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Reactions of the Pentacyanocobaltate(II) Ion
II. Liquid Phase Hydrogenation and Decomposition*

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In connection with the homogeneous catalytic activation of molecular hydrogen by pentacyanocobaltate(II) ions in aqueous solution, several features of the complex have been investigated. The reaction between hydrogen and pentacyanocobaltate(II) results in an equilibrium, the position of which is independent of the total Co concentration. From the changes of the equilibrium constant with temperature a reaction enthalpy of 11 kcal/mole H_2 has been calculated.

The results of kinetic investigations of the hydrogen absorption show that, similarly to the decomposition of $[Co(CN)_5]^{3-}$ under the influence of water, the rate-determining step is of second order with respect to cobalt. If the hydrogenation is assumed to be a termolecular reaction it shows zero energy of activation. It is, however, also possible to explain the kinetic results by means of other reaction schemes. The most satisfactory is that in which in a rapidly established equilibrium, pentacyanocobaltate(II) first forms a small amount of dimer which subsequently either absorbs hydrogen to form a hydrogenated monomer complex, or decomposes under the influence of water.

On mixing a solution of a cobalt(II) salt with excess potassium cyanide, the pentacyanocobaltate(II) ion is formed. In aqueous solution it exhibits several interesting properties. In contrast with the diamagnetic crystalline potassium salt (*2*) it is mononuclear and has one unpaired electron per cobalt ion (*3*).

It absorbs molecular hydrogen (*4*) to an amount which approaches the stoichiometry of reaction (1).

$$2[Co(CN)_5]^{3-} + H_2 \rightarrow 2[Co(CN)_5H]^{3-} \quad (1)$$

The hydrogenated solutions catalyze the D_2–H_2O exchange (*3*), the ortho-para hydrogen conversion (*3*), and effect the hydrogenation of unsaturated compounds such as cinnamic and sorbic acid (*4, 1*). The catalytic hydrogenation activity has been shown to possess a very specific character. After the addition of one equivalent of H_2 to octadeca-9,11,13-trienoic acid no further addition takes place, while octadeca-9,11-dienoic acid cannot be hydrogenated (*5*). Recently several other catalytic hydrogenations have been described (*16*). It was considered that a more detailed knowledge of the reaction between $[Co(CN)_5]^{3-}$ and H_2 might lead to a better understanding of the above-mentioned catalytic properties and of the mechanism of heterogeneous catalytic hydrogenation as well (*6, 7, 8*).

The present work deals with the kinetics and equilibrium of the hydrogen uptake by pentacyanocobaltate(II). Since this reaction is invariably accompanied by a decomposition of the complex ion (*1, 3, 9, 10*), the latter reaction was also investigated.

METHODS

Hydrogen Absorption

All reactions were carried out in the absence of molecular oxygen. The reaction vessel (A), of volume 400 ml, was equipped with an efficient vibro mixer and was con-

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* For Part I, see ref. (*1*).

nected with a 100 ml gas burette. Before mixing the solutions of $CoCl_2$ and KCN pure H_2 was passed through them to remove dissolved O_2. After forcing the $CoCl_2$ solution into A, containing the KCN solution, the mixture was vigorously stirred and the H_2-absorption measured as a function of the time. By means of a mercury relay, magnetic valve, and gas burette the pressure of the system could be kept accurately at 1 atm. Water of constant temperature (±0.02°C) circulated around gas burette and reaction vessel. The dead space of the system was ca. 10 ml.

The rate of hydrogen absorption was not limited by mass transport. Addition of 0.2% (W/V) of a strong foaming agent (polyethyleneglycol derivative) gave a much better contact between gas and liquid without changing the absorption rate or the ultimate amount of absorbed hydrogen.

UV-Absorption Measurements

Under cover of an atmosphere of H_2 or N_2 the solution present in A could be forced into a cuvette which was then sealed with a ground joint stopper. Measurements of spectrum and decomposition of $[Co(CN)_5]^{3-}$ were carried out with N_2-saturated solutions. During kinetic experiments the cuvette compartment of the Beckman DU spectrophotometer was kept at constant temperature by means of a thermostatic cell.

RESULTS

Absorption Spectrum

The absorption spectrum between 220 and 1000 mμ of an aqueous solution containing $[Co(CN)_5]^{3-}$ is shown in Fig. 1. It agrees well with that recently described by King and Winfield (*10*). The band near 970 mμ is very characteristic for the complex and can be used to determine $[Co(CN)_5]^{3-}$ concentrations (*9*). Dilute solutions follow Beer's law. Their optical density at 970 mμ is directly proportional to the cobalt concentration (Fig. 2). Neither a change in temperature (0–25°C) nor the presence of salts (0.9 M KCN) alters the position or the intensity of the maximum. The results as given in Fig. 2 were corrected for decomposition of $[Co(CN)_5]^{3-}$. The density measurements were extrapolated to the time of mixing the KCN and $CoCl_2$ solutions. The slope in Fig. 2 corresponds to ϵ_{mol} = 277 cm^{-1} liter $mole^{-1}$. This is slightly less than the value 298 determined by King and Winfield (*10*). Throughout the experiments Fig. 2 was used to determine $[Co(CN)_5]^{3-}$ concentrations from measurements of optical densities at 970 mμ.

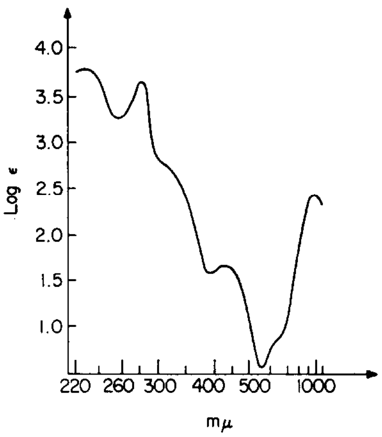

FIG. 1. Absorption spectrum of pentacyanocobaltate(II). CN/Co = 15; 0.01 N NaOH.

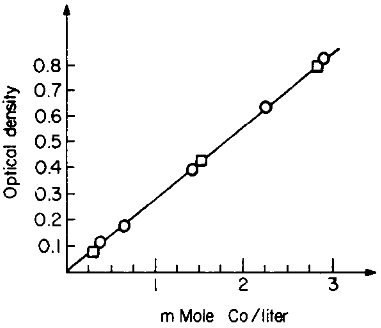

FIG. 2. Absorption at 970 mμ by pentacyanocobaltate(II); ○, temp. 25°C; 0.86 M KCN; □, temp. 0°C; CN/Co = 6; cell length 1.00 cm; D = optical density = log [100/% transmission].

Decomposition of Pentacyanocobaltate(II)

The intensity of the absorption at 970 mμ decreases with time due to decomposition of the pentacyanocobaltate(II) ion.

The decrease is considerably accelerated by increasing the total ionic strength of the solution (*3*). In a previous paper (*1*) it has been suggested that the decomposition is in fact a disproportionation of $[Co(CN)_5]^{3-}$:

$$2[Co(CN)_5]^{3-} \xrightarrow{H_2O} [Co(CN)_5H]^{3-} + [Co(CN)_5OH]^{3-} \qquad (2)$$

The results of accurate UV measurements by King and Winfield (*10*) also lend support to the above decomposition. By NMR measurements Griffith and Wilkinson (*11*) have shown the presence of metal–hydrogen bonds in aged solutions of pentacyanocobaltate(II).

The course of the decomposition of $[Co(CN)_5]^{3-}$ in 0.86 *M* KCN as a function of time was followed by optical density measurements at 970 mμ. Experiments were carried out at various initial cobalt concentrations and at various temperatures. In all cases the cobalt complex decomposed fairly rapidly in the beginning, viz. 5–7% of the amount initially present. After that the decomposition slowed down and proceeded with second order kinetics with respect to cobalt. The reciprocal of the optical density (*D*) plotted against time yielded a straight line over a range in which *D* decreased by a factor of 2.7 (Fig. 3).

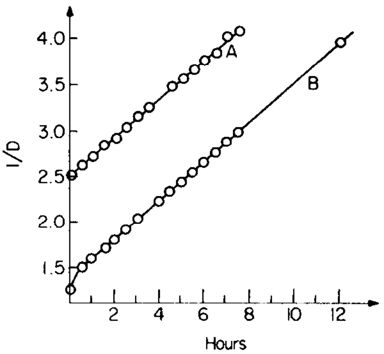

FIG. 3. Decomposition of pentacyanocobaltate (II). Temp., 25°C; 0.86 *M* KCN; cell length 1.00 cm; A: initial Co conc. 1.43 mmole/liter; B: initial Co conc. 2.86 mmole/liter.

This linear relationship was also observed at other reaction temperatures. An Arrhenius plot of the observed second order rate constants is drawn in Fig. 4. The

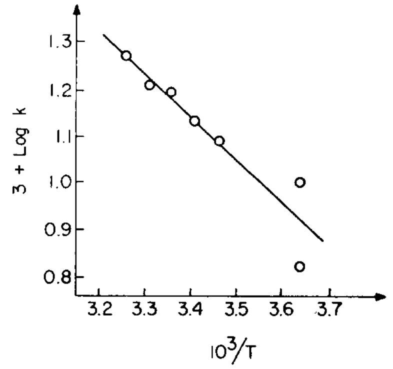

FIG. 4. Arrhenius plot for decomposition of pentacyanocobaltate(II) in 0.86 *M* KCN; $k =$ rate constant, $(sec)^{-1}$ $(mole/liter)^{-1}$.

apparent energy of activation and the apparent frequency factor are 4 kcal/mole and 780 min^{-1} $(mole/liter)^{-1}$, respectively.

Reaction with Hydrogen

The equilibrium. Pentacyanocobaltate(II) ions in an aqueous solution rapidly absorb molecular hydrogen. Under favorable conditions the amount of hydrogen absorbed corresponds closely to an over-all reaction between two cobalt ions and one hydrogen molecule. In 1 *N* NaOH, Mills *et al.* (*3*) observed at 0°C 95% of the amount of H_2 uptake required by Eq. (1), and about 80% at 25°C. The observed deviations from the stoichiometric amount of hydrogen have been ascribed (*3*) to the simultaneously occurring decomposition of $[Co(CN)_5]^{3-}$. This is, however, only a partial explanation. It is easily demonstrated that the hydrogenation is a reversible reaction. At 25°C the 970 mμ band diminishes during hydrogen uptake to about 10% of its original value, but rises again when the hydrogenated solution is flushed with nitrogen. Thereafter hydrogen can again be taken up. In this respect the observations made by King and Winfield (*10*) are confirmed.

The equilibrium position was examined at several temperatures and at several cobalt concentrations. The following variables were determined at equilibrium:

(*i*) The optical density of the solution at 970 mμ, which determined the amount of nonhydrogenated pentacyanocobaltate(II). The absorption at this wavelength of the products of both the decomposition and the hydrogenation reactions is negligible (*10*).

(*ii*) The total amount of absorbed hydrogen which determined the percentage of hydrogenated cobalt complex.

The sum of the two percentages never reached 100%. It varied from 99% in experiments carried out with 1 N sodium hydroxide at 0°C, to 89% in experiments with 0.9 M potassium cyanide at 35°C. The amounts of cobalt which could not be accounted for were considered to have been decomposed in accordance with the disproportionation reaction. Since the disproportionation generates one-half equivalent of hydrogenated cobalt complex (Eq. 2) half the amount of decomposed cobalt was added to the percentage mentioned under *ii*, in order to calculate the total percentage of hydrogenated pentacyanocobaltate(II).

Table 1 shows the equilibrium composition at several intial cobalt concentrations. From the hydrogen uptake the equilibrium appeared to be reached within 60 min time. It appears that a change in the initial concentration by a factor of seven has hardly any influence upon the relative composition at equilibrium. The equilibrium ratio of hydrogenated to nonhydrogenated complex [CoH]/[Co] seems to be constant. From this we may conclude that both species will be either mononuclear or binuclear complexes.

According to the most likely over-all reaction scheme

$$2[\mathrm{Co(CN)_5}]^{3-} + \mathrm{H_2} \underset{k_2}{\overset{k_1}{\rightleftarrows}} 2[\mathrm{Co(CN)_5H}]^{3-} \qquad (3)$$

the equilibrium constant may be written as

$$K = \frac{[\mathrm{CoH}]^2}{[\mathrm{Co}]^2[\mathrm{H_2}]} \qquad (4)$$

Additional evidence for the validity of this equation was found in experiments which were carried out under 1/3 atm of hydrogen and 2/3 atm of nitrogen. In this case the equilibrium ratio $[\mathrm{CoH}]^2/[\mathrm{Co}]^2$ was also reduced by a factor of three, compared with that obtained at 1 atm of hydrogen.

The value of the equilibrium constant clearly appeared to be temperature dependent. At lower temperatures more hydrogen can be absorbed and less nonhydrogenated cobaltate remains. In Tables 2 and 3 the results of experiments carried out in two different aqueous solutions, 0.86 M KCN and 1.0 N NaOH, are summarized.

With the solutions containing NaOH equilibria were reached within about 3 hr.

TABLE 1

EQUILIBRIA IN HYDROGENATION OF PENTACYANOCOBALTATE(II)[a]

Expt. no.	$\mathrm{CoCl_2}$ added (mmoles)	[Co][b] (%)	$\mathrm{H_2}$ absorbed[c] (%)	Decomp.[d] (%)	[CoH][e] (%)
1	7	9.3	81.0	9.7	85.9
2	5	9.5	81.0	9.5	85.8
3	4	9.4	81.0	9.6	85.8
4	2	9.4	80.9	9.7	85.8
5[f]	1	8.5	78.7	12.8	85.1

[a] Temp. 25°C; 0.86 M KCN; total volume 350 ml; $\mathrm{H_2}$ pressure, 735 mm Hg.

[b] [Co] = percentage of cobalt present as pentacyanocobaltate(II).

[c] $\mathrm{H_2}$ absorbed = percentage of cobalt equivalent to the amount of $\mathrm{H_2}$ absorbed.

[d] Decomp. = percentage of cobalt not accounted for.

[e] [CoH] = percentage of cobalt present as hydrogenated pentacyanocobaltate(II).

[f] Because of the small amount of cobalt used the possible errors in [Co] and the absorbed amount of $\mathrm{H_2}$ are relatively high.

The results of the experiments carried out with solutions of 1 *N* NaOH at 0°C (Table 3, Expts. 11 and 12) show a near 100% cobalt recovery at equilibrium. This makes it unlikely that in the other experiments as described in Tables 1, 2, and 3 the larger amounts of cobalt which could not be accounted for, were due to the presence of uncompletely removed oxygen.

Arrhenius plots for both series of experiments as given in Tables 2 and 3 are drawn in Fig. 5. The enthalpy and entropy of reaction calculated from Fig. 5 are 11.2 ± 0.2 kcal/mole H_2 and ca. —14 e.u./mole H_2, respectively.

In order to calculate the *K* values solubilities of hydrogen were measured in deaerated aqueous solutions containing 1 mole of sodium hydroxide and 0.2 mole of potassium cyanide per liter (Table 4). The solubilities in 0.86 *M* KCN which have not been determined were taken as equal to those in 1 *M* NaOH. The former, however, will be larger because of a lower total ionic strength of the solution and the presence of more polarizable ions.

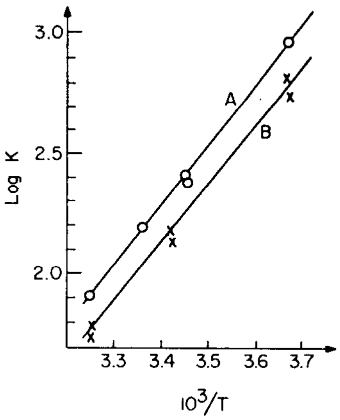

FIG. 5. Equilibria in hydrogenation of pentacyanocobaltate(II); the results in A and B are taken from Tables 2 and 3, respectively.

Kinetics of H_2 uptake. In several experiments the rate of reaction between molec-

TABLE 2

EQUILIBRIA IN HYDROGENATION OF PENTACYANOCOBALTATE(II)[a]

Expt. no.	Temp. (°C)	[Co][b] (%)	H_2 abs. (%)	Decomp. (%)	[CoH] (%)	K[c] $\left[10^3 \cdot \left(\frac{\text{mole}}{\text{liter}}\right)^{-1}\right]$
6	0	3.74	91.0	5.3	93.6	930
7	17	7.35	82.9	9.7	87.8	260
8	17	7.51	83.8	8.7	88.2	250
9	25	9.35	80.9	9.7	85.8	160
10	35	12.7	76.5	10.8	81.9	82

[a] 0.86 *M* KCN; $CoCl_2$ 4.0 mmole; volume 350 ml; H_2 pressure, 735 mm Hg.

[b] Explanations as in Table 1, footnotes *b–e*.

[c] The equilibrium constant *K* was calculated according to Eq. (4).

TABLE 3

EQUILIBRIA IN HYDROGENATION OF PENTACYANOCOBALTATE(II)[a]

Expt. no.	Temp. (°C)	[Co][b] (%)	H_2 abs. (%)	Decomp. (%)	[CoH] (%)	K $\left[10^3 \cdot \left(\frac{\text{mole}}{\text{liter}}\right)^{-1}\right]$
11	0	4.8	94.6	0.6	94.9	590
12	0	4.5	93.8	1.7	94.6	660
13	20	9.8	86.2	4.0	88.2	140
14	20	9.5	84.5	6.0	87.5	150
15	35	15.3	79.9	5.3	82.2	57
16	35	14.6	75.6	9.8	80.5	60

[a] 1.00 *M* NaOH; KCN 65 mmole; $CoCl_2$ 2 mmole; volume 390 ml; H_2 pressure, 735 mm Hg.

[b] Explanations as in Tables 1 and 2.

TABLE 4
SOLUBILITY OF MOLECULAR HYDROGEN IN 1 M NaOH, 0.2 M KCN[a]

Temp. (°C)	Solubility	
	ml H_2/liter (NTP)	10^{-3} mole/liter
0	15.0	0.67
20	12.6	0.57
25	12.0	0.54
35	11.3	0.51

[a] H_2 pressure, 735 mm Hg.

ular H_2 and pentacyanocobaltate(II) was followed by measuring the amount of hydrogen adsorbed as a function of time. Our experiments demonstrated that under the conditions applied, the hydrogen uptake follows second order kinetics with respect to cobalt. The initial rate of hydrogen absorption is proportional to the square of the cobalt concentration (Fig. 6), provided the reactions are carried out in solutions of high ionic strength. This is necessary to prevent changes in reaction rates due to changes in the activities of the reactants.

The course of the hydrogen absorption during each experiment also gave evidence for second order kinetics with respect to cobalt. In such a case the integrated rate equation can be written as

$$\frac{1}{A_t} - \frac{1}{A_{t=0}} = kt \qquad (5)$$

in which

A_t = nonhydrogenated cobaltate(II) concentration as estimated from the amount of H_2 consumed
t = time
k = apparent rate constant.

In Fig. 7 the values of $1/A_t$ for some experiments (Nos. 12, 13, and 15 from Table 5) are plotted as a function of time. The linear relationship between $1/A_t$ and t up to time $t = 12$ is obvious. At this point in all three experiments ca. 70% of the equilibrium amount of hydrogen was absorbed. After $t = 12$ min the values of $1/A_t$ lay below the straight lines drawn. This deviation is probably mainly due to the constantly increasing influence of the reverse reaction.

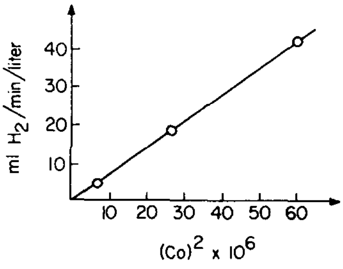

FIG. 6. The second order dependence of initial rate upon cobalt concentration. Temp., 20°C; 1.05 M KCl; 0.048 M KCN; H_2 pressure, 740 mm Hg.

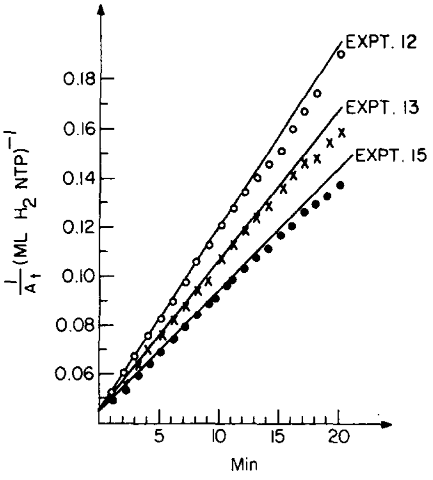

FIG. 7. Kinetics of hydrogen absorption by pentacyanocobaltate(II); forward reaction has been considered only; conditions as given in Tables 3 and 5.

The observed absorption agrees excellently with the picture of a termolecular forward reaction and a bimolecular reverse reaction as given in (3).

The rate equation for the disappearance of pentacyanocobaltate(II) then becomes

$$d\,\mathrm{Co}/dt = -k_1[\mathrm{H_2}][\mathrm{Co}]^2 + k_2[\mathrm{CoH}]^2 \qquad (6)$$

in which [Co] and [CoH] represent amounts of nonhydrogenated and hydrogenated cobalt complexes, respectively.

Integration of Eq. (6) yields:

$$\ln\frac{A_t + C}{A_t - A_\infty} = \ln\frac{A_0 + C}{A_0 - A_\infty} - k_1[\mathrm{H_2}]\left[1 - \frac{1}{K[\mathrm{H_2}]}\right]t \qquad (7)$$

in which

A_t = Amount of nonhydrogenated cobaltate(II) at time t, as estimated from the amount of H_2 consumed

A_0 = Amount of nonhydrogenated cobaltate (II) at time $t = 0$

A_∞ = Amount of nonhydrogenated cobaltate (I) at time $t = \infty$ (equilibrium)

$$C = \frac{A_0 A_\infty}{A_0 - 2A_\infty}$$

$K = k_1/k_2$ = equilibrium constant.

In Fig. 8 the values of ln $(A_t + C)/(A_t - A_\infty)$ for experiments 12, 13 and 15 are plotted as functions of t. For all three experiments the relationship is almost rectilinear up to $t = 40$ min. At this point 90% of the equilibrium amount of hydrogen has been absorbed. Experiments 12 and 13 even yield straight lines up to $t = 90$ min, when 97% of the equilibrium amounts of hydrogen have been taken up. From the slopes of the corresponding straight lines in Figs. 7 and 8 equal values are calculated for k_1. On calculating the functions $1/A_t$ and ln $(A_t + C)/(A_t - A_\infty)$ from H_2 absorption measurements, it was assumed that the disproportionation of the total amount of decomposed cobalt complex had taken place directly on mixing the KCN and $CoCl_2$ solutions ($t = 0$). Furthermore, the influence of formation of $[Co(CN)_5H]^{3-}$ due to disproportionation, upon the kinetics of H_2-absorption was neglected. It constitutes only a small fraction of the total amount of $[Co(CN)_5H]^{3-}$ present at equilibrium. Table 5 summarizes the results of the kinetic measurements. The values of the rate constant k_1 are given as those of the termolecular forward reaction (Eq. 3). Table 5 shows that k_1 between 0 and 35°C is constant within the experimental error. This would correspond with a zero apparent energy of activation.

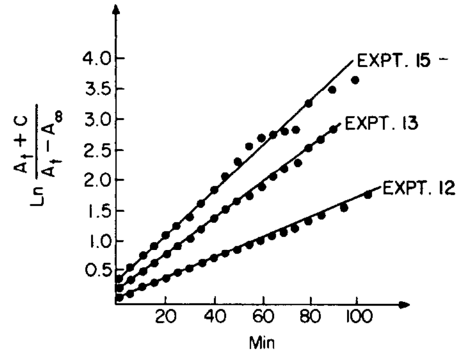

FIG. 8. Kinetics of hydrogen absorption by pentacyanocobaltate(II); both forward and reverse reactions have been considered; conditions as given in Tables 3 and 5; for symbols see Eq. (7).

TABLE 5
RATES OF HYDROGENATION OF PENTACYANOCOBALTATE(II)[a]

Expt. no.	Temp. (°C)	Disprop. (%)	k_1 $\left[10^3 \cdot \text{min}^{-1} \cdot \left(\frac{\text{mole}}{\text{liter}}\right)^{-2}\right]$	
				Average
11	0	0.6	51	50
12	0	1.7	49	
13	20	4.0	48	49.5
14	20	6.0	51	
15	35	5.3	45	48
16	35	9.8	51	

[a] 1.00 M NaOH; $CoCl_2$ 2 mmole; KCN 65 mmole; volume 390 ml; H_2 pressure, 735 mm Hg.

Influence of Salt Concentration

Decomposition and hydrogenation of $[Co(CN)_5]^{3-}$ in aqueous solution has been found to be accelerated by the presence of ions (*3, 4, 9*). Mills *et al.* (*3*) observed that the influence of KCN, NaOH, KCl, and $BaCl_2$ on hydrogenation were of approximately equal effectiveness. King and Winfield (*9*) showed the alkali metal ions to possess different activities.

We carried out comparative rate experiments on hydrogenation and decomposition at two different concentrations of KCl. Under the conditions applied (0.048 M KCN, 0.0077 M $CoCl_2$, temp. 20°C) we found the influence of an increase of the KCl concentration from 0.3 M to 1.0 M to have identical accelerating effects on decomposition and hydrogenation. Both second order rate constants increased with a factor of 3.0. This gives evidence that in both reactions the rate-determining steps are identical or proceed between similar reactants (*12*).

DISCUSSION

In all the reactions described, viz. disproportionation, hydrogenation, and dehydrogenation, highly charged ions take part. Mention has already been made of the marked influence of the presence of salts on the rates of these reactions. To prevent influences of changing cobalt concentration on the total ionic strength (*12*), all kinetic and equilibrium experiments were carried out in solutions having a large total ionic strength, viz. 1 *M* in NaOH, KCl, or KCN. In such solutions the activity coefficients of the complex cobalt ions in the concentration range investigated (0.003–0.02 *M*) may be considered to be constant. From the slope in Fig. 5 the value of $-\Delta H$ is estimated to be 11.2 kcal/mole, which, combined with the bond dissociation energy of the H_2 molecule (104 kcal/mole) leads to a bond energy of 58 kcal/mole for the newly formed bond in $[Co(CN)_5H]^{3-}$.

As mentioned above both the decomposition (disproportionation) and the hydrogenation of $[Co(CN)_5]^{3-}$ are strongly accelerated by an increase in ionic strength of the solution. This indicates that in both cases reactions between ions of equal charge signs are rate-determining (*12*), as has been suggested by Mills *et al.* (*3*). Also in agreement with this view are the results of our kinetic experiments which for both reactions point to second order dependences upon the cobalt concentration. The fact that both reaction rates are influenced to the same extent by changes in the KCl concentration, provides further evidence for the disproportionation and hydrogenation reactions having identical dependences on the $[Co(CN)_5]^{3-}$ concentration.

Mills *et al.* (*3*), however, found the hydrogen absorption to be of first order with respect to cobalt. It is not unlikely that in their experiments the application of too high concentrations may have caused relatively too low rates of absorption. The hydrogen diffusion then becomes rate-determining as well. Confusion may also have been caused by the course of the hydrogen absorption, which towards the end of the reaction exhibits first order kinetics with respect to cobalt. In Eq. (7) the expression ln $(A_t + C)/A_t - A_\infty)$ then becomes equivalent to: Constant − ln $(A_t - A_\infty)$, which is essentially the integrated rate equation for a first order reaction.

The reasonably large heat effect (11 kcal/mole H_2) of the hydrogen absorption, and the correspondingly very low apparent activation energy of this presumed termolecular reaction, suggest analogy to the absorption of hydrogen on surfaces of various transition metals.

Other reaction routes, however, are also possible, e.g.,

$$2[Co(CN)]^{3-} \underset{k_4}{\overset{k_3}{\rightleftarrows}} [Co_2(CN)_{10}]^{6-} \tag{8a}$$

$$[Co(CN)_{10}]^{6-} + H_2 \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2[Co(CN)_5H]^{3-} \tag{8b}$$

or

$$[Co(CN)_5]^{3-} + H_2 \underset{k_4}{\overset{k_3}{\rightleftarrows}} [Co(CN)_5H_2]^{3-} \tag{9a)*}$$

$$[Co(CN)_5H_2]^{3-} + [Co(CN)_5]^{3-} \underset{k_6}{\overset{k_5}{\rightleftarrows}} 2[Co(CN)_5H]^{3-} \tag{9b}$$

These two routes are both in agreement with the kinetics observed for the H_2 absorption, provided the relation $k_4 \gg k_3 \gg k_5 > k_6$ is valid. The same considerations that were given to the kinetics of the termolecular forward and the second order reverse reactions apply here, e.g., compare Eqs. (6) and (7). In both schemes (8) and (9) the over-all apparent rate constants of the forward and the reverse reactions can be written as

$$k_1 = k_3 k_5 / k_4 \qquad \text{and} \qquad k_2 = k_6$$

respectively. Consequently the over-all energy of activation is given by

$$\begin{aligned} E_t &= E_3 - E_4 + E_5 \\ &= \Delta H_{34} + E_5 \end{aligned}$$

in which E_3 represents the energy of activation of the reaction with rate constant

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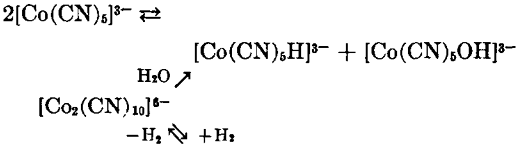
* The probability of (9) has been considered by Mills *et al.* (*3*) who rejected this route because of the observed salt effect and the first order kinetics with respect to cobalt.

k_3, etc., and $-\Delta H_{34}$ represents the enthalpy of reaction of the process (8a) or (9a). If this enthalpy of reaction is positive an appropriate value of E_5 may cause an over-all energy of activation which is zero or even negative. A case in point is reaction (8a), viz. the dimerization of pentacyanocobaltate(II) ions. This reaction may be accompanied by the evolution of heat, as it is known from magnetic measurements that in the solid state the potassium salt of this complex probably exists as a dimer (*2*). For Eqs. (8) and (9) to meet the kinetic requirements, however, only small amounts of the associated species should be present in the equilibria (8a) and (9a). For that reason it will be difficult to distinguish between either one of the mechanisms (8) and (9) or the termolecular reaction.

Although the experiments do not give any clear indication as to which of the possible reaction routes is correct, scheme (8) is the most attractive. Diagram (10) represents the reactions which may take place



$$\begin{array}{l} 2[Co(CN)_5]^{3-} \rightleftarrows \\ \qquad\qquad\qquad [Co(CN)_5H]^{3-} + [Co(CN)_5OH]^{3-} \\ \qquad\qquad H_2O \nearrow \\ \quad [Co_2(CN)_{10}]^{6-} \\ \qquad\qquad -H_2 \nwarrow\!\searrow +H_2 \\ \qquad\qquad\qquad 2[Co(CN)_5H]^{3-} \end{array}$$

(10)

This picture has the advantage that both the hydrogenation and the decomposition reactions are considered to proceed via the same binuclear cobalt complex. In accordance with this view King and Winfield (*10*) have shown the presence of small amounts of the binuclear complex in solutions of methanol. However, these investigators were unable to find any relationship between the concentration of the complex and the rate of hydrogen absorption.

It is interesting to quote some results obtained by Webster and Halpern (*13*) and by Calvin, Wilmart, and Barsh (*14,15*). They showed that the activation of molecular hydrogen both by silver ions in aqueous solution and by cuprous ions in quinoline, might also follow third order kinetics. The resemblance to the reaction between H_2 and $[Co(CN]_5]^{3-}$ is striking, especially when it is borne in mind that the hydrogen absorption by Cu(I) and Ag(I) as well as by $[Co(CN)_5]^{3-}$ is believed (*10*) to proceed by homolytic fission of the hydrogen molecule.

Further investigations into these reactions will be necessary in order to verify whether the observed similarity is fortuitous, or whether a more general mechanism applies to this type of reaction.

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