceeds only via the intact cobalt(II) complex.

The hydrogenation activity of [Co(dpnH)]⁺ at various pH levels has been measured by the hydrogenation of benzil in a water/n₂propanol mixture (50% v/v), and the pH of the solution has been adjusted by the usual phosphate buffers. Unfortunately [Co(dmgH)₂] is not stable in the presence of phosphate [9], and therefore the following experiments were carried out with the more stable [Co(dpnH)]⁺ complex.

Under the above mentioned conditions the hydride formation is the rate determining step and the hydrogen uptake by the solution takes place according to the following rate law [9]:

$$r = k[\text{H}_2][\text{Co}]^2 \quad (5)$$

Therefore, each change of the cobalt(II) complex concentration, effected by the reactions (1)–(4), can easily be recognized by a respective change of the hydrogenation velocity. By plotting the amount of hydrogen absorbed against time, one obtains the expected straight lines between pH = 6.0 and pH = 12.0 (see Fig. 1). At first their slopes remain constant, but then increase quickly with increasing pH. At pH = 13.1 the velocity of the hydrogen consumption during the benzil hydrogenation decreases continuously, indicating a continued decrease of the cobalt(II) complex concentration. This decrease can be attributed either to a decomposition of the cobalt(II) complex, started by the dissociation of the proton from the oxime group (eqn. (4)) whereby in a similar way to the acid decomposition [10, 11] the macrocyclic structure of the ligand is destroyed and the stability of the complex correspondingly decreased, or to a relatively fast covalent hydration of the C=N double bond in the coordinated dpnH-ligand.

In Fig. 2 *k*_{obs}, obtained from the slope of the straight lines (and the initial rate at pH = 13.1), has been plotted against -p[OH⁻]. When comparing this curve with the analogous plot of *k*_{obs} against -pL for the adduct formation with pyridine [1], the same course can be observed in both cases to a large extent. Therefore we supposed that the increase of *k*_{obs} above pH = 10.7 can be analogously attributed to an adduct formation with OH⁻ (or a deprotonation of an axially bound water molecule). Simandi *et al.* [12], however, suggested that the analogous increase of activity of the [Co(dmgH)₂] complex is due to the dissociation of a proton from the -O-H-O-bridge of

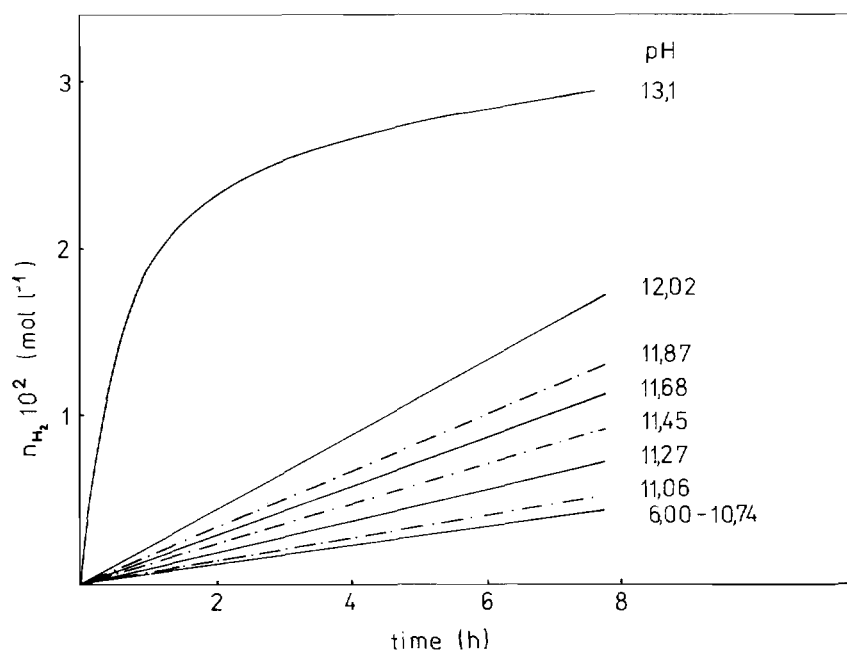


Fig. 1. Hydrogen uptake at various pH values ($[\text{Co}]_{\text{T}} = 5 \times 10^{-3} \text{ mol l}^{-1}$; $[\text{S}]_{\text{T}} = 5 \times 10^{-2} \text{ mol l}^{-1}$; $T = 298 \text{ K}$; $I = 0.05$).

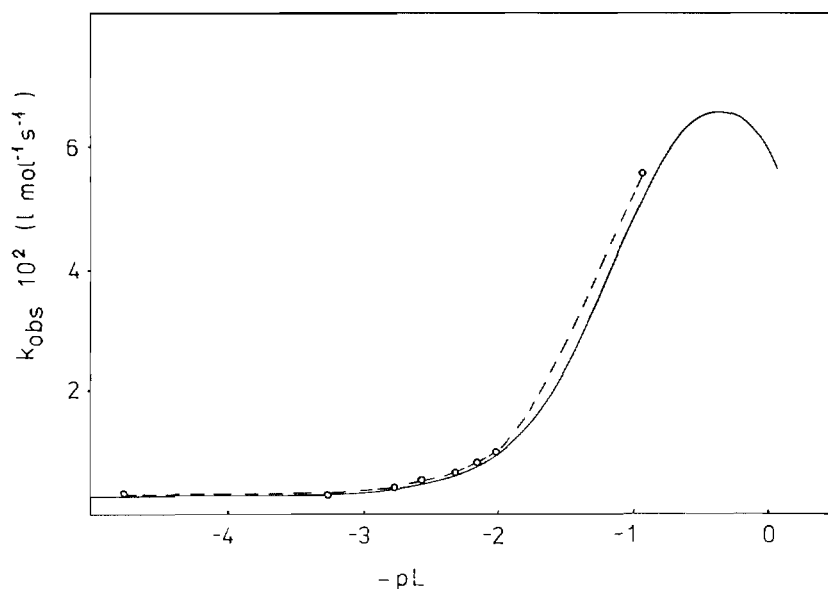


Fig. 2. Change of the rate constant k_{obs} with the pL value of the ligand ($pL = -\lg [L]$; $L = \text{py}$ (—), OH^- (---)).

the ligand. At present we cannot decide between the two possibilities unambiguously.

Furthermore, spectroscopic investigations in an argon atmosphere have shown that the position and the intensity of the charge transfer band ($\tilde{\nu} = 19\,000 \text{ cm}^{-1}$) is constant with time up to $\text{pH} = 11$, i.e. no side reaction can be observed in this pH range. At $\text{pH} = 12.1$ the charge transfer band has a lower

intensity. A similar decrease of intensity has been found as the result of a 1:1 adduct formation of $[\text{Co}(\text{dmgH})_2]$ [13] and $[\text{Co}(\text{dpnH})]^+$ [14] with pyridine. At $\text{pH} = 13.1$ on the contrary, already shortly after adjustment of the pH value a new band at about $15\,000 \text{ cm}^{-1}$ appears, which is typical for the cobalt(I) complex (see Fig. 3). The intensity of this band, however, is small and decreases like the

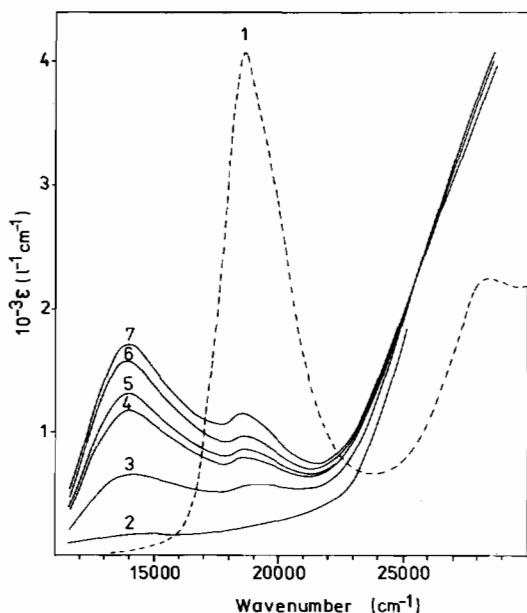


Fig. 3. Time dependence of the UV-Vis spectra of $[\text{Co}(\text{dpnH})]\text{ClO}_4$. 1, in unbuffered solution; 2-7 at pH = 13.1 after about 10 min; 20 min; 40 min; 60 min; 2 h and 18 h.

charge transfer band at 20000 cm^{-1} relatively fast. Thus, the spectroscopic findings corroborate the conclusions derived from the hydrogenation experiments and show that a disproportionation of $[\text{Co}(\text{dpnH})]^+$

according to eqn. (2) occurs only at such high pH values, at which the complex probably is no longer stable.

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