[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OKLAHOMA]

Dissociation of *trans*-Dichlorobis-(ethylenediamine)-cobalt(III) Chloride Hydrochloride

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In disagreement with the work of previous investigators, it has been shown that the complex salt *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride hydrochloride, prepared according to standard methods, exists as $[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}6H_2O$ instead of $[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}2H_2O$. Pressure–composition diagrams at constant temperature were obtained for the equilibrium between the anhydrous and hydrated hydrochloride forms of the complex, and the width of the constant pressure plateau precludes the possibility of the existence of a dihydrated hydrochloride. Analyses of the equilibrium vapors indicated that they consist of a mixture having a 6 to 1 mole ratio of water to hydrogen chloride. The dissociation pressure p was determined as a function of temperature from 5 to 30° and is represented to within experimental error (±0.1 mm.) by the function $\log p = -2500/T + 9.505$, where p is given in millimeters and T in °K. From this expression the following thermodynamic constants have been calculated for the reaction $[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}6H_2O = [Co(en)_2Cl_2]Cl + HCl + 6H_2O$, using 1 atm. as the standard state for both gases: K_d (dissociation constant) $= 2.70 \times 10^{-14}$ atm.^{7}, $\Delta H^0 = 79{,}900$ cal., $\Delta S^0 = 206$ e.u., $\Delta F^0 = 18{,}500$ cal.

Introduction

Although the *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride has been extensively studied, little information is available about the hydrochloride of this compound. The *trans*-compound and the hydrochloride were reported by Jorgensen,[1] who gave the formula for the hydrochloride $Co_2(en)_4Cl_6{\cdot}2HCl{\cdot}4H_2O$. Succeeding workers[2,3] have accepted his stoichiometry for the compound, with correction for the fact that a double formula seems not to be warranted, and have written the compound as

$$[Co(en)_2Cl_2]Cl{\cdot}HCl{\cdot}2H_5O$$

The purpose of the present work was to determine the way in which the unstable hydrochloride dissociates, whether there are intermediate steps in the dissociation process and how much energy is involved in breaking the bonds between the complex and the HCl and H_2O molecules.

Experimental

Chemicals.—The *trans*-dichlorobis-(ethylenediamine)-cobalt(III) chloride was prepared by the method described in "Inorganic Syntheses," Vol. II, p. 223. The pure *trans*-salt was dissolved in water and then precipitated as the insoluble hydrochloride by the addition of concentrated HCl. Since the hydrochloride is unstable in air, losing the HCl and H_2O readily, it was kept in a desiccator over concentrated HCl and samples were removed as needed.

The compound was analyzed by converting to the anhydrous form (by completely removing the associated HCl and H_2O by evacuation) and precipitating the chloride; theoretical value, 37.3% chloride; experimental, 37.3 ± 0.1%.

All chemicals used were reagent grade.

Phase Studies Apparatus.—The apparatus used for determining pressure *vs.* composition and pressure *vs.* temperature diagrams for the dissociation equilibrium is shown in Fig. 1. A two or three gram sample of the complex in the hydrochloride form was removed from the desiccator and placed directly into finger tube A. Tube A was connected by means of standard taper joint B to the removable stopcock C, and the entire sample tube (consisting of the finger tube, stopcock C and connecting tapers) was weighed. The empty weight of the same tube previously had been obtained. The sample tube was then connected to the vacuum line through taper D. By manipulating stopcocks C, E and F, increments of vapor were removed from the sample and readings of pressure were taken on manometer G, corresponding to weighings made by removing the sample tube. The finger tube was immersed in a constant temperature bath during the period of equilibrium and pressure measurement. Bath temperature could be varied from 5 to 30° and could be maintained at any desired temperature to ±0.05°. The dependence of dissociation pressure on temperature was studied by removing successive increments of HCl and H_2O from the hydrochloride and noting the pressure. When constant pressure was attained, the temperature was varied and corresponding pressures were recorded.

Titration of Vapors.—Direct analysis of vapors removed was made by introducing a sample of the complex in the hydrochloride form into the sample tube as previously described, pumping at a given temperature until a constant pressure was reached, opening stopcock E to the left, placing a liquid air-bath around the detachable U-tube H and evacuating. The weight of HCl and H_2O was determined from the difference between sample tube weight before and after freezing vapors into the U-tube. The HCl in the mixture was titrated with aqueous NaOH.

Vapor Density Measurements.—The vapor density apparatus shown in Fig. 2 was used to determine the molecular weight of vapors removed from the complex. The fused silica microbalance A supported a 1 cm. radius silica bulb B and a pointer C. The instrument was calibrated by simultaneously determining the pressure of a known gas within the cylinder D and height of pointer C as measured with cathetometer. Vapors of unknown molecular weight were then introduced into the cylinder and from the slope of a plot of pressure *vs.* height of pointer, molecular weight was determined, assuming all species to be ideal gases. The instrument was accurate to about ±1 molecular weight until over a pressure range of 0 to 12 mm.

Results

Phase Diagrams.—Results of pressure *vs.* composition determinations are shown in Fig. 3 for runs made at 9.7, 21.6 and 25.4°. Pressure due to all vapors (mm.) is plotted against values of the ratio of sample weight to weight of dry complex (*i.e.*, sample weight after all H_2O and HCl have been removed). The results of three separate determinations of dissociation pressure as a function of temperature (over the temperature range 5 to 30°) were fit by the expression

$$\log p = -2{,}500/T + 9.505 \qquad (1)$$

where p is the dissociation pressure (mm.) and T is the absolute temperature (°K.) to within experimental error (±0.1 mm.).

Vapor Composition.—Table I shows the results of titrations made on three condensed vapor samples. Values of the ratio of moles H_2O to moles HCl are given for these determinations.

Vapor density measurements made in the pressure range 0 to 10 mm. yielded values of molecular weight of 20.2, 21.4 and 21.1 ± 1.0.

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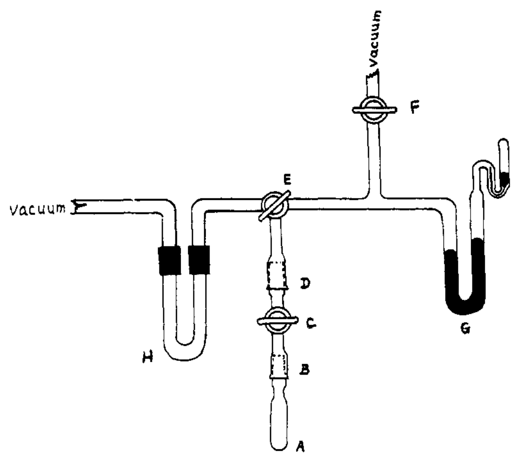

Fig. 1.—Phase studies apparatus.

Discussion

An examination of Fig. 3 reveals that the complex hydrochloride releases all molecules of HCl and H_2O in a single dissociation step. From the width of the plateau one can determine the total molecular weight of species lost during the dissociation process. A line drawn on the plot indicates the plateau width which would correspond to the loss of $6H_2O$ and 1HCl from one mole of the complex, a total molecular weight decrease of 144.6. From Fig. 3 alone, however, it is not possible to distinguish between such combinations as $8H_2O$, $6H_2O$ + HCl, $4H_2O$ + 2HCl, $2H_2O$ + 3HCl and 4HCl.

Direct titration of condensed vapors taken from the plateau region yields the result that the ratio of H_2O to HCl in the complex is 5.9 ± 0.1, which result obviously supports the hypothesis that the hydrochloride has the formula $[Co(en)_2Cl_2]Cl \cdot HCl \cdot 6H_2O$. Furthermore, the molecular weight of vapors released by the complex as determined by the vapor density measurements is 20.9 ± 1.0, which is within experimental error equal to the molecular weight of a 6:1 molar mixture of H_2O to HCl (20.7).

TABLE I

TITRATION OF VAPOR SAMPLES

Wt. of sample collected, g.	HCl, meq.	H_2O, meq.	Ratio of H_2O to HCl
0.6061	4.29	25.0	5.83
.5024	3.49	20.8	5.96
.6107	4.27	25.3	5.92

The rounding occurring at the upper end of the plateau in Fig. 3 has not been completely explained. It is believed that excess HCl and H_2O are sorbed on the complex as it is kept over concentrated hydrochloric acid and that in the evacuation process this excess is removed gradually as the total pressure is lowered. The lower end of the plateau breaks very sharply and further pumping will not significantly reduce the weight of the complex after the pressure has reached values below the dissociation pressure.

From equation 1 the values of K_D (dissociation constant), ΔH^0, ΔF^0 and ΔS^0 have been calculated

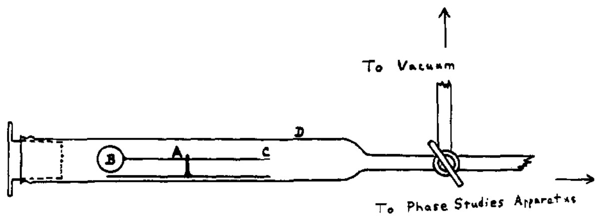

Fig. 2.—Vapor density apparatus.

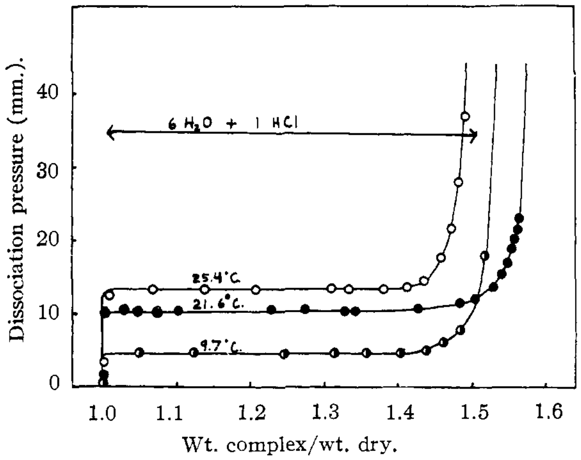

Fig. 3.—Dissociation pressure *vs.* composition.

for the dissociation process at 25°, assuming the equilibrium reaction to be

$$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 6H_2O = [Co(en)_2Cl_2]Cl + HCl + 6H_2O \qquad (2)$$

These values are given in Table II using gas at 1 atm. as the standard state for the HCl and H_2O and using the solid crystal as standard state for both the hydrochloride and the anhydrous forms of the complex.

The value of ΔH^0, 79,900 cal., corresponds to the removal of 6 moles of H_2O and 1 mole of HCl from the complex. It is interesting to compare this value with the enthalpy change corresponding to the combined processes

$$6H_2O \text{ (solid)} = 6H_2O \text{ (vapor)}$$

and

$$HCl \text{ (solid)} = HCl \text{ (vapor)} \qquad (3)$$

at 25°, which is approximately 75,000 cal. Thus the sum of the energies of all the bonds between H_2O, HCl and the complex is roughly 5 kcal. greater than the sum of the corresponding bond energies in solid, crystalline H_2O and HCl. The value of ΔS^0 for reactions 3 is approximately 250 e.u., which is somewhat greater than the value of 206 e.u. obtained for the dissociation of the complex.

TABLE II

THERMODYNAMIC CONSTANTS FOR THE REACTION AT 25°

$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 6H_2O = [Co(en)_2Cl_2]Cl + HCl + 6H_2O$

K_d (dissociation constant), atm.[7]	2.70×10^{-14}
ΔH^0, cal.	79,900
ΔF^0, cal.	18,500
ΔS^0, e.u.	206

Some other interesting results of the present work should be mentioned. First of all, the bonding of 6 molecules of H_2O and 1 molecule of HCl in the complex is such that all are released in a single dissociation step. In fact, it is not possible within the temperature and pressure ranges studied to form an anhydrous hydrochloride or a hydrate not involving HCl. Thus, the presence of both H_2O and HCl is necessary in order to stabilize the bonding of either of them. Second, the complex hydrochloride is quite unstable with respect to dissociation. The error of previous workers in reporting a compound having the formula $[Co(en)_2Cl_2]\cdot Cl\cdot HCl\cdot 2H_2O$ probably was due to their failure to use vacuum rack techniques in handling the compound under a pressure of H_2O and HCl sufficient to maintain it as the hydrochloride.

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Intramolecular Hydrogen Bonds to π-Electrons and Other Weakly Basic Groups

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Intramolecular hydrogen bonds between hydroxyl groups and π-electrons are shown to exist in compounds of the type 2 allylphenol. The $\Delta\nu_{OH}$ shifts are shown to depend on basicity of the π-bond and on the geometrical configuration around the bonding groups. These $\Delta\nu_{OH}$ shifts are compared with those of compounds where the hydrogen bonds involve electronegative acceptor atoms.

The phenomenon of hydrogen bonding has been investigated extensively in many laboratories through the use of infrared spectroscopy. Consequently, much is known concerning the types of groups most likely to participate in such bonding, the energies and lengths of the bonds and the approximate form of the associated potential energy function.[1] The energies of intermolecular hydrogen bonds have been shown to be about 3 to 10 kcal./mole, although in some cases, the energies, as measured by $\Delta\nu_{X-H}$ shifts,[2,3] have been estimated to be much less than this lower limit. However, the situation is somewhat confused for low-energy hydrogen bonds because the effects on $\Delta\nu_{X-H}$ shifts of non-specific interactions such as dipole–dipole association have, in general, been completely overlooked. Certainly, as the energy of hydrogen bonds decreases, the importance of these other effects in solutions of high dielectric strength increases and may become more significant than effects due to hydrogen bonding.

The situation is very much simpler for intramolecular hydrogen bonds because they can be studied in dilute solutions which have very low dielectric strength. In these cases, we find that bonds can be formed quite readily between rather unlikely groups and that the bond energies can indeed be very small. This is particularly true for groups substituted *ortho* to each other on an aromatic ring,[4] thus giving rise to the so-called "*ortho* effect." In such compounds, the groups are more nearly constrained to the same plane and the probability of interaction is greatly increased (decrease in entropy of interaction).

This enables hydrogen bonds of low strength to be formed between hydroxyl groups and the halogens, π-electrons in both aromatic[5,6] and olefinic systems, sulfur or other electronegative groups having at least one available electron pair. Strengths of these bonds probably lie between 1–4 kcal./mole, although in some systems discussed below, the strength is less than 1 kcal./mole.

This paper will discuss the bonding of phenolic hydroxyl groups to π-electrons in such compounds as allyl and propenyl phenols and will show how the steric and inductive properties of substituent groups on both the aromatic ring and the olefinic double bond affect the frequency and the breadth of the bands. These bonds will be compared with those formed between phenolic hydroxyl groups and halogen, sulfur, nitro and pyrryl groups.

Experimental

The hydroxyl stretching frequencies were investigated in the fundamental region at 3,600 cm.$^{-1}$ by means of a Beckman DK-II spectrophotometer. The day-to-day reproducibility was better than ±2 cm.$^{-1}$ for sharp bands. The resolution of the instrument at maximum performance was about 4 cm.$^{-1}$ but a spectral slit width of about 7 cm.$^{-1}$ was used to obtain most of the data. In order to determine the relative values of frequencies which differ by less than 4 cm.$^{-1}$, the respective samples were run differentially at equal total O–H absorbance. Relative differences of 0.5 to 1.0 cm.$^{-1}$ could be unequivocally determined.[7]

All materials, except as mentioned below, were either purchased from commercial sources or were synthesized according to directions found in the literature. The *cis*- and *trans*-isomers of 2-(γ-chlorallyl)-phenol were prepared in a manner similar to the described synthesis of the mixed product[8] except that the original dichloropropene was first separated into its *cis* (b.p. 105–105.5°) and *trans* (b.p. 112.5–113°) forms by fractionation on a 30-tray Oldershaw column. The *cis*-2-(γ-chlorallyl)-phenol had a b.p. 87–88° at 1.0 mm., $n^{25}D$ 1.5610, and *trans*-2-(γ-chlorallyl)-phenol a b.p. 98–99° at 1.2 mm., $n^{25}D$ 1.5645.

Commercially obtained chemicals were distilled or recrystallized, where practical, before use.

The samples were run in CCl_4 at concentrations from approximately 0.7 to 0.0007 molar in cells with path lengths up to 10 cm. Moisture was removed by direct addition of P_2O_5 to the CCl_4 solution; in the time taken to obtain the spectra, no reaction could be detected with any of the samples.

Results

Jaffé[9] recently pointed out that one prime differ-

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