

By comparing δ_1 and δ_2 with the lattice constant of the bulk silver, 4.0722 Å (8), it seems that the first superficial layer of silver atoms is involved in the oxygen chemisorption process.

As the electric resistance depends also on the number of conduction electrons, its increase during the chemisorption might be due *not only* to the thickness decrease but also to a change of this number. On basis of this assumption δ can be deduced from the following relation (4):

$$\frac{d_0}{d_0 - \delta} = \left(\frac{\alpha_0 R_1}{\alpha_1 R_0} \right)^{3/8} \quad (5)$$

(valid in the range $d_0 \leq 0.15 l_\infty$). The thus found value is smaller than those obtained in the first case, but has the same order of magnitude:

$$\delta = (3.08 \pm 0.24) \text{Å} \quad (6)$$

It results therefore that even in this case there is an important influence of the thickness decrease on the electric resistance. As a matter of fact, our experimental data about the Hall tension behavior of thin silver films during oxygen chemisorption seem to indicate that the hypothesis of the thickness decrease is more probable than the hypothesis of the change in the number of conduction electrons (3).

In conclusion, we can say that our results concerning the influence of oxygen chemi-

sorption on the electric resistance and on the TCR of thin silver films support qualitatively as well as quantitatively Sachtler and Dorgelo's hypothesis.

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I. G. MURGULESCU
GERDA H. COMȘA
N. I. IONESCU

*Institute of Physical Chemistry
Academy of the Socialist Republic
of Romania
Bucharest 9, str. Dumbrava Roșie 23,
Romania
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Catalytic Hydrogenation by Dicyanobipyridinecobaltate (II) in Homogeneous Solution

In recent years, a number of metal complexes have been found (Co, Cu, Ru, Rh, Ag, Hg) which can activate hydrogen in solution (1-6).

From this published data, it is generally agreed that catalytic activity exists, if the catalyst has an unfilled *d* shell. In addition, as Schindewolf (7) pointed out, a complex compound must also be coordinately "un-

saturated," in order that activation of hydrogen is possible. As such, with the ferrihexacyanide ion, in spite of the fact that it has an unpaired electron, no hydrogen absorption is observed, because it has six ligands (thus being coordinately "saturated").

Since, dicyanobipyridinecobaltate(II), Co(CN)₂Dip, first isolated by Cambi (8), has

both an unfilled electron shell and also is coordinately "unsaturated" (having only four ligands), this complex should show activation of hydrogen. In the following, we want to report the hydrogenation of a variety of organic substrates, catalyzed by this system in homogeneous aqueous-alcoholic solutions.

EXPERIMENTAL

The whole apparatus consisted of an 80-ml four-necked round-bottomed flask equipped with a glass stirrer. At the top end of this stirrer was a tube equipped with a magnet driven by Rühromag motor. The hydrogen uptake was measured with a gas burette with leveling bulb.

For each run, the catalyst solution was freshly prepared by mixing the appropriate amounts of potassium cyanide, cobalt(II) acetate, and 2,2'-bipyridine. The ratio Co/CN/Dip was 1:2:3 at a cobalt concentration of 3 mmole. After the hydrogen absorption of the catalyst solution was complete, substrate was added.

The reductions described here were carried out at room temperature and at a hydrogen pressure of 1 atm. Before mixing the solutions of potassium cyanide, cobalt acetate(II), and 2,2'-bipyridine, the whole system was evacuated and flushed several times with hydrogen, and finally filled with hydrogen.

RESULTS

Table 1 gives a list of substrates which were hydrogenated.

The course of the hydrogenation of 1,3-cyclohexadiene catalyzed by dicyanobipyridinecobaltate(II) is shown in Fig. 1, curve 11. The substrate is reduced very rapidly; the rate of hydrogen uptake being 3.40 ml/min. One mole equivalent of hydrogen was absorbed to yield cyclohexene exclusively.

As a comparison, the hydrogenation of 1,3-cyclohexadiene in an aqueous solution of pentacyanocobaltate(II), $[\text{Co}(\text{CN})_5]^{3-}$, was measured (Fig. 1, curve 12), since it is known that this system has a high catalytic activity. It is seen, that the rate of hydrogenation

with the dicyanobipyridinecobaltate(II) catalyst is approximately 3 times faster.

Figure 2 shows the reduction of sorbic acid (added as its potassium salt) in a solution of dicyanobipyridinecobaltate(II) (curve 1) and, as a comparison, in an aqueous solution of pentacyanocobaltate(II) (curve 2). Again the more rapid hydrogen uptake with the dicyanobipyridinecobaltate(II) catalyst is noted.

TABLE I
LIST OF SUBSTRATES REDUCED^a

Substrate	Ratio, moles substrate/ (CN) ₂ Dip	Initial rate of H ₂ absorption (ml/min)
1,3-Cyclohexadiene	2.2	3.40
Sorbic acid (potassium salt)	1.1	2.50
Cinnamalacetic acid (potassium salt)	1.1	2.55
Cinnamyl alcohol	1.1	0.58
Cinnamyl acid (sodium salt)	1.1	0.05
Acrylic acid (potassium salt)	1.1	0.10
Methacrylic acid (sodium salt)	1.1	0.00
Cyclohexene	2.2	0.00

^a Cobalt concentration 3 mmole; temp., 30°C.

However, a gradual decrease of the rapid hydrogen uptake in the dicyanobipyridinecobaltate(II) solution is noted, whereas in the pentacyanocobaltate(II) system, the rate of hydrogenation remains the same as was measured at the beginning of the reaction. Therefore, the two curves intersect in point D of Fig. 2, and from this period, the pentacyanocobaltate(II) has now to be considered as the more "active" catalyst.

This decrease in the rate of hydrogen absorption is due to the fact that the dicyanobipyridinecobaltate(II) catalyst is being poisoned by the substrate (sorbic acid), thereby being oxidized to the respective Co^{III} complex. In the trivalent state, the catalyst is however inactive, having a filled electron shell.

Poisoning of the catalyst is also observed when *p*-benzoquinone, nitrobenzene, or crotonaldehyde are added. These substrates

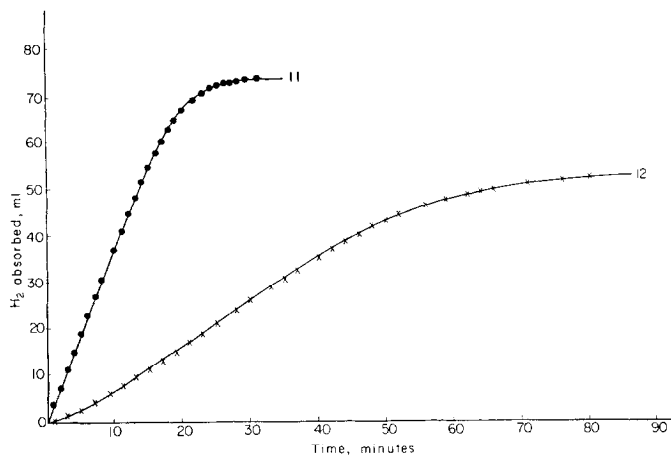


FIG. 1. Hydrogenation of 1,3-cyclohexadiene with ●, dicyanobipyridinecobaltate(II); ×, pentacyanocobaltate(II).

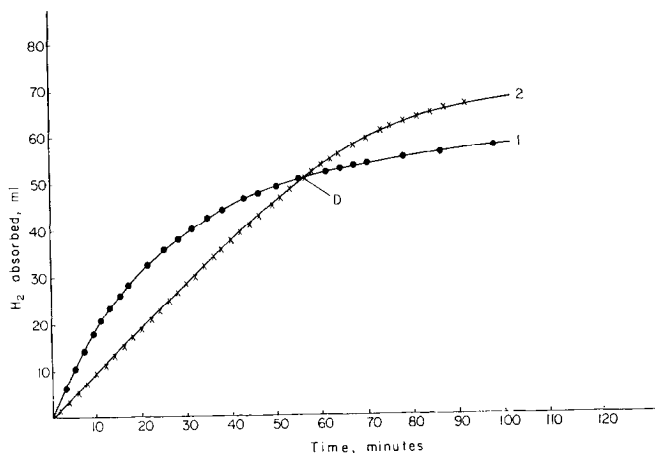


FIG. 2. Hydrogen uptake of sorbic acid with ●, dicyanobipyridinecobaltate(II); ×, pentacyanocobaltate(II).

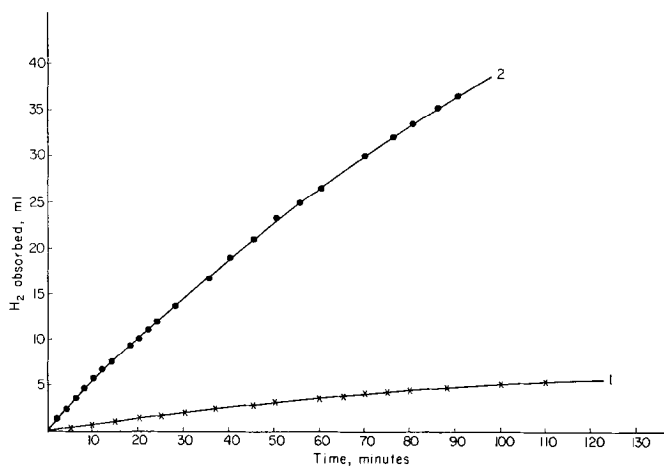


FIG. 3. Reduction of ●, cinnamyl alcohol; ×, acrylic acid; with dicyanobipyridinecobaltate(II) at 30°C.

oxidize the catalyst immediately, so that no hydrogen adsorption is noted.

The hydrogenation of cinnamyl alcohol is rather slow (Fig. 3, curve 2), and even slower is the hydrogen uptake of acrylic acid (added as its sodium salt, curve 1). With methacrylic acid no hydrogen absorption at all is noted.

The dicyanobipyridinecobaltate(II) catalyst is therefore not only specific to the type of functional group used (a general requirement of reduction of the C=C seems to be conjugation), but is also sensitive to other structural features. For example, acrylic acid is reduced, while acrylic acid substituted in the α -position by a methyl group is not reduced.

Summarizing these results, the most important feature is that a system of very high activity has been found. Substrates which do not poison the catalyst are reduced in the dicyanobipyridinecobaltate system at a considerably more rapid rate than in the highly active pentacyanocobaltate(II) system.

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G.-M. SCHWAB
G. MANDRE

*Physikalisch-Chemisches Institute of
the University of Munich,
Munich, Germany*

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