[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

The Heats of Formation of Cobalt(II) and Nickel(II) Pyridinated Cyanates and Thiocyanates[1,2]

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The preparation of the hexapyridinated cyanates and the tetrapyridinated thiocyanates of cobalt(II) and nickel(II) is described and their analyses are reported. Measurements of the heats of solution of the above pyridinates and their constituents in hydrochloric acid are described. The results obtained and the heats of formation of the pyridinates calculated from them are reported.

Some earlier work has been done on the determination of dissociation pressures[4] of cobalt(II), nickel(II) and copper(II) pyridinated salts to obtain information concerning the effects of different atoms and groups on the strength of the coördinate bond. Additional data were collected concerning volume changes[4,5] occurring during the formation of the metal pyridinated salts.

We felt that the determination of the heats of formation of the metal pyridinated salts would be a more direct method of comparing the relative strengths of the coördinate bonds formed by cobalt and nickel with pyridine. If in the formation of a pyridinated compound

$$\mathrm{Co(CNS)_2(s)} + 4\ \mathrm{Py(liq)} \longrightarrow \mathrm{Co(CNS)_2{\cdot}4\ Py(s)} + \Delta H$$

the heats of reaction of the metal pyridinated salts, of pyridine and of the anhydrous metal salt with dilute hydrochloric acid were known, it would be possible to calculate the heat of formation of the pyridinated complex.

$$\Delta H = L_s + L_a - L_c$$

L_s, L_a and L_c representing the heats of reaction of the anhydrous salt, pyridine and the complex, respectively. A somewhat similar procedure was used by Lamb[6] in determining the heats of solution and transformation of cobalt pentammines. Hieber,[7] using an ice calorimeter, followed the same procedure in determining the heats of formation of α- and β-cobalt(II) pyridinated thiocyanates.

In calculating the heats of formation of the complexes, we have assumed that the complex metal pyridinate reacts immediately and completely with the 2 *N* HCl to form the acid, the metal chloride and the pyridine hydrochloride. To test the validity of this assumption and eliminate from consideration the possibility of the formation of a stable chloride of the complex pyridinate, additional experiments were conducted.

A quantity of $\mathrm{Ni(CNS)_2}$ was dissolved in 1500 ml. of 2 *N* HCl. Into this solution an amount of pyridine sufficient to form $\mathrm{Ni(CNS)_2{\cdot}4Py}$ was injected and the heat of solution measured. The heat of this reaction checked with the values obtained when pyridine reacted with HCl alone. In a second experiment 750 ml. of 2 *N* HCl containing $\mathrm{Ni(CNS)_2}$ was mixed isothermally with 750 ml. of 2 *N* HCl containing pyridine in an amount required to form the nickel complex. The temperature rise observed was approximately 0.003° for each gram of $\mathrm{Ni(CNS)_2}$ added. A second 750 ml. of 2 *N* HCl containing $\mathrm{Ni(CNS)_2}$ was mixed with 750 ml. of 2 *N* HCl. The temperature rise observed was approximately the same as had been observed in the preceding experiment and can be attributed to the heat of dilution of the nickel salt. It can be concluded from the above experiments that the formation of a stable chloride of the complex pyridinate does not occur and that we are justified in our original assumption.

Preparation of Compounds.—The pyridinated salts were prepared by a method described in earlier papers.[4,8] A water solution of the metal chloride was mixed with an equivalent amount of potassium cyanate or thiocyanate, pyridine was added in slight excess and the resulting complex salt extracted with chloroform. The pyridinated salt crystallized as the solvent evaporated, the crystals were freed from excess pyridine and stored in a desiccator.

The anhydrous metal thiocyanates were prepared by a method described by Grossman.[9] The metal sulfate solution was added to a solution of an equivalent amount of barium thiocyanate. The barium sulfate was removed by filtration, the filtrate was evaporated to dryness and the cobaltous and nickelous thiocyanates recrystallized from ethyl alcohol.

The metal cyanates were prepared by warming the complex salts under vacuum to remove the pyridine. Solutions of the cyanates are unstable so we were unable to prepare pure samples by any precipitation and recrystallization method. The anhydrous salts are unstable at temperatures above 90°. The removal of the pyridine from the dipyridinated compounds required a long period of careful warming under vacuum.

Determination of Heats of Reaction.—The calorimeter employed in the measurements was similar to that used by Lamb.[6] The reaction vessel was a two-liter dewar flask immersed in a thermostated bath controlled to ±0.002°.

The sample holder was ground flat on the base so that a microscope cover glass could be cemented tightly to it. The piston for ejecting the sample had a conical base which was ground to fit tightly into the neck of the sample holder when the piston was moved to its uppermost position. This expedient was used to prevent loss of pyridine from the complex salt while the apparatus was being assembled. The pyridine was introduced by a slightly different assembly. The base of a small vial was fused to the end of the piston. The open end of the vial was closed with a stopper which carried a glass rod slightly longer than the opening of the sample tube. An upward movement of the piston removed the stopper allowing the pyridine to enter the reaction vessel.

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(3) This article is based on theses submitted by D. C. Bush and C. J. Rogers, in partial fulfillment of the requirements for the degree of Master of Science at Oregon State College, June, 1950.

(4) (a) T. L. Davis and H. R. Batchelder, THIS JOURNAL, **52**, 4069 (1930); (b) T. L. D. and C. W. Ou, *ibid.*, **56**, 1061 (1934); (c) T. L. Davis and A. V. Logan, *ibid.*, **62**, 1276 (1940).

(5) Tenney L. Davis and A. V. Logan, *ibid.*, **58**, 2153 (1936).

(6) Arthur B. Lamb and J. P. Simmons, *ibid.*, **43**, 2190 (1921).

(7) W. von Hieber and F. Muhlbaur, *Z. anorg. allgem. Chem.*, **186**, 97 (1930).

(8) T. L. Davis and A. V. Logan, *ibid.*, **50**, 2493 (1928).

(9) H. Grossmann and F. Hünseler, *Z. anorg. Chem.*, **46**, 361 (1905).

The determination of the heat capacity of the calorimeter containing 1500 ml. of 2 N hydrochloric acid was carried out at 25°. A potential of 14 volts was used for the solution heater circuit. The current passing into the heater was determined by the potential drop across a standardized one ohm resistance while the potential across the heater was measured by means of a shunt box. All measurements were made with a typical potentiometer circuit.

In the determination of the heat capacity, corrections for heat of stirring and heat losses were made by observing temperature changes over a long period of time before and after heat had been added to the solution. The temperature readings were plotted *versus* time; the resulting curves were extrapolated to obtain the corrected temperature. The determination of the heat capacity was made when the calorimeter contained 2 N hydrochloric acid alone and additional runs were made when the pyridinated complexes had been previously dissolved in the acid. The change in concentration when salt was added was so small that no measurable change in heat capacity was observed, nor did the added salt affect the heat of stirring.

Following the above procedure the heats of reaction of the simple salts, the pyridine and the pyridinated compounds with 2 N hydrochloric acid were determined, at 25°.

Results and Discussion

The results of our experimental work are summarized in Table I.

The heats of formation obtained show conclusively that the negative ion has considerably greater effect upon the heat of formation of the complex than does the metal. The simple interpretation of the data obtained previously[5] in regard to dissociation pressures and volume changes seems to be inadequate in light of the values reported here. The fact that the thiocyanates coordinating with four pyridines have higher heats of formation and lower volume changes than do the cyanates complexed with six pyridines seems anomalous. The need is indicated to obtain information concerning the crystal structures of the complexes. This work is in progress at the present time.

TABLE I

Substance	Metal,[a] % Calcd.	Metal,[a] % Found	Heat of solution, cal./mole[b] at 25°	Heat of formation, cal./mole at 25°
Pyridine	...	...	−7,860 (±25)	......
$Co(CNS)_2$	33.66	33.63	−340 (±10)	......
$Co(CNO)_2$	41.26	40.87	−34,900 (±100)	......
$Ni(CNS)_2$	33.59	33.50	1,140 (±10)	......
$Ni(CNO)_2$	41.13	41.70	−32,070 (±10)	......
$Co(CNS)_2\cdot 4Py$	12.00	11.96	5,870 (±60)	−37,700
$Co(CNO)_2\cdot 6Py$	9.55	9.52	−59,800 (±100)	−22,300
$Ni(CNS)_2\cdot 4Py$	11.97	12.00	7,940 (±100)	−38,300
$Ni(CNO)_2\cdot 6Py$	9.52	9.58	−60,700 (±200)	−18,500

[a] Nickel was determined by cyanide–silver titration; cobalt gravimetrically as the sulfate. [b] Averages obtained from 2 to 6 determinations on each compound.

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[CONTRIBUTION NO. 193 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

Thermochemistry of the Rare Earths. I. Cerium and Neodymium

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The heats of solution of the metals and chlorides in hydrochloric acid, the hydrated chlorides in water, and the heats of precipitation of the oxalates in oxalic acid of cerium and neodymium have been measured. The data have permitted a calculation of the standard heats of formations of these substances as well as an estimate of their free energies of formation. The electrode potentials have been calculated to be 2.335 volts for cerium metal and 2.246 volts for neodymium metal.

Introduction

Previous investigations on the thermal properties of rare earth solutions[2] have been extended, by means of calorimetric measurements, to include the basic thermal properties of a number of compounds of cerium and neodymium. In order to obtain precise calorimetric data, from which good values for the heats of formation and other thermodynamic properties of these compounds could be calculated, considerable care was exercised to maintain well-defined initial and final calorimetric systems. The present paper describes the experimental data from such systems and the thermodynamic properties derived therefrom. In addition, the heats of solution and dilution of oxalic acid hydrate, as well as a recalculation of its heat of formation, is presented.

Experimental

Preparation of Materials.—The purity and methods of preparation of the anhydrous chlorides of cerium and neodymium have been described.[3] The metals of cerium and neodymium were prepared by methods described by Spedding, *et al.*[4] The metals were cast in vacuum into large cylindrical billets which were then turned down on a lathe under oil. Fine turnings from the billets were washed free from oil with benzene and loaded into sample bulbs while submerged in the benzene. After the excess solvent was drained off, the bulb was evacuated and refilled with purified argon to nearly atmospheric pressure. The bulb was then sealed. Samples prepared in this manner retained their luster indefinitely. Both the cerium and neodymium metals were found, by spectrographic analysis, to be free of other rare earths and all common elements. The hydrated crystals of the chlorides were grown over a period of 14 months from solutions of the chlorides in 2–3 N hydrochloric acid. The crystal masses, in this period of time, grew to a height of about one inch in a 400-ml. beaker. The crystals were rinsed with a small amount of water several times and then with alcohol. After being crushed, they were stored in a dry-box. The pH values of solutions of the crystals, as measured with a Beckman model pH meter were from 6.3 to 6.6 (identical values were observed for solutions of the anhydrous chlorides) indicating that the crystals contained no hydrochloric acid. The solid crystals and their resulting solutions were both analyzed for composition by accepted gravimetric methods. Analytical grade oxalic acid was used; it was twice recrystallized from conductance water. The crystals were first air-dried and then placed in a dry-

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(1) Work was performed in the Ames Laboratory of the A.E.C.

(2) F. H. Spedding and Carl F. Miller, THIS JOURNAL, 74, 3158 (1952).

(3) F. H. Spedding, P. Porter and J. Wright, *ibid.*, 74, 2055 (1952).

(4) F. H. Spedding, H. A. Wilhelm, W. H. Keller, D. H. Ahmann, A. H. Daane, C. C. Hach and R. P. Ericson, *Ind. Eng. Chem.*, 44, 553 (1952).