the aquation of *cis*-$[Coen_2ClH_2O]^{+2}$ at 30° in various buffers leads to

$$k = 3 \times 10^{-5} + 1 \times 10^{-9}/[H^+] \text{ sec.}^{-1} \quad (11)$$

This result is in agreement with the value of k_3 (aquation of the *cis*-chlorohydroxo complex) found in this work provided that K_a is taken as about 4×10^{-8}, allowing a factor of two in rate constants for the five degree temperature difference.

Mathieu also reports an experiment similar to the one described in connection with Table I in which he adds one equivalent of NaOH to a solution of *cis*-$[Coen_2Cl_2]^+$, and follows the subsequent kinetic processes. He reports $k = 7.7 \times 10^{-4}$ sec.$^{-1}$ at 30° for the aquation of the chlorohydroxo complex. This value is too low for he failed to account for the large amount of dichloro complex remaining in the reaction mixture and for the mixture of isomers.

Table IV shows the final assignment of rate constants for several chlorohydroxo complex ions. For comparison the rate constants for acid hydrolysis of the corresponding dichloro complexes are included. It is seen that, even though the electrical charges on the ions are the same, the chlorohydroxo complexes react 20–100 times faster than the dichloro complexes in spite of the statistical factor of two favoring the latter. It is also noteworthy that like the dichloro complexes of bis-(ethylenediamine)–cobalt(III) ion, the *cis*-chlorohydroxo ion reacts faster than the *trans*-isomer.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORIES OF NORTHWESTERN UNIVERSITY]

Mechanism of Substitution Reactions of Complex Ions. IX. Contribution of Inductive Effects to the Rates of Acid and Base Hydrolysis of Cobalt(III) Complexes[1,2]

BY FRED BASOLO, JOHN G. BERGMANN, ROBERT E. MEEKER AND RALPH G. PEARSON

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Rates of acid and base hydrolysis have been measured for a series of $[Coen_2X\text{-}pyCl]^{+2}$ complexes. The rates of acid hydrolysis increase with increasing base strength of X-py whereas that of base hydrolysis decreases. Inductive factors contribute less than do steric factors to the rates of reaction of cobalt(III) complexes. These results are discussed in terms of the mechanisms for acid and base hydrolysis reactions.

The rate of acid hydrolysis (aquation) of cobalt(III) complexes was shown to increase with increasing size of the "inert" ligands. The greater rate of reaction of the more sterically hindered complexes is cited in support of a dissociation mechanism (S_N1).[3] Thus, in a series of complex ions containing substituted ethylenediamine such as *trans*-$[Co(AA)_2Cl_2]^+$, an alkyl substituent increases the rate of aquation. Although the accelerated rate has been attributed to steric factors, it is also possible that this may result from the inductive effect of the alkyl group, piling up negative charge on the cobalt atom and hence repelling the chloride ion.[4] It is therefore necessary to have some estimate of the contribution of both steric and inductive effects to the speed of these reactions. The object of this investigation is to determine the rates of acid and base hydrolysis for some cobalt(III) complexes with ligands of different base strengths but of approximately the same steric requirements.

Experimental

Preparation of Compounds.—The method described by Bailar and Clapp[5] was used to prepare the substituted pyridine complexes $[Coen_2X\text{-}pyCl]Cl_2$. These salts were dried in a desiccator over potassium hydroxide and analyzed for nitrogen and ionic chloride.

Compound[a]	Ionic chlorine, % Calcd.	Found	Nitrogen, % Calcd.	Found
$[Coen_2pyCl]Cl\cdot H_2O$	18.5	18.3	18.5	18.3
$[Coen_2\beta\text{-}CH_3\text{-}pyCl]Cl_2$	18.7	18.6	18.5	17.9
$[Coen_2\gamma\text{-}CH_3\text{-}pyCl]Cl_2$	18.7	18.3	18.5	18.2
$[Coen_2\gamma\text{-}OCH_3\text{-}pyCl]Cl_2$	17.9	17.9	17.7	18.3

[a] en = ethylenediamine, py = pyridine, β-CH_3-py = β-picoline, γ-CH_3-py = γ-picoline, γ-OCH_3-py γ-methoxypyridine. The geometric configuration of these complexes is not known. However as they were all prepared by the same method and they all have their similar absorption spectra, it is believed that they all have the same structure.

Attempts to prepare compounds containing pyridine substituted with electron attracting groups were not successful. The pyridine derivatives used were 3- and 4-cyanopyridine, nicotinic acid and nicotinamide. In no case did the pyridine appear to coördinate and the only product isolated from these reaction mixtures was *cis*-$[Coen_2Cl_2]Cl$. Bailar and Clapp[5] report similar observations for reactions of several other weak bases.

trans-Dichloro-tetrakis-(pyridine)–cobalt(III) nitrate was prepared by the method of Werner and Feenstra.[6] Analogous compounds containing β- and γ-picoline were prepared by this same method. These nitrate salts were recrystallized from water, washed with ether, dried overnight in a desiccator over drierite, and analyzed for chlorine and nitrogen.

Compound	Chlorine, % Calcd.	Found	Nitrogen, % Calcd.	Found
$[Copy_4Cl_2]NO_3$	14.0	13.8	13.8	14.1
$[Co(\beta\text{-}CH_3\text{-}py)_4Cl_2]NO_3\cdot 3H_2O$	11.5	11.3	..	..
$[Co(\gamma\text{-}CH_3\text{-}py)_4Cl_2]NO_3\cdot H_2O$	12.2	12.0	11.9	12.2

The procedure described by Jaeger and Van Dyk[7] was employed to obtain *trans*-dichloro-bis-(2,2'-dipyridyl)–cobalt(III) chloride. The compound was dried overnight in a desiccator.

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(1) For previous paper in this series see R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 2673 (1956).

(2) This investigation was supported by a grant from the United States Atomic Energy Commission under Contract AT(11-1)-89. Project No. 2.

(3) R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953).

(4) D. D. Brown, C. K. Ingold and R. S. Nyholm, *J. Chem. Soc.*, 2674 (1953).

(5) J. C. Bailar, Jr., and L. B. Clapp, THIS JOURNAL, **67**, 171 (1945).

(6) A. Werner and R. Feenstra, *Ber.*, **39**, 1538 (1906).

(7) F. M. Jaeger and J. A. Van Dyk, *Z. anorg. allgem. Chem.*, **227**, 317 (1936).

Kinetic Measurements. (a) Rates of Acid Hydrolysis of $[Coen_2X\text{-}pyCl]^{+2}$ Complexes.—Solutions of the complexes were prepared which were approximately 0.0025 *M* complex and 0.0025 *M* $HClO_4$. The reaction mixtures were thermostated at 50 ± 0.1° and aliquots removed at suitable intervals and quenched by transferring them to a flask containing crushed ice. The ionic chloride in these solutions was then determined by a potentiometric method to be described elsewhere.[8] First-order rate plots gave straight lines from which the rate constants were obtained. It was also necessary to make certain that the pyridines remain coördinated during these reactions. This was determined by making aliquots of these reaction mixtures alkaline and then extracting the solutions with ether. The ultraviolet absorption spectra of the ether extracts were examined to determine whether or not any of the pyridines had been released. In no case was there any detectable release of pyridine during the first half-life of these reactions.

(b) Rates of Base Hydrolysis of $[Coen_2X\text{-}pyCl]Cl_2$ Complexes.—Base hydrolysis reactions of these compounds are much too rapid to be studied by conventional methods even at 0°. Therefore, it was necessary to employ the flow method described earlier.[9] Again the reaction mixtures were tested for possible release of pyridines by the procedure described above and in no case had any appreciable amount of pyridine been released.

(c) Rates of Acid and Base Hydrolysis of *trans*-$[Co(X\text{-}py)_4Cl_2]Cl$ Complexes.—Hydrolysis reactions of *trans*-$Co(X\text{-}py)_4Cl_2]Cl$ complexes were determined in buffer solutions at *p*H 1–2 in HNO_3 and at *p*H 9.18 in 0.05 *M* $Na_2B_4O_7$, at a temperature of 25 ± 0.1°. The course of these reactions was followed by withdrawing aliquots of the reaction mixture at suitable intervals, quenching in cold acetone and determining ionic chloride potentiometrically. First-order plots showed no deviations from linearity until after approximately 10 hours. These deviations were accompanied by a change in color from green to brown and by a strong odor of the pyridines.

Results and Discussion

The rate constants for the acid hydrolysis (1) and the base hydrolysis (2) reactions

$$[Coen_2X\text{-}py\ Cl]^{+2} + H_2O \longrightarrow [Coen_2X\text{-}py\ H_2O]^{+3} + Cl^- \quad (1)$$

$$[Coen_2X\text{-}py\ Cl]^{+2} + OH^- \longrightarrow [Coen_2X\text{-}py\ OH]^{+2} + Cl^- \quad (2)$$

are summarized in Table I. Also given here are the acid dissociation constants of the corresponding pyridinium ions.[10]

TABLE I

RATES OF ACID AND BASE HYDROLYSIS OF $[Coen_2X\text{-}pyCl]Cl_2$

X-py	pK_a[10]	Acid (50°) k(sec.$^{-1}$) × 10^5	Base (25°) k(mole^{-1} sec.$^{-1}$) × 10^{-3}
py	5.18	1.1[a]	1.6[b]
β-CH_3-py	5.81	1.3	1.3
γ-CH_3-py	6.08	1.4	1.3
γ-OCH_3-py	6.47	1.5	1.2

[a] Duplicate runs agreed to within 5%. [b] Duplicate runs agreed to within 3%.

The compounds chosen for this investigation represent a suitable series of analogous complexes to allow an evaluation of the importance of inductive effects on these rates of reaction. A consideration of molecular models shows that methyl or methoxy substituents on the β- or γ-positions of pyridine result in little or no change in the steric conditions at the cobalt atom. However, the base strengths of the pyridines used differ by a factor of approximately twenty. Therefore the observed differences in rate of reaction must be attributed to changes in the inductive effect of the "inert" ligands.

That the rates of acid and base hydrolysis of cobalt(III) complexes are subject to alterations in inductive effect is clearly shown in Table I. It is of interest that increased base strength of the ligand results in an increase in the rate of acid hydrolysis but a decrease in the rate of base hydrolysis. The fact that these reactions are affected differently by changes in the inductive character of the "inert" ligands shows that the reaction paths are not the same.[4] Recent publications[11] support an S_N1CB mechanism[12] for the base hydrolysis reaction compared to the S_N1 mechanism assigned[3,13] to acid hydrolysis.

The greater the base strength of the coördinated pyridine, the greater the electron density of cobalt(III) and the more labile the Co–Cl bond. This is consistent with the observed increased rates of acid hydrolysis with increasing base strength. However, although the base strengths of the pyridines differ by a factor of approximately twenty, the rates differ by less than a factor of 1.5 (Table I). Changes in the rate of these reactions due to the inductive effect are not very large. Therefore, the contribution of this effect to the differences (factors of 10^2 to 10^3) in rates of acid hydrolysis observed for a series of *trans*-$[Co(AA)_2Cl_2]Cl$ complexes[3] must be very small indeed. The base strengths of the AA groups (substituted ethylenediamines) used in this previous study do not change by more than a factor of 1.5.[14] Thus these large changes in rate of reaction cannot be due to inductive effects[4] and must be primarily a result of steric effects.[3]

The decrease in rate of base hydrolysis with an increase in base strength of the coördinated pyridines is in accord with an S_N1CB mechanism.[11] In this case the larger electron density on the cobalt(III) makes the complex a weaker acid so that less of the reactive conjugate base is produced in alkali and consequently the reaction is slower. This is in agreement with the effect of acid weakening and acid strengthening groups found previously.[9]

The rates of hydrolysis of some *trans*-$[Co(X\text{-}py)_4Cl_2]Cl$ complexes are summarized in Table II. That these compounds which contain no acidic hydrogens hydrolyze at a rate independent of hydroxide ion concentration has been cited in support of an S_N1CB mechanism for the base hydrolysis of complexes which do contain acidic hydrogens.[11]

TABLE II

RATES OF HYDROLYSIS OF *trans*-$[Co(X\text{-}py)_4Cl_2]Cl$ AT 25°

X·py	pK_a[10]	k(sec.$^{-1}$) *p*H 1–2	k(sec.$^{-1}$) *p*H 9.2
py	5.18	8.2×10^{-6}	8.5×10^{-6}
β-CH_3py	5.81	2.5×10^{-5}	2.5×10^{-5}
γ-CH_3py	6.08	1.5×10^{-5}	1.5×10^{-5}

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[8] P. M. Henry, Doctorate Thesis, Northwestern University, 1956.

[9] R. G. Pearson, R. E. Meeker and F. Basolo, THIS JOURNAL, **78**, 709 (1956).

[10] R. K. Murmann and F. Basolo, *ibid.*, **77**, 3484 (1955).

[11] R. G. Pearson, R. E. Meeker and F. Basolo, *J. Inorg. Nuc. Chem.*, **1**, 341 (1955); A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1261 (1955).

[12] The notation S_N1CB means substitution, nucleophilic, first order, conjugate base. See reference 4.

[13] R. G. Pearson, C. R. Boston and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

[14] F. Basolo, R. K. Murmann and Y. T. Chen, THIS JOURNAL, **75**, 1478 (1953).

On the basis of inductive effect alone, one would predict that the order of increasing rates should be py < β-CH_3-py < γ-CH_3-py. However, models show that the $[Co(\beta\text{-}CH_3\text{-}py)_4Cl_2]^+$ complex suffers from greater steric strain than either of the other two complexes. This additional steric acceleration may be responsible for the observed order of py < γ-CH_3-py < β-CH_3-py. Steric factors are also believed to account for the fact that *trans*-$[Copy_4Cl_2]^+$ hydrolyzes with a half-time of 23 hr. at 25°, whereas *trans*-$[Codipy_2Cl_2]^+$ reacts with water within a fraction of a second. A consideration of molecular models shows that the pyridine complex is readily constructed provided the four planar pyridines are pitched at an angle about the cobalt like the blades of a propeller. It is impossible to bring pairs of these pyridines into the same plane, as is required for the construction of the model of the 2,2'-dipyridyl complex. Still another contribution to this more rapid rate of reaction might be a greater stabilization of the reaction intermediate through resonance of the 2,2'-dipyridyl complex compared to the pyridine compound.

EVANSTON, ILLINOIS

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

The Structure and Characteristics of the Fluorescent Metal Chelates of o,o'-Dihydroxyazo Compounds[1]

BY DONALD C. FREEMAN, JR., AND CHARLES E. WHITE

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A series of compounds has been synthesized and investigated in order to determine the characteristics of structure and bond type necessary for the formation of fluorescent chelates. The parent type of structure for the compounds in this series is that of *o,o'*-dihydroxyazobenzene. Some modifications of this basic configuration such as the bis-salicylidenediamines, salicylidene-*o*-aminophenols, and salicylaldehyde azines were also studied. Both non-aqueous N,N-dimethylformamide and 34% N,N-dimethylformamide in water were found to be excellent solvents for fluorescent chelation reactions. The bonds between the metal ion and the chelating agent were found to be primarily ionic in character. Transition elements do not form fluorescent chelates with this type of compound. A strong dependence of fluorescence intensity on the size of the metal ion was observed. The acidity of the medium necessary for maximum fluorescence was found to be a critical but predictable factor.

Introduction

Non-fluorescent organic compounds capable of forming fluorescent chelates with metal ions in solution have been shown to be of considerable value as analytical reagents. The aim of this work was to determine some of the characteristics of the structural configuration and bond type necessary for fluorescence in metal chelates of the *o,o'*-dihydroxyazo compounds.

Experimental

Apparatus.—A fluorometer with some of the units similar to those described by Fletcher and Warner[2] was constructed in the authors' laboratory. The exciting source was a H100BL4 mercury vapor lamp and the measuring unit consisted of a 1P28 electronmultiplier phototube attached to an R.C.A. WV-84A ultra-sensitive microammeter. The sample holder was designed to accommodate 25-ml. glass stoppered test-tubes or square cuvettes. Excellent linearity of response was obtained throughout the visible spectrum. A Beckman DU spectrophotometer equipped with an electronmultiplier phototube was used for absorption measurements.

Reagents.—All inorganic reagents used were C.P. grade or equivalent. Distilled water was obtained from a Barnstead still. The presence in distilled water of traces of aluminum from the piping necessitated redistillation in glass for the most sensitive applications. Water purified by ion exchange is undesirable for fluorometric work since it may contain fluorescent impurities.

Three of the organic ligands used in this research were commercially available dyes that have been previously employed as fluorometric reagents for aluminum. These were: 2,2'-dihydroxy-1,1'-azonaphthalene-3-sulfonic acid, sodium salt (I), 2,2'-dihydroxy-1-naphthaleneazobenzene-5'-sulfonic acid, sodium salt (II), 2,4,2'-trihydroxyazobenzene-5'-sulfonic acid, sodium salt (III). The purity of these commercial dyes was found to vary between 59 and 75% as determined by means of a titanium(III) chloride titration of the azo group which was adapted from a method of Knecht and Hibbert.[3] To purify the dyes further the following procedure was used. The dyes were precipitated from aqueous solution with concentrated hydrochloric acid, washed and extracted with ethanol in a Soxhlet extractor. The product was precipitated on evaporation of the ethanol. This procedure increased the purity of I to 75%, II to 91% and III to 90%. Spectrographic analysis of the purified dyes indicated the absence of all metals other than alkali metals, salts of which constitute the chief impurities in II and III.

Since the commercial dye I was found to contain a considerable amount of organic impurity, it was decided to synthesize this compound. 1-Diazo-2-naphthol-4-sulfonic acid was treated with β-naphthol in 15% potassium hydroxide. After removal of the unreacted yellow diazo oxide by filtration, the solution was allowed to stand for 12 hours. The deep blue solution was continuously extracted with carbon tetrachloride until the extract was no longer red. The blue aqueous solution was then continuously extracted with isoamyl alcohol from which the blue basic form of the dye was obtained by filtration. This product is easily dissolved in water or alcohol.

1-(2-Hydroxybenzeneazo)-2-naphthol (IV), 2,4,2'-trihydroxyazobenzene (V) and 2,6-dihydroxy-3-(2-hydroxyphenylazo)-pyridine (VI) were prepared by standard diazotization and coupling procedures. The 2,6-dihydroxypyridine for VI was synthesized by the method of Errera.[4] 2,2'-Dihydroxyazobenzene (VII), 2,2'-dihydroxy-5,5'-dimethylazobenzene (VIII), 2,2'-dihydroxy-4,4'-dimethylazobenzene (IX) and 2,2'-dihydroxy-5,5'-dinitroazobenzene (X) were prepared by a method to be published elsewhere.

Salicylidene-*o*-aminophenol (XI) was prepared as follows. Salicylaldehyde, 124.4 g., was added to 21.8 g. of *o*-aminophenol dissolved in 1 liter of commercial absolute ethanol. The solution was refluxed for 30 minutes and cooled. The product was recrystallized from ethanol to give a 79% yield

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(1) Abstracted from the thesis of D. C. Freeman, Jr., submitted to the Graduate School of the University of Maryland, June, 1955, in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

(2) M. H. Fletcher and E. R. Warner, *Nuc. Sci. Abstr.*, **5**, 4700 (1951).

(3) E. Knecht and E. Hibbert, "New Reduction Methods in Volumetric Analysis," Second Edition, Longmans, Green and Co., 1925.

(4) G. Errera, *Ber.*, **31**, 1241 (1898).