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Cobalt Chelates as Hydrogenation Catalysts. V. The pH Dependence of the Benzil Hydrogenation with $[Co(dpnH)]^+$ as Catalyst in the Presence of Pyridine

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In analogy to the investigations described in Part IV [1] we have studied the pH dependence of the benzil hydrogenation with the same catalyst and under the same conditions, but in the presence of pyridine ($Co(dpnH)^+$:py = 1:80). Under these conditions and on account of the equilibria (1) and (2)

$$[Co(dpnH)]^+ + py \overset{K_1}{\rightleftharpoons} [Co(dpnH)py]^+ \qquad (1)$$

$$[Co(dpnH)py]^+ + py \overset{K_2}{\rightleftharpoons} [Co(dpnH)py_2] \qquad (2)$$

($K_1 = 22.0 \pm 0.8$ l mol^{-1}, $K_2 = 0.18 \pm 0.005$ l mol^{-1}, $I = 0.05$, $T = 298$ K) the complex in solution is present to 84% as $[Co(dpnH)py]^+$, 11% as $[Co(dpnH)]^+$ and 5% as $[Co(dpnH)py_2]^+$ [2] and shows a distinctly different behaviour from the base-off form of the complex.

The hydrogen uptake curves between pH = 6–12 are presented in Fig. 1. As can be inferred from this, between pH = 6 and pH = 7.2, similar to the base-off form of the catalyst, the straight lines coincide, *i.e.* the catalyst concentration in the pH range is constant. With increasing pH, however, a more and more curved initial part of the hydrogen uptake curve appears followed by a straight line whose slope becomes more gentle the higher the pH of the solution. The curved initial part of these curves obeys a second order rate law, and in solution a growing amount of the respective cobalt(I) complex is to be found. The slopes of the following straight lines, which become more and more gentle, show that with increasing pH of the solution the concentration of the cobalt(II) complex available for the benzil hydrogenation also is continuously decreased. This quite different behaviour, compared to the base-off form of the complex, can be explained with the following diagram.

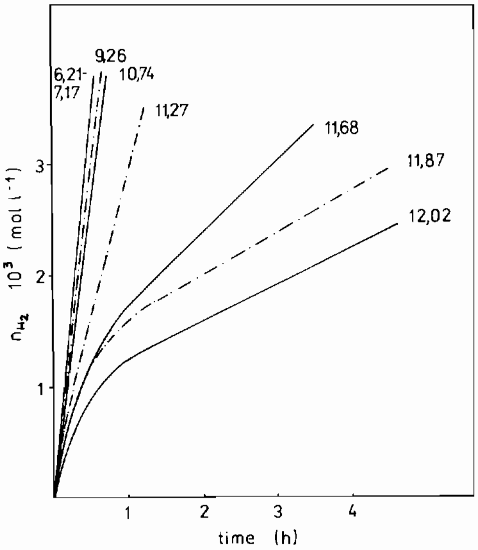
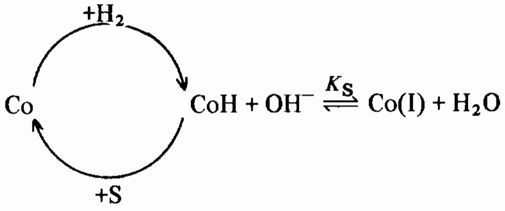


Fig. 1. Hydrogen consumption curves at various pH values ($[Co]_T$:$[py]_T$ = 1:80; $[Co]_T = 5 \times 10^{-3}$ mol l^{-1}; $T = 298$ K; $I = 0.05$).



For as long as the OH^- concentration is small, the reaction runs off within the circle on the left side: the cobalt(II) complex reacts with hydrogen by forming the monohydride $[HCo(dpnH)py]^+$ which is captured by the substrate. Thereby within the cycle a small, but stationary hydride concentration is formed, which is proportional to the initial concentration of the cobalt(II) complex and whose magnitude depends on the velocity of the forward and the reverse reaction. For the hydride concentration eqn. (3) must also be valid.

$$K_s[OH^-] = \frac{[Co(I)][H_2O]}{[CoH]} \qquad (3)$$

As soon as the OH^- concentration increases (pH > 7.2) the hydrido complex dissociates until the ratio $[Co(I)]/[CoH]$ corresponds to the product on the left side of eqn. (3). Simultaneously the concentration of the cobalt(II) complex is diminished by this means. The cobalt(II) concentration, which is responsible for the benzil hydrogenation and which is regulated in this way, can be calculated from the slope of the straight line (Fig. 1), provided that the

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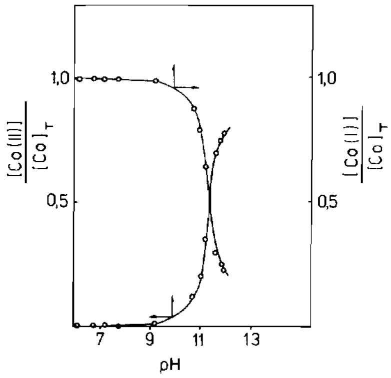

Fig. 2. pH dependence of the relative cobalt(II) ([Co(II)]/[Co]$_T$) or resp. cobalt(I) ([Co(I)]/[Co]$_T$) concentration.

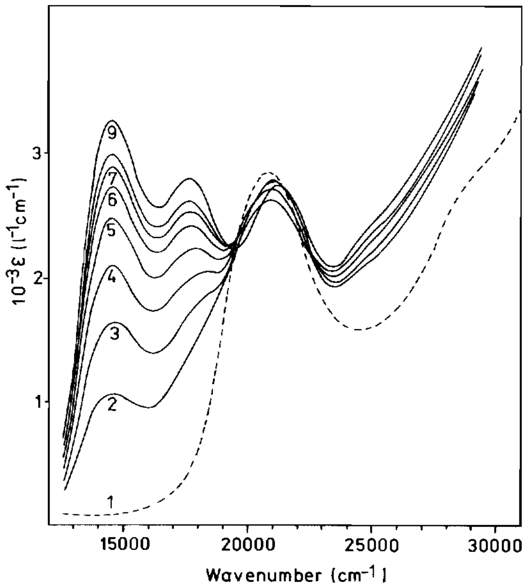

Fig. 3. Time dependence of the UV–Vis spectra of [Co(dpnH)py]$^+$. 1, at pH = 9.2; 2–9 at pH = 12.1; 2, 10 min; 3, 2.3 h; 4, 4.3 h; 5, 6.3 h; 6, 8.3 h; 7, 10.3 h; 8, 12.3 h and 9, 41.8 h.

k_{obs} values do not change with pH. The course of the relative cobalt(II) concentration [Co(II)]/[Co]$_T$ at different pH values can be seen in Fig. 2.

Moreover, the increase of the cobalt(I) concentration at a simultaneously decreasing velocity of the benzil hydrogenation shows that the benzil hydrogenation does not proceed by way of the cobalt(I) complex as has been suggested by some authors [3,4].

By spectroscopic investigations under anaerobic conditions it was proved that the formation of the cobalt(I) complex does not proceed by disproportionation of the cobalt(II) complex [Co(dpnH)py]$^+$ but by way of the intermediately formed hydrido complex. In the pH range 6–11 the position ($\tilde{\nu}$ = 20800 cm^{-1}) and the intensity of the charge transfer band remains constant for 5 h. At pH = 12.1 shortly after adjustment of the pH two new absorption bands at 14500 and 17600 cm^{-1}, which are typical for the cobalt(I) complex, can be observed and their intensity increases slowly during the next hours (see Fig. 3). Accordingly the disproportionation of [Co(dpnH)py]$^+$ indeed occurs somewhat earlier than with the base-off form of the cobalt(II) complex [1], but not in this pH range in which the cobalt(I) formation already proceeds during the benzil hydrogenation. At pH = 13.1 the disproportionation reaction runs distinctly faster and from the decrease of absorbance with time a decomposition of the complex can also be presumed.

References

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