in other less obvious ways. This implies specific ion effects. For the present system, the reaction is insensitive to changes in ionic strength; however, all measurements have, of necessity, been conducted at higher than ideal ionic strengths. The rates are essentially the same in the absence of added salt (μ = 0.2) and at μ = 0.7 in the presence of $NaNO_3$, KNO_3, $RbNO_3$ or $CsCl$. The process is accelerated by about 10% at μ = 0.7

in the presence of $Ba(NO_3)_2$ in agreement with the report by Adamson and Vorres.[6]

Electron Transfer Rates through the Use of Optical Activity. II. The Electron Transfer Racemization of Propylenediaminetetraacetatocobaltate(III)—an Example of Electron Transfer with Retention of Configuration

By Yong Ae Im and Daryle H. Busch

The rate of electron transfer has been studied in the system composed of the hexadentate propylenediaminetetraacetate complexes of cobalt(II) and cobalt(III) by the use of optical activity. The extreme stereospecificity of the optically active ligand is established, and it has been demonstrated that the less stable isomer of the cobalt(III) complex must exist in relative concentrations of less than 1% at equilibrium, if it exists at all. The form of the rate law clearly delineates this system as involving electron transfer with complete retention of configuration for both exchanging species. It is most reasonably concluded that the labile cobalt(II) complex exists predominantly as a single enantiomer, the configuration of the octahedron being determined by that of the ligand. The cause of this stereospecificity is discernable in terms of the structures of the compounds. A novel statistical resolution of optical isomers is presented.

Introduction

The system composed of propylenediaminetetraacetatocobaltate(III) and propylenediaminetetraacetatocobaltate(II) (the ligand shall be abbreviated as PDTA hereafter) has been chosen for the purpose of extending investigations[1] of electron transfer processes which catalyze racemization.

The cobalt(III) complex has been resolved into optical antipodes by Dwyer and Garvan[2] who employed active cis-dinitrobis-(ethylenediamine)-cobalt(III) bromide. The cobalt(II) complex, which ordinarily is expected to be labile and configurationally unstable, exhibits a characteristic optical rotation in solution.[3] It has been concluded by Bosnick, Dwyer and Sargeson[3] that the cobalt(II) complex exhibits configurational stability as a result of the fact that propylenediaminetetraacetic acid exists in a preferred enantiomeric form when combined with divalent and trivalent metal ions.

The fact that both the oxidant and the reductant conserve configuration determines that the system $[Co(PDTA)]^- - [Co(PDTA)]^=$ be an example of electron transfer catalyzed racemization proceeding with conservation of configuration through the course of the reaction. In this respect, it is comparable to the system composed of $[Os(dipy)_3]^{+3} - [Os(dipy)_3]^{+2}$. It previously has been shown that such systems should obey the same rate law as those involving isotopic tracers.[1]

The study of the rate of electron transfer in the PDTA system also was expected to provide funda-

mental information on the nature of certain stereospecific relationships, since both the ligand and the cobalt complex are optically active. Comprehensive accounts of stereospecificity have been given by Bailar and Corey[4,5] and Basolo and Pearson.[6]

Theoretically, the hexadentate complex $[Co(PDTA)]^-$ can exist in four different isomeric forms, d-l, d-d, l-d and l-l (the capital letters refer to the sign of rotation of the whole complex and the small letters, to that of the ligand, usually at the d-line of sodium). Dwyer and Garvan[2] attempted to isolate all the possible isomers but were only able to obtain d-l and l-d. The highly stereospecific nature of the complexing agent was demonstrated by experiments in which they found that the configuration of the ligand obtained from the separately resolved metal complex was optically pure and identical in rotation with the ligand which was prepared from optically active propylenediamine. The fact that only l-PDTA is obtained from d-$[Co(PDTA)]^-$ and only d-PDTA from l-$[Co(PDTA)]^-$ provides strong, though not conclusive, evidence for the non-existence of the isomers l-l and d-d. This experimental result may be a consequence of the difference in physical properties (solubility, etc.) and/or thermodynamic stability of the diastereoisomers. Small amounts of some isomers may not be detectable by a preparative technique. If the thermodynamically less stable d-d and l-l isomers of $[Co(PDTA)]^-$ exist in such small amounts as to escape detection

(1) Y. A. Im and D. H. Busch, J. Am. Chem. Soc., 83, 3357 (1961).

(2) F. P. Dwyer and F. L. Garvan, ibid., 81, 2955 (1959).

(3) B. Bosnick, F. P. Dwyer and A. M. Sargeson, Nature, 186, 966 (1960).

(4) J. C. Bailar, Rec. Chem. Progr., 10, 17 (1949).

(5) E. J. Corey and J. C. Bailar, Jr., J. Am. Chem. Soc., 81, 2620 (1959).

(6) F. Basolo and R. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.

during synthetic experiments and if equilibrium is attained through the labile cobalt(II) complex, rate studies on the electron transfer racemization of [Co(PDTA)]⁻ and [Co(PDTA)]⁼ should provide a way to detect the equilibrium amounts of the unstable L-*l* and D-*d* isomers. In order for this to be true, they must, of course, occur to an extent which is detectable by the measurement employed.

Experimental

Synthesis.—Potassium D(or L-)-propylenediaminetetra-acetatocobaltate(III) ion was prepared by the method of Dwyer and Garvan.³ The procedure involved the preparation of *d,l*-propylenediaminetetraacetic acid and *d,l*-barium propylenediaminetetraacetatocobaltate(III) 8-hydrate; resolution of the barium salt, effected by *d-cis*-dinitro-bis-(ethylenediamine)-cobalt(III) bromide; and conversion of the optically active barium salt to the potassium salt by double decomposition with potassium sulfate. The very soluble, red-purple, K[Co(PDTA)]·3H₂O exhibited the rotation, [α]₅₄₆₁ ±1000° for 0.01% aqueous solutions in a one dm. tube.

D(or L-)-propylenediaminetetraacetatocobaltate(II) ion was prepared by mixing appropriate amounts of cobalt(II) nitrate 6-hydrate and disodium dihydrogen propylenediaminetraacetate at the beginning of each experiment. The synthesis of optically active propylenediaminetetraacetic acid involved the resolution of the propylenediamine,⁷ using *d*-tartaric acid, and the preparation of H₄PDTA from monochloroacetic acid, sodium hydroxide and propylenediamine. The optically active H₄PDTA–H₂O is a white crystalline substance which is much more soluble than the racemate. It exhibited the rotation [α]D ±47° (0.5% aqueous solution in a one dm. tube).

Kinetic Procedure.—Solutions for the kinetic experiments were prepared by mixing appropriate amounts of optically active K[Co(PDTA)]·3H₂O and of the stock solutions of Na₂H₂PDTA, or Na₂H₂PDTA·H₂O in the case of the optically active ligand, and Co(NO₃)₂·6H₂O, followed by adjusting the pH of the solution. The stoppered flask containing the solution was then placed in a thermostat and samples were withdrawn periodically for the measurement of the optical rotations. Usually, an aliquot of 2 ml. was diluted to 42 ml. with distilled water for convenience in the measurement of rotation. The optical rotations were determined with a precision of ±0.003° using a Rudolf Model 80 photoelectric polarimeter. All rotations were measured using a one decimeter tube and a mercury lamp, at the wave length of 436 mμ.

Results and Discussion

The data reveal that the hexadentate complex, D-[Co(*l*-PDTA)]⁻, does not undergo thermal racemization even at 100° and at a pH of 2.0. Thermal decomposition takes place, however, after long periods of heating. The apparent decrease in the optical rotation of the solution after a period of heating was found to be due to the decomposition of the complex, as evidenced by the fading of the vivid color of the solution. This was effectively demonstrated by establishing the fact that both the optical rotation and the optical density of the solution decrease at the same rate (Fig. 1). The decomposition rate is quite small, and it seems that there is an induction period prior to which the decomposition is extremely slow. After the induction period, the rate increases, suggesting autocatalysis.

No racemization is observed upon mixing an equimolar solution of D-[Co(*l*-PDTA)]⁻ and the *l*-PDTA complex of cobalt(II). The expected reaction is that given below. (To simplify the

D-[Coᴵᴵᴵ (*l*)]⁻ + [Coᴵᴵ (*l*)]⁼ ⟶ L-[Coᴵᴵᴵ (*l*)]⁻ + [Coᴵᴵ (*l*)]⁼

(7) F. P. Dwyer, F. L. Garvan and A. Shulman, *J. Am. Chem. Soc.*, **81**, 1943 (1959).
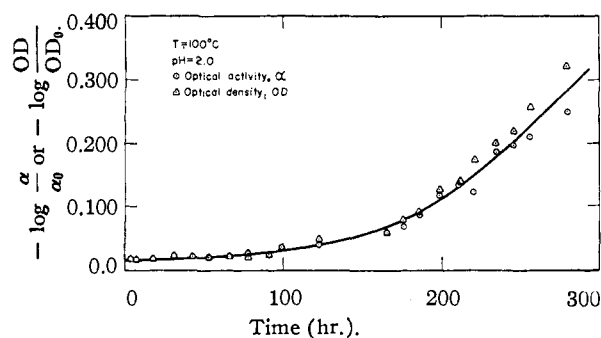

Fig. 1.—Variation of optical rotation and optical density of D-[Co(*l*-PDTA)]⁻ with time at 100°.

writing of this and other equations,¹ the ligand is occasionally denoted by its configuration alone.) Table I shows typical data, where it may be seen that little change is observed in optical rotation during 48 hr. ±Δα represents the deviation

TABLE I
DEPENDENCE OF ROTATION ON TIME IN SOLUTION CONTAINING BOTH COBALT(II) AND COBALT(III) COMBINED WITH *levo*-LIGAND

[*d*-K (Co(*l*-PDTA)]·3H₂O] = 0.02 *M*; [Na₂[Co(*l*-PDTA)·H₂O] = 0.02*M*; pH = 2.0; *T* = 100ᵇ

Time (hr.)	Experiment A — α	±Δα	Experiment B — α	±Δα
0	0.241	+0.003	0.236	+0.002
1	.241	+ .003	.241	+ .007
3	.244	+ .006	.236	+ .002
5	.244	+ .006	.239	+ .005
7	.239	+ .001	.243	+ .009
9	.236	+ .001	.239	+ .005
11	.234	− .004	.239	+ .005
13	.237	− .001	.234	.000
21	.236	− .002	.230	− .004
24	.237	− .004.	.229	− .005
26	.234	− .004	.228	− .006
28	.235	− .003	.231	− .003
30	.234	− .004	.242	+ .008
32	.240	− .002	.242	+ .008
34.3	.235	− .003	.231	− .003
36.3	.234	− .004	.229	− .005
48	.238	.000	.220	− .014
Av.	.238	± .003	.234	± .005
	1.3% change		2.1% change	

from the mean for the particular datum. The variation of Δα is actually confined to a span of rotation of the magnitude of the uncertainty of the measurement. However, the inversion in algebraic sign of Δα with time reflects the fact that the rotation has changed very slightly. This corresponds to the extent of change expected from decomposition alone. As can be seen from corresponding data for experiments in which L-[Coᴵᴵᴵ(*d*-PDTA)]⁻ and the *l*-PDTA complex of cobalt(II) are used, the 48 hr. period represents over 98% reaction. On this basis it may be concluded that the equilibrium concentration of the less probable isomer, L-*l*, is substantially less than 1%. The extreme stereospecificity exhibited by the PDTA ligand² is confirmed by these experiments.

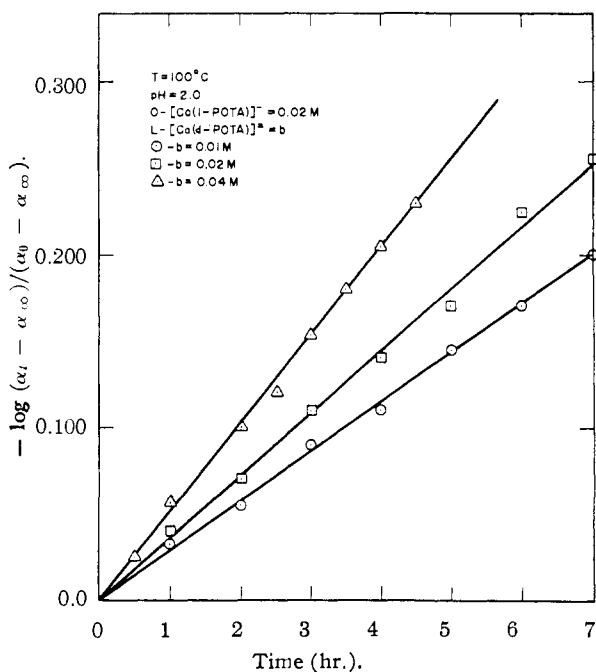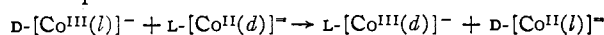Complete racemization occurs when equivalent amounts of D-[Coᴵᴵᴵ(*l*-PDTA)]⁻ and the *d*-PDTA

Fig. 2.—Variation of optical rotation with time for the system D-[Co(l-PDTA)]⁻-L-[Co(d-PDTA)]⁼.

complex of cobalt(II) are mixed. This corresponds to the process

$$\text{D-}[Co^{III}(l)]^- + \text{L-}[Co^{II}(d)]^= \rightarrow \text{L-}[Co^{III}(d)]^- + \text{D-}[Co^{II}(l)]^=$$

As discussed previously,[1] the appropriate rate law for electron transfer catalyzed racemization in systems in which configuration is conserved is as given in equation 1 (α_t is the rotation at time t; α_∞ is the equilibrium rotation; α_0 is the initial rotation; and a and b are the concentrations of the cobalt(III) and cobalt(II) complexes).

$$-\ln\left(\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) = R[(a + b)/ab]t \qquad (1)$$

where R is a function of the initial concentrations of reactants (equation 2)

$$R = ka^n b^m \qquad (2)$$

If m and n are assumed to be unity, equation 3 is obtained

$$-\ln\left(\frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}\right) = k(a + b)t \qquad (3)$$

For equimolar mixtures of oppositely rotating cobalt(III) and cobalt(II) complexes, the rate constant may be obtained from the slopes of plots of $-\ln(\alpha_t/\alpha_0)$ versus time, for α_∞ is then zero. The applicability of equation 3 is shown by the graphs of Fig. 2. In general the pseudo first-order rate constant R' is of the form given in equation 4.

$$R' = k(a + b) \qquad (4)$$

The proportionality of R' to $(a + b)$ has been verified (Fig. 3). The zero intercept of Fig. 3 confirms the absence of thermal racemization.

Table II summarizes the rate data, including the investigations of the concentration, pH and temperature dependence. The pH dependence over the range from 2.0 to 7.0 has been analyzed in terms of two parallel paths connected by an acid–
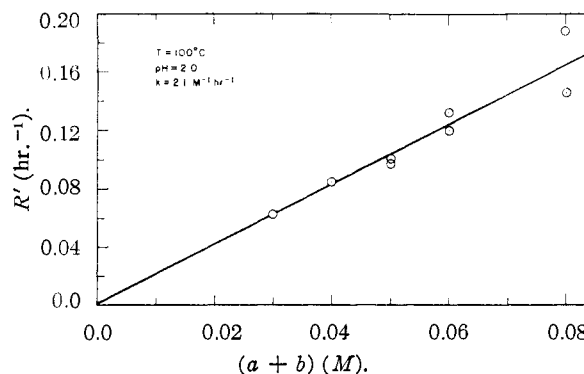

Fig. 3.—Variation of pseudo first-order rate constant R' with the total initial concentration of reactants, $a + b$, for D-[Co(l-PDTA)]⁻ and L-[Co(d-PDTA)]⁼.

base equilibrium in analogy to that found for the similar ethylenediaminetetraacetate (EDTA) system[1] (equations 5, 6 and 7).
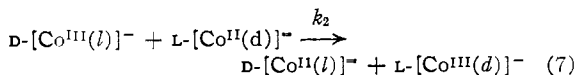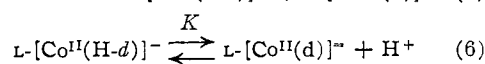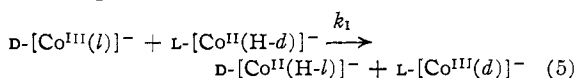
$$\text{D-}[Co^{III}(l)]^- + \text{L-}[Co^{II}(H\text{-}d)]^- \xrightarrow{k_1}$$
$$\text{D-}[Co^{II}(H\text{-}l)]^- + \text{L-}[Co^{III}(d)]^- \qquad (5)$$

$$\text{L-}[Co^{II}(H\text{-}d)]^- \underset{\longleftarrow}{\overset{K}{\longrightarrow}} \text{L-}[Co^{II}(d)]^= + H^+ \qquad (6)$$

$$\text{D-}[Co^{III}(l)]^- + \text{L-}[Co^{II}(d)]^= \xrightarrow{k_2}$$
$$\text{D-}[Co^{II}(l)]^= + \text{L-}[Co^{III}(d)]^- \qquad (7)$$

TABLE II

RATE OF ELECTRON TRANSFER IN THE SYSTEM
[Co(PDTA)]⁻-[Co(PDTA)]⁼

Temp., °C.	pH	(D-[Coᴵᴵᴵ (l)]⁻)	(L-[Coᴵᴵ (d)]⁼)	R'(hr.⁻¹)ᵃ	$k = \frac{R'}{a + b}$
100	2.0	0.02	0.01	0.062	2.1
100	2.0	.02	.02	.084	2.1
100	2.0	.02	.03	.099	2.0
100	2.0	.02	.04	.132	2.2
100	2.0	.02	.06	.145	1.8
100	2.0	.04	.04	.178	2.2
100	3.15	.02	.02	.039	0.96
100	4.0	.02	.02	.024	.59
100	7.0	.02	.02	.024	.60
90	2.0	.02	.02	.027	.68
90	2.0	.02	.04	.043	.70
90	3.0	.02	.02	.114	.29
90	4.0	.02	.02	.090	.22
80	2.0	.02	.02	.013	.31
80	3.0	.02	.02	.0060	.15
80	4.0	.02	.02	.0046	.11

ᵃ All values of R' are the average of two or more separate determinations.

At 100°, the following values were obtained and are compared with the corresponding values for the EDTA system

	k_i (M^{-1} hr.⁻¹)	k_2 (M^{-1} hr.⁻¹)	
PDTA system	2.5	0.71	2.4 × 10⁻³
EDTA system	2.9	0.50	2.0 × 10⁻³

The close correspondence in the form of the pH dependence and in the actual values of the pertinent constants attests to the close similarity in the electronic configurations of the two sets of reactants and in their respective solution structures. The only notable difference in this aspect of the behaviors of the EDTA and PDTA systems is

associated with measurements at higher pH. Electron transfer experiments are rendered impractical in the EDTA case at pH values greater than four because of the base catalysis of the racemization of $Co^{III}(EDTA)^{-}$.[1,8] In contrast, the electron transfer process has been measured at a pH of 7 in the PDTA system with no evidence of competing reactions. This is in agreement with the observation that the base hydrolysis of the cobalt(III) complex of PDTA is very slow[9] (again in contrast to the EDTA complex[8]).

The data obtained on the temperature dependence of the rate of electron transfer are not so extensive as in the case of the EDTA system. Consequently, as detailed an analysis of the results is not justified. However, a useful comparison may be made. At a pH of 2.0, the *apparent* enthalpy of activation and entropy of activation are $\Delta H^{\ddagger} = 24$ kcal./mole and $\Delta S^{\ddagger} = -9.3$ e.u. These values are comparable to those derived from k_1 (involving the protonated species) for the EDTA system; *i.e.*, $\Delta H^{\ddagger} = 24$ kcal./mole; $\Delta S^{\ddagger} = -9.0$ e.u. The corresponding values for the PDTA system at a pH of 4, $\Delta H^{\ddagger} = 21$ kcal./mole and $\Delta S^{\ddagger} = -21$ e.u., compare with those derived from k_2 for the EDTA system; $\Delta H^{\ddagger} = 20$ kcal./mole and $\Delta S^{\ddagger} = -21$ e.u.

The close conformance of the rate data to the equations derived for electron transfer catalyzed racemization with conservation of configuration establishes the general nature of the process. The fact that analysis of this system and the related EDTA system in terms of their respective rate laws[1] yields kinetic parameters which are closely similar for the two, as they are expected to be, further confirms the interpretations presented. From the agreement in their kinetic behaviors, the transition states for electron transfer in the two systems must be very similar. Consequently, these considerations will not be discussed here.[1]

The isomer distributions for both the cobalt(II) and cobalt(III) complexes of PDTA merit further consideration. The results presented here clearly demonstrate the essentially exclusive existence of the D-l and L-d isomers of the cobalt(III) complex, at the expense of the diastereoisomers, D-d and L-l. The source of this selectivity must be sought in the stereochemistry of the isomers. Cooke and Busch[10] have presented evidence for the absolute configuration of L-$[Co(d\text{-PDTA})]^{-}$ and have assigned the methyl group to an equatorial orientation with regard to its parent chelate ring. The gauche conformation of the chelate ring in the corresponding EDTA complex has been established by the X-ray work of Weakliem and Hoard.[11] For a given absolute configuration of the complex, the configuration of the ligand determines whether the methyl group is axially or equatorially located, and, of course, the converse configurational relationships also apply. Two such diastereoisomers are depicted in Figs. 4 and
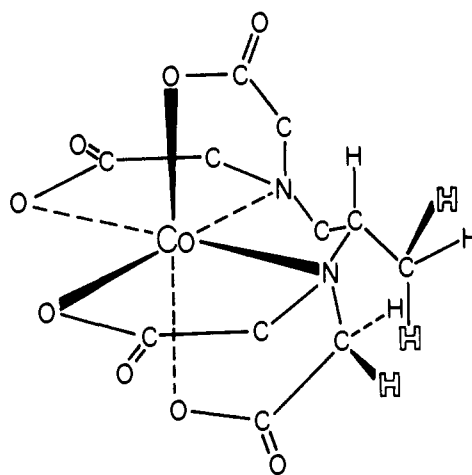
(8) D. W. Cooke and D. H. Busch, paper presented before the 136th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.

(9) K. Swaminathan and D. H. Busch, unpublished results.

(10) D. W. Cooke and D. H. Busch, *J. Inorg. Nucl. Chem.*, in press.

(11) H. A. Weakliem and J. L. Hoard, *J. Am. Chem. Soc.*, **81**, 549 (1959).

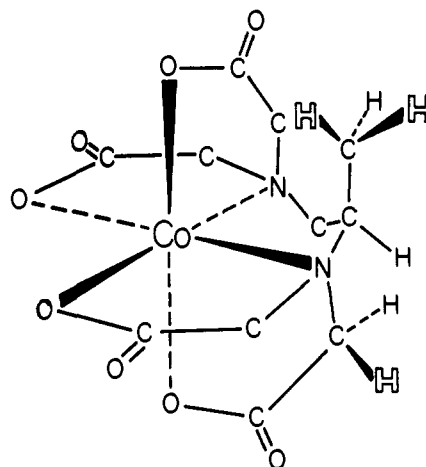Fig. 4.—Configuration of the L-d isomer of [Co(PDTA)].

Fig. 5.—Configuration of the L-l isomer of [Co(PDTA)]$^{-}$.

5. The stable L-d form (Fig. 4) contains the equatorial methyl group and the proximity of this group to the most disadvantageously located hydrogen atoms is shown. Considerable repulsion might even be expected in this form. However, as Fig. 5 shows, an axial methyl group is much less favorably placed, for in this case it rises alongside a methylene group with which it must share drastically limited space. Because of the problems of illustration, the offending methylene hydrogen atoms are not shown; however, their effect should be obvious.

Although the steric relationships are useful in a post-datum accounting for the excess of the isomers D-l and L-d in the case of the cobalt(III) complex, they are of greater importance in understanding the cobalt(II) species. It must be realized that a novel situation exists in the cobalt(II) case, for the usual lability of cobalt(II) complexes requires that this system be always at "configurational equilibrium." Yet, the compound is clearly asymmetric. It is obvious from this and earlier work[3] that an equilibrium mixture of the isomers D-l and L-l must always exist and that one of the forms is more abundant. The open question is with regard to the relative abundance of the more stable isomer. Without further inquiry, the isomer dis-

TABLE III

RESOLUTION THROUGH ELECTRON TRANSFER IN THE SYSTEM $[Co(PDTA)]^-$-$[Co(PDTA)]^-$

$T = 100°$; pH 2.0

([Co(PDTA)]⁻), a	([Co(PDTA)])⁼, b	$\overbrace{\text{Expt.}}^{\alpha_\infty}$	Calcd.	% Resolution^a	k $(M^{-1}$ hr.$^{-1})b$
Racemic, 0.02 M	D-l, 0.04 M	.....	−0.202	84	1.9
Racemic, 0.02 M	D-l, 0.02 M	−0.138	− .138	75	2.2
D-l, 0.02 M	Racemic, 0.02 M	− .133	− .138	75	2.2
D-l, 0.02 M	Racemic, 0.03 M	− .119	− .116	70	2.1

^{a} Per cent. resolution is the ratio of the calculated concentration of the more abundant isomer in the equilibrium mixture to the concentration of the initial racemate. ^{b} Each value of k is the average of more than two experiments.

tribution might vary anywhere from about 51% (D-l)—49% (L-l) to something like 99+% (D-l)—1% (L-l), since the kinetic equations will be obeyed so long as the rotation is instantly proportional to the concentration of the cobalt(II) complex.

From the nature of the steric interaction of the methyl group with the remainder of the ligand, an increase in the size of the metal ion should increase this repulsion, for this would fold back the methylene hydrogen atoms into the methyl group. One therefore expects the methyl group to be at least as selective for ions bigger than cobalt-(III) as it is for that ion. Since the results given here prove the cobalt(III) complex to exist at equilibrium as 99+% D-l (or L-d) isomer and since cobalt(II) is larger than cobalt(III), it is only reasonable to conclude that the cobalt(II) complex is essentially all (99+%) of the single preferred configuration.

From the foregoing, a novel method of resolution may be suggested for certain very special systems. In systems retaining configuration, these configurations (d and l) are distributed statistically between the exchanging species as a result of electron transfer (just as an isotopic tracer is).

In consequence, an excess of an optically active ion will confer a high degree of resolution on the second ion (originally racemic) at equilibrium. This has been demonstrated (Table III) by following such solutions to their equilibrium rotations, which may be calculated from equation 8

$$\alpha_\infty = \frac{b}{(a+b)}\{[\alpha]_{II}b - [\alpha]_{III}a\} \qquad (8)$$

where a and b are as previously defined and $[\alpha]_{II}$ and $[\alpha]_{III}$ are the rotations of one molar solutions of the divalent and trivalent complexes. In all cases the experimental and predicted values for the equilibrium rotation agree closely. Other novel resolution methods based on equilibria have been demonstrated among complexes.[12,13]

(12) F. P. Dwyer, M. F. O'Dwyer and E. C. Gyarfas, *Nature*, 167, 036 (1951); F. P. Dwyer and E. C. Gyarfas, *ibid.*, 168, 29 (1951).
(13) D. H. Busch, *J. Am. Chem. Soc.*, 77, 2747 (1955).

The Liquid Phase Hydrogenation of Cyanocobaltate(II)

BY N. KELSO KING AND M. E. WINFIELD

Solutions containing $[Co^{II}(CN)_5]^{3-}$ react reversibly with molecular hydrogen to give a colorless hydride ion of probable structure $[Co^{III}(CN)_5H]^{3-}$, which has considerable stability in alkaline water or methanol, or in the solid state. The same product results from reduction of $[Co^{II}(CN)_5]^{3-}$ electrolytically or by means of NaBH₄. It is formed also in the first step in the aging of $[Co^{II}(CN)_5]^{3-}$, which proves to be disproportionation to hydride and $[Co^{III}(CN)_5OH]^{3-}$ rather than a simple dimerization as formerly believed. Since cations accelerate both disproportionation and H₂ uptake, the influence of added salt on the latter reaction is not readily analyzed but is probably a combination of cation promotion and a general salt-effect diminished by loss of reactant by disproportionation. Cs⁺ provides a clear example of excellent promotion of gas uptake vitiated by excessive stimulation of disproportionation. K⁺ is the best compromise promoter in the series of alkali metal ions. Use of methanol in place of water as solvent increases the rate of H₂ uptake 4-fold (taking into account a 10-fold increase in gas solubility). Descriptions are given of the sequence of reactions which follow mixing of CoCl₂ and KCN solutions and of the spectra of essentially pure solutions of $[Co^{II}(CN)_5]^{3-}$ and $[Co^{III}(CN)_5H]^{3-}$. The hydride has a single absorption band in the visible and ultraviolet regions, situated at 305 mμ. The H₂ evolution and exchange reactions, which have been observed in mixtures of CoCl₂ and KCN by previous investigators, can be explained in terms of $[Co^{III}(CN)_5H]^{3-}$ as the source of the liberated gas.

Introduction

Cobaltous chloride added to excess aqueous KCN yields a greenish solution containing the pentacyanocobaltate(II) ion[1-3] which can be re-

(1) M. A. Descamps, *Compt. rend.*, 67, 330 (1868).
(2) D. N. Hume and I. M. Kolthoff, *J. Am. Chem. Soc.*, 71, 867 (1949).
(3) A. W. Adamson, *ibid.*, 73, 5710 (1951).

duced by various means to an ion whose color and absorption spectrum have not previously been determined correctly because of masking by other compounds present. Treadwell and Huber,[4] as well as later investigators, have regarded the ion as a complex of Co^I, the expected product of a 1-electron reduction of $[Co^{II}(CN)_5]^{3-}$.

(4) W. D. Treadwell and D. Huber, *Helv. Chim. Acta*, 26, 10 (1943).