Column Chromatography Studies on the Acid Hydrolysis Products of Some Solid Tris(Pyridine)Cobalt(III) Complexes

N. Loan[a]; K. E. Hyde[a]

[a] Department of Chemistry, State University of New York, College at Oswego, Oswego, New York, USA

PLEASE SCROLL DOWN FOR ARTICLE

COLUMN CHROMATOGRAPHY STUDIES ON THE ACID HYDROLYSIS PRODUCTS OF SOME SOLID TRIS(PYRIDINE)COBALT(III) COMPLEXES

N. LOAN and K. E. HYDE*

Department of Chemistry, State University of New York, College at Oswego, Oswego, New York 13126, USA

Cold column chromatography of partially hydrolyzed solutions of solid tris(pyridine)cobalt(III) salts dissolved in perchloric acid media have resulted in the isolation of an acetatocomplex, a chlorobridged complex involving mercury(II) and an unsymmetric dimeric complex. These complexes have been characterized in solution by the determination of their visible spectra and pyridine:cobalt(III) ratios. The pK_a values have been determined for the bridged complex (3.39) as well as those for $[Co(py)_2(CO_3)(H_2O)_2]^+$ (2.48), $[Co(py)_3(CO_3)(H_2O)]^+$ (2.41) and $[Co(py)_3Cl(H_2O)_2]^{2+}$ (2.38).

INTRODUCTION

The dichlorotetrakis(pyridine)cobalt(III) complex has received attention because it undergoes hydrolysis at the same rate in both acidic and basic media.[1] This observation and the fact that the complex possesses no acidic hydrogens are consistent with classifying it as a complex in which the S_N1CB pathway is not available for base hydrolysis. The kinetics of this and similar substituted pyridine complexes have been subjected to investigations in various solvents in an effort to understand the influence of hydrophobic surfaces on solvolysis.[2,3]

This same complex is found to exhibit properties that are atypical for aminecobalt(III) complexes. It has been noted that its hydrolysis products readily lose coordinated pyridine.[4] This property has been used to advantage in synthesis.[5] The complex is much more susceptible to spontaneous reduction than its corresponding ammine complex.[4]

Our interest in tris(pyridine)cobalt(III) complexes is related to our most recent study[6] in which it was shown that anation of the diaquacomplex, trans-$[(Co(py)_4(H_2O)_2]^{3+}$ by chloride results in formation of diaquachlorotrispyridinecobalt(III) as the first observable product. Anation of the diaqua complex to form dichlorotetrakis(pyridine)cobalt(III) occurs only in chloride solutions of very high acidity $([H]^+ > 1M)$.[7]

Our goal in the present study is to identify the products that form when several solid tris(pyridine)cobalt(III) complexes are hydrolyzed in acidic media (2M $HClO_4$). At this acidity, spontaneous reduction and loss of ligand pyridine are slow enough to use column chromatography to separate hydrolysis products. The separated species are characterized by their charge, py/CO(III) ratio, visible spectrum and pKa. In

---

* Author for correspondence.

addition to the expected tri- and diaquatrispyridinecobalt(III) complexes, an acetato-complex, a chlorobridged complex with mercury(II) and a dimeric cobalt(III) complex have been identified and characterized in solution.

EXPERIMENTAL

Preparations

The solid tris(pyridine)complexes [Co(py)$_3$CO$_3$Cl], [Co(py)$_3$Cl(H$_2$O)$_2$](ClO$_4$)$_2$.2H$_2$O, [Co(py)$_3$CO$_3$(H$_2$O)](ClO$_4$).2H$_2$O and [Co(py)$_3$H$_2$O(H$_2$O)](ClO$_4$)$_3$.2H$_2$O were prepared as previously described.[8-10] Our preparation for the aqua-carbonatotris(pyridine)cobalt(III) complex was developed before the description by Laier[10] was available and is presented here. A 5 g quantity of [Co(py)$_3$CO$_3$Cl] was added to 20 cm^3 of a 2 M HClO$_4$ solution that contained 6.9g of Hg(ClO$_4$)$_2$. The crude product formed within 20 min and was recrystallized from a minimum amount of warm (40°C) methanol. The yield is improved by using reduced pressures to remove approximately half of the solvent and enhancing precipitation by the addition of diethylether. The yield after air drying was 33% based on crude [CO(py)$_3$CO$_3$Cl]. Elemental analysis gave: calc. for [Co(py)$_3$CO$_3$(H$_2$O)](ClO$_4$).2H$_2$O: Co, 11.6; py, 46.5; C, 37.7; H, 4.2; N, 8.25%. Found: Co, 11.3; py, 46.1; C, 37.9; H, 4.1; N, 8.17%. The white compound that precipitates during the preparation of this compound has been identified as [Hg(py)Cl]ClO$_4$ by analysis: calc.: py, 19.1; Hg, 48.4; C, 14.48; N, 3.38; H, 1.21; Cl, 8.54%. Found: py, 18.9; Hg, 46.6; C, 14.60; N, 3.51; H, 1.30; Cl, 8.36%.

Analyses

Mercury was determined by atomic absorption (Varian AA 575 spectrophotometer) and chloride was determined gravimetrically as AgCl. The UV absorption at 254 nm was used for the analysis of pyridine in 2 M HClO$_4$ solutions. At this wavelength and in this medium, the molar absorptivity of pyridine is 5488 M^{-1} cm^{-1}. Potentiometric procedures were used for the analyses of both cobalt(III) and Co^{2+}.

Cation Exchange Column Techniques

Short columns (1.5 by 4.0 cm) of Bio-Rad 50W-X2 cation exchange resin were used to separate the cationic complexes. The eluant was 2M HClO$_4$ and a cooling jacket maintained the column at 0°C. Eluates were collected at about −5°C. Spectra and pyridine to cobalt(III) ratios were determined immediately.

Acidity Constant Determinations

A Metrohm E 436 automatic titrator was used to obtain titration curves for the complexes dissolved in 0.1 M NaClO$_4$ and additional 0.1M HClO$_4$ was added to establish a starting pH of about 1.5. The resulting solutions were titrated in a thermostated vessel with 0.1 M NaOH. A similar procedure was used with eluates from the chromatography experiments. Both acidity constants for malonic acid were determined (pK$_1$ = 2.66 and pK$_2$ = 5.35) with these procedures and were in agreement with accepted values.

Hydrolysis Experiments

Three different acidic media were used to dissolve the solid complexes: 2M $HClO_4$, 2M $HClO_4$ with added $Hg(C_2H_3O_2)_2$, and 2M $HClO_4$ with added $Hg(ClO_4)_2$. In the initial studies, mercury(II) acetate was used to accelerate the loss of bound chloride from cobalt(III) complexes and the amount selected to ensure a 20% excess of Hg(II) over Co(III). The mercury(II) perchlorate medium was selected as an additional medium after it was noted that the acetate ion complicated the hydrolyses reactions by providing an anation pathway.

In the hydrolysis procedure, a known quantity of solid complex was dissolved in one of the above media at the desired temperature (ambient, 0 or 60°C). After a known time, the reaction mixture was cooled to $-10°C$, filtered and immediately charged onto the cooled chromatography column.

RESULTS

Column Chromatography

The cation column was calibrated with the pyridinecobalt(III) cations $[Co(py)_4(CO_3)]^+$, $[Co(py)_3Cl(H_2O)_2]^{2+}$, and $[Co(py)_3(H_2O)_3]^{3+}$. The resulting (eluent volume — cation charge) matrix was used to estimate the charge on an unknown complex. Peripheral experiments indicated that the ammine complex cations $[Co(NH_3)_5(H_2O)]^{3+}$ and $[Co(NH_3)_5Cl]^{2+}$ passed through the column with a smaller volume of eluent than similar pyridine complexes of the identical charge.

Hydrolysis of [Co(py)₃CO₃Cl]

2 M HClO₄

After one hour at ambient temperatures in this medium, chromatography produces a single band that may unambiguously be identified as $[Co(py)_3Cl(H_2O)_2]^{2+}$ by its charge, spectrum and Co:py ratio. At these conditions decarboxylation is complete before appreciable loss of chloride occurs.

2 M HClO₄/Hg(ClO₄)₂

In the presence of mercury(II) ion, loss of chloride is accelerated relative to decarboxylation. This fact has been used as the basis for the synthesis[10] of $[Co(py)_3CO_3(H_2O)](ClO_4.2H_2O)$. However, column chromatography after the ambient hydrolysis had proceeded for from 3 to 30 min resulted in two bands. The slower moving band is identified as $[Co(py)_3(CO_3)(H_2O)]^+$ on the basis of its charge, visible spectrum and Co:py ratio. By analyzing portions of the eluate for both cobalt and mercury, it was determined that the faster moving band consisted of a complex that contained both cobalt(III) and mercury(II). We assign this band as a "chloro-bridged intermediate" complex. Its column characteristics suggest a charge of $1+$ or less, but this assignment should be viewed with caution because of the polynuclear nature of the complex. Table I gives the parameters that characterize its visible spectrum. Further support for the bridged nature of this complex comes from the identification of Hg(py)Cl as the white precipitate that forms when the reaction is carried out on a preparative scale. When $AgNO_3$ is used in place of $Hg(ClO_4)_2$, two bands similar to those described above are noted.

TABLE I

Solution characteristics of the cobalt(III) complexes identified during the hydrolysis of solid tris(pyridine)cobalt(III) complexes.

Formulation of complex[a]	Wavelength maxima (λ) nm	Wavelength maxima (ϵ) $M^{-1}cm^{-1}$	Wavelength minima (λ) nm	Wavelength minima (ϵ) $M^{-1}cm^{-1}$	py/Co Ratio (std. dev.)	pK_{a1}	pK_{a2}	Temp. (°C)	Ionic strength (M)
acetatocomplex (3)	543	65	444	11	2.91 ±.06				
	375	110	364	108					
chlorobridged intermediate (4)	520	119	447	26	2.99 ±.12	3.59	6.80	5	~1
	385	160	358	122					
unsymmetric dimer (10)	553	63	449	12	2.53 ±.18				
	379	103	336	101					
$[Co(py)_3(CO_3)(H_2O)]^{1+}$	541	118	450	20		2.38	5.71	25	0.1
	379	146	358	118					
$[Co(py)_3Cl(H_2O)_2]^{2+}$	602	32	535	34		2.41	5.85	9	0.1
$[Co(py)_3(H_2O)_3]^{3+}$ (4)	523	51	443	15	2.98 ±.10				
$[Co(py)_2(CO_3)(H_2O)_2]^{1+}$ (4)	536	87	455	18	2.00 ±.15	2.48	6.98	2	1.0
	388	107	358	81					
$[Co(py)_2(H_2O)_4]^{3+}$ (5)	547	45	448	10	1.98 ±.13				

[a] The numbers in parentheses represent individual chromatography experiments. Visible spectra and cobalt-pyridine analyses were performed for each.

Hydrolysis for about 1 hr at ambient temperatures or for shorter periods at 60°C results in a single band whose exchange column behaviour and spectrum permit it to be identified as $[Co(py)_3(H_2O)_3]^{3+}$. Both loss of chloride and the expected decarboxylation have occurred during the time of this hydrolysis experiment.

Hydrolysis of $[Co(py)_3Cl(H_2O)_2](ClO_4)_2.2H_2O$

2 M HClO₄

Hydrolysis for 5 min at ambient temperatures results in a single band identified as $[Co(py)_3Cl(H_2O)_2]^{2+}$. Under these conditions there is no appreciable loss of coordinated chloride. Hydrolysis for longer periods at ambient temperatures (or for several min at 60°C resulted in the formation of larger amounts of a second, slower moving band that is identified as the expected hydrolysis product *mer*-$[Co(py)_3(H_2O)_3]^{3+}$.

2 M HClO₄/Hg(ClO₄)₂

At both 0°C and ambient temperatures, the mercury(II)-induced loss of coordinated chloride is immediate and *mer*-$[Co(py)_3(H_2O_3]^{3+}$ in the only observable product. Upon incubation for long periods (2 days), increasing amounts of *cis*-$[Co(py)_2(H_2O)_4]^{3+}$ are identified in the chromatography separations.

2 M HClO₄/Hg(C₂H₃O₂)₂

When mercury(II) acetate is used in the hydrolysis medium and chromatography is initiated after 30 min, *mer*-$[Co(py)_3(H_2O)_3]^{3+}$ is again the only observable product. If incubation is carried out for 2 hrs prior to column separation, two bands are observed. Analysis of the column eluate indicates that the slow moving band is the expected aquacomplex $[Co(py)_3(H_2O)_3]^{3+}$ but the first band's behaviour suggests a singly charged species. We take this complex to be the result of dianation of the aquacomplex by acetate ion. The spectral parameters of this "diacetatocomplex" are shown in Table I. The data indicate that the wavelength maxima shift to lower energies as acetate ions replace ligand water in the first coordination sphere of the cobalt complex. The same shift is observed for other aquaaminecobalt(III) complexes as acetate replaces water.[11-14]

Further incubation before column separation resulted in an unexpected observation. Chromatography resulted in a single band that behaved approximately as a 1+ cation. Its visible spectrum and Co:py ratio of 2.5 make it unlike any of the complexes so far encountered in pyridinecobalt(III) chemistry. The solution characteristics of this complex are shown in Table I. It should be noted that the incubation and chromatography separation were repeated 10 times. The spectral parameters and Co:py ratio are invariant within experimental error whether the band was sampled at its tip or tail. We are forced to assign this complex as an unsymmetric aquaacetatopyridinecobalt(III) dimer. Similar results are obtained with 60°C incubations for 15 min but at longer times at either ambient temperatures or 60°C, a second band of 3+ charge appears. This band is found to be solely *cis*-$[Co(py)_2(H_2O)_4]^{3+}$. The assignment is based on charge, spectrum and analytical Co:py ratio of the eluate.

In an effort to investigate the possibility that chloride ion might be involved as a bridging ligand, the hydrolysis in this acetate-containing medium was repeated with $[Co(py)_3CO_3(H_2O)](ClO_4).2H_2O$ as the starting complex. Again, the unsymmetric

dimer was observed in 2 M $HClO_4/Hg(C_2H_3O_2)_2$. Care was taken to ensure that the solution acidity was maintained at 2 M after decarboxylation.

Hydrolysis of $[Co(py)_3(H_2O)_3](ClO_4)_3.2H_2O$

2 M $HClO_4/Na(C_2H_3O_2)$

The unsymmetric dimer could also be obtained in the absence of mercury(II). When solid $[Co(py)_3(H_2O)_3](ClO_4)_3.2H_2O$ is incubated for 15 min at 60°C in a 2 M $HClO_4$ solution to which sodium acetate had been added in an amount to ensure an excess of acetate over cobalt, two bands are observed in the chromatography experiment. They are identified as the unsymmetric dimer and cis-$[Co(py)_2(H_2O)_4]^{3+}$. In the absence of sodium acetate, the same experiment produced a single band that may be assigned a 3+ charge. Its visible spectrum and Co/py ratio allow one to assign cis-$[Co(py)_2(H_2O)_4]^{3+}$ to the leading edge and $[Co(py)_3(H_2O)_3]^{3+}$ to the trailing edge.

Dynamic Thermogravimetry

$[Hg(py)Cl]ClO_4$

No mass loss occurs upon heating the white solid to 130°C with a dry nitrogen purge. A 35% mass loss is observed in the temperature range 185 to 310°C and at 350°C the decomposition is explosive with little residue remaining.

$[Co(py)_3CO_3(H_2O)](ClO_4).2H_2O$

The mass loss observed (4 to 12%) upon heating the solid to 100°C in a nitrogen purge was dependent on the purge time before heating commenced. The mass loss is consistent with 1 to 3 waters of hydration. A stoichiometry of Co_3O_4 is reported[15] for the final residue when several tetraaminecobalt(III) complexes are heated to 500°C. Our average mass loss (73.4%) observed when the hydrate is heated to this temperature is less than the expected loss (84.3%). The poor agreement is probably related to our use of a nitrogen purge.

$[Co(py)_3Cl(H_2O)_2](ClO_4)_2.2H_2O$

Nitrogen purging and heating to 100°C results in mass losses in the range 8.0 to 9.5%. This suggests between 2 and 3 waters of hydration for the solid complex. Additional heating resulted in a gradual mass loss and an explosive decomposition at 200°C.

Acidity Constant Determinations

The pK_a's for three of the species studied herein have been determined and are listed in Table I. Rapid decomposition of solutions of mer-$[Co(py)_3(H_2O)_3]^{3+}$ and cis-$[Co(py)_2(H_2O)_4]^{3+}$ during titration prevented reliable estimates of acidity constants for this complex.

DISCUSSION

The most interesting result of the present work is the identification and characteriza-

tion of the unsymmetric dimer with a py:Co ratio of 2.5. Cobalt(III) dimers have been used to explain the oxidation of bromide ions by cobalt(III) in acetic acid.[16] We found no evidence for dimer formation in any of the strongly acidic solutions that did not contain acetate ion.

Although there is no evidence that any of the solid tris(pyridine)cobalt(III) complexes used in the present hydrolysis studies are dimeric in that state, Laier and Springborg[17] have prepared solid tris-μ-hydroxobis[tris(pyridine)cobalt(III)]. They have characterized the corresponding triol that forms in acidic solutions of the above salt and have noted the slow hydrolysis of the dimeric species.

It is unlikely that a dimeric species forms when any of the monomeric solids dissolve in 2M $HClO_4$ as used in our hydrolysis studies. An interpretation of our results is that the mercury(II) acetate present in the hydrolysis medium induces dimer formation. Other workers[18] have concluded that acetate ion may be inserted as that bound to the Hg^{2+} ion as well as from free acetate in solution. The solution species that we have identified during the hydrolysis of $[Co(py)_3Cl(H_2O)_2]^{2+}$ as an acetato-complex may well be a dimeric complex with bridging hydroxide and/or acetate ions. The facile loss of pyridine from a tris(pyridine)cobalt(III) moiety of the dimeric species is not unexpected.[4,6] The product thus produced is easy to identify as dimeric because of its py:Co ratio of 5:2. Our results after additional incubation follow from the known ease of reduction of pyridinecobalt(III) centers.[4] Namely, the unsymmetric dimer is involved in an internal redox reaction with a bound ligand at the $Co(py)_3^{3+}$ moiety of the unsymmetric dimer to produce labile Co^{2+} and the last cobalt(III) complex, cis-$[Co(py)_2(H_2O)_4]^{3+}$, observed in our hydrolyses.

The chloride-bridged intermediate with mercury has been characterized in solution during the mercury-induced loss of chloride from $[Co(py)_3CO_3Cl]$. A similar bridged complex could not be isolated during the induced aquation of $[Co(py)_3Cl(H_2O)_2]^{2+}$. Such a complex has long been suggested to explain the observed kinetics of mercury(II)-catalyzed loss of ligand halide from cobalt(III)[18-20] and other metal[10] centres. With the pseudohalide SCN^-, bridged intermediates have been identified as solid complexes for both mercury(II)[22] and silver(I).[23,24] The present study represents one of the few cases in which a chloride-bridged complex persists long enough to be separated by column chromatography and characterized in solution. Its pK_a values (3.39 and 6.80) are comparable to those reported for Hg^{2+}(aq), 3.70 and 6.30.[25]

The pK_{a1} values for the aquapyridinecobalt(III) complexes reported in Table I fall in a narrow range (2.38 to 2.48) and indicate that they are much stronger acids than similar ammine complexes but not as strong as trans-$[Co(py)_4(H_2O)_2]^{3+}$.

REFERENCES

1. F. Basolo, J.G. Bergmann, R.E. Meeker and R.G. Pearson, *J. Am. Chem. Soc.*, **78**, 2676 (1956).
2. C.N. Elgy and C.F. Wells, *J. Chem. Soc., Dalton Trans.*, 2405 (1980).
3. K.H.M. Halawnni and C.F. Wells, *J. Chem. Soc., Faraday Trans. I*, **85**, 2999 (1989).
4. K.E. Hyde and G.M. Harris, *J. Phys. Chem.*, **82**, 2204 (1978).
5. U. Sakaguchi, K. Tomioka and H. Yoneda, *Chem. Lett.*, 349 (1984).
6. D.A. Gooden, H.A. Ewart and K.E. Hyde, *Inorg. Chim. Acta*, **166**, 263 (1989).
7. S. Tompkins, unpublished research project, State University of New York, College at Oswego, 1983.
8. J. Springborg and C.E. Schaffer, *Acta Chim. Scand.*, **A27**, 3312 (1973).
9. T. Mallen and K.E. Hyde, *Inorg. Chim. Acta*, **130**, 177 (1987).
10. T. Laier, C.E. Schaffer and J. Spingborg, *Acta Chim. Scand*, **34A**, 343 (1980).
11. R. Van Eldik and P.R. Joubert, *Inorg. Chim. Acta*, **12**, 245 (1973).

12. A. Haim, T.J. Praystas and R.J. Ward, *Inorg. Chem.*, **12**, 743 (1973).
13. R.G. Yalmon and T.J. Kuwana, *J. Phys. Chem.*, **59**, 298 (1955).
14. G. Harris and R. Van Eldik, *Inorg. Chim. Acta*, **70**, 147 (1983).
15. W.W. Wendlandt, T.D. George and K.V. Krishamurty, *J. Inorg. Nucl. Chem.*, **21**, 69 (1961).
16. J. Schlosserova, M. Hronec and V. Vesely, *J. Chem. Soc., Faraday Trans. 1*, **81**, 2055 (1985).
17. T. Laier and J. Springborg, *Acta Chem. Scand.*, **A35**, 145 (1981).
18. G. Jackson, G. A. Lawrence and A.M. Sargeson, *Inorg. Chem.*, **19**, 1001 (1980).
19. W.L. Reynolds and R.E. Alton, *Inorg. Chem.*, **17**, 3355 (1978).
20. D.A. Buckingham, C.R. Clark and M.J. Gaudin, *Inorg. Chem.*, **27**, 293 (1988).
21. W. Weber, D.A. Palmer and H. Kelm, *Inorg. Chim. Acta*, **54**, L177 (1981).
22. G.C. Lalor and H. Miller, *J. Inorg. Nucl. Chem.*, **37**, 307 (1975).
23. A. Pfeil, T.P. Dasgupta, D.A. Palmer and H. Kelm, *Inorg. Chim. Acta*, **38**, 623 (1980).
24. A. Pfeil, D.A. Palmer and H. Kelm, *Spectrochim. Acta*, **36A**, 1013 (1980).
25. C.F. Baes and R.E. Mesmer, *The Hydrolysis of Cations*, (Wiley-Interscience, New York, 1976), p. 302.