Invited Review

# Rate Parameters for Ligand Replacement Processes in Octahedral Complexes of Metals in Oxidation State Three

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## 1. Introduction

The reactivity of octahedral metal complexes has been the subject of a large number of experimental investigations, and the results have been reviewed

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several times. The basic problem which justifies such a wide interest is the mechanism of the ligand substitution process occurring at the metal atom.

In spite of the large amount of data, there are few cases for which the detailed aspects of the reaction mechanism have been settled. Generally, the usual kinetic approach leaves considerable uncertainty as to the structure of the transition state. In this respect, substitution reactions of octahedral metal complexes are not amenable, as yet, to as ready an analysis as are the nucleophilic displacements on saturated carbon substrates or as are the ligand replacements on $d^8$ square planar metal complexes.

The most widely used approach to the problem is a comparative analysis of the behavior shown by a suitably selected class of compounds. In practice, this "behavior" is represented by the rate constants measured at a common temperature when the compounds are varied in such a way as to explore the rate changes due to variation of a given structural parameter such as leaving group, chelation, steric hindrance, *etc.*

However, rate constants, being related to the free energy change of the activation process, may be divided into the enthalpic and entropic contributions. Thus, at least in principle, the knowledge of both $\Delta H^+$ and $\Delta S^+$ (while equivalent as a whole to the corresponding rate constants) is more advantageous. These parameters and the activation volume $\Delta V^+$ give useful information on different, although to some extent related, aspects of the reaction mechanism. We stress the fact that small but detectable differences in rate constants may not be ready for analysis as they presumably are related to minor changes in mechanism. Also we are aware of the condition that identical rate constants at one given temperature may belong in differently reacting systems as a consequence of the compensation of enthalpy terms with entropy terms.

There have been, unfortunately, many workers who did not attempt to evaluate activation enthalpies, and even more who neglected to calculate the activation

TABLE I. Mechanistic Classifications of Langford and Gray.

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There are three categories of *stoichiometric* mechanisms distinguished *operationally* by kinetic tests.

1. *Dissociative* (D): intermediate of reduced coordination number, which may be detected by its selective reactivity.

2. *Associative* (A): intermediate of increased coordination number, which may be detected by departure of the rate expression from strict second-order kinetics when the reaction is followed in the direction for which the transition state lies after the intermediate.

3. *Interchange* (I): no kinetically detectable intermediates. There are two major categories of *intimate* mechanism that may be distinguished *operationally* if it can be assumed that a group of reactions with related mechanism can be identified.

1. *Associative activation* (a): the reaction rate is approximately as sensitive (or more sensitive) to variation of the entering group as to variation of the leaving group.

2. *Dissociative activation* (d): the reaction rate is much more sensitive to variation of the leaving group than to variation of the entering group.

D mechanisms must be dissociative. A mechanisms must be associative. Therefore, we adopt the following as the simplest combined notations designating both *stoichiometric and intimate* mechanism: A, $I_a$, $I_d$, D.

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entropies. One reason for the deliberate omission is that, while it is relatively easy to distinguish among rate constants differing by more than 10% by conventional kinetic techniques, the experimentally-based activation enthalpies are less discriminating. Suffice it to say here that, in spite of the lower degree of accuracy for the activation parameters, the value of $\Delta S^{\neq}$ for the base hydrolysis mechanism provided a clear decision between the proposed alternatives that were so long and so unnecessarily debated in the inorganic mechanism literature.

In this review we have collected rate constants plus activation parameters for the ligand substitution and isomerization reactions of metal complexes with the metal always in the oxidation state +3. This choice has been suggested both by the fact that much of the available data concern this class of complexes and because the rates cover a large range encompassing both labile and inert species.

The data reported here are those that appeared in the literature through 1971 and in some cases those that appeared in 1972 and 1973 in the most common periodicals. We have tried to be reasonably complete, however certainly we have missed some relevant articles and we apologize for our incompleteness to the authors of such articles.

Throughout the review the terminology introduced by Langford and Gray[1] will be adopted. Their interchange mechanism – either dissociative (Id) or associative (Ia) – is in our opinion suitable for our purposes being sufficiently flexible to cover most of the cases discussed herein. The definitions on which this

terminology is based are given in Table I. Further details about their description may be found in their text.[1]

We feel that the numbers collected here will provide a basis for discussion and speculation to chemists interested in this research area. It is not our purpose to attempt a complete analysis of the data; rather we shall present possible approaches to such an analysis. Also we shall probe somewhat more deeply into some specific cases, which, at the moment, appear to be sufficiently clear to us to warrant detailed discussion.

The mechanisms for ligand replacement reactions in octahedral complexes have been discussed often and elsewhere. The background plus many details in this field of research are presented in published books and reviews.[1-14]

## 2. Errors, Precision, and Accuracy

It is possible in certain instances to compare rate data on the same reaction as measured by several investigators. Taking as example the reaction

$$Cr(NH_3)_5Cl^{2+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + Cl^-$$
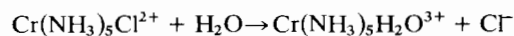
we have found eight articles giving relevant numbers. These numbers are presented in Table II.

Ignoring for the moment the fact that the media are not identical, it can be seen that the variation in rate constants is about a factor of two. This represents a difference of 0.41 kcal $mol^{-1}$ in the free energy of activation. It is immediately apparent that the values of $\Delta H^{\neq}$ are much more divergent, with the lowest reported value being 20.7 kcal $mol^{-1}$ and the highest being 23.6. Since an energy change of 1.36 kcal $mol^{-1}$ represents a change of one power of ten in rate – all other things being equal – the variability in $\Delta H^{\neq}$ shows that the change in rate constant with temperature is less well known than the rate constant itself,

TABLE II. Hydrolysis of Chloropentaamminechromium(III) Cation.

| $\mu$ | k(25°C) | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Ref.[d] |
|---|---|---|---|---|
| 0.106 | $6.8 \times 10^{-6}$ | 20.7 | -12.7 | 34 |
| _[a] | $6.0 \times 10^{-6}$ | 21.5 | -10.3 | 45 |
| _[b] | $6.0 \times 10^{-6}$ | 21.6 | -10.0 | 45 |
| – | $8.0 \times 10^{-6}$ | 21.8 | - 8.7 | q,40 |
| 0.1 | $9.3 \times 10^{-6}$ | 21.8 | - 8.4 | 41 |
| 0.5 | $6.8 \times 10^{-6}$ | 22.2 | - 8. | 43 |
| 1.0 | $3.9 \times 10^{-6}$ | 22.3 | - 8.5 | 42 |
| 0.2[c] | $5.6 \times 10^{-6}$ | 22.4 | - 7.5 | 44 |
| 1.0 | $7.4 \times 10^{-6}$ | 23.6 | - 2.8 | 37 |

[a] MeOH–$H_2O$ mixture. [b] EtOH–$H_2O$ mixture. [c] $D_2O$.
[d] These reference numbers refer to that list which is entitled *Data Table References*.

provided of course that the differences appear to result from both random fluctuations and genuine variations. Separation into these two causes of differences is not yet possible. From the data of Table II, one can see the compensation of $\Delta H^{+}$ and $\Delta S^{+}$ often ascribed to errors but the rate constants show some divergences that we believe are genuine. The variation in $\Delta H^{+}$ values usually leads to a related variation in $\Delta S^{+}$ values. In this case a variation of 4.58 cal mol$^{-1}$ deg$^{-1}$ is equivalent to a change of one power of ten in the rate constant.

Although it is not our primary concern here, the interrelationship between $\Delta H^{+}$ and $\Delta S^{+}$ is of sufficient importance to our discussions of mechanism that some mention be made here. More broad discussions of this "compensation effect" are to be found elsewhere.[15]

There are a number of different reasons because of which the activation parameters may not be completely reliable quantities; fortunately most of these reasons are easily recognized and can possibly be avoided. For a given reaction, both the entropy and the enthalpy of activation may be obtained from the ln(K/T) versus 1/T Eyring plot. The slope of the plot is equal to $\Delta H^{+}/R$, while the intercept is related to the entropy through the equation

$$\Delta S^{+} = \{\text{Intercept} - \ln(K/h)\}R$$

where K, h and R are the Boltzmann, the Planck and the ideal gas constants, and T is the absolute temperature, respectively.

The maximum error in ln(K/T) is the sum of the relative errors for both k and T. The latter is usually measured to within $\pm 0.1°$C in the temperature range from $0°$ to $100°$C where by far most of the kinetic runs have been carried out. This comes out to be a sufficient degree of accuracy in temperature since the relative error $\Delta T/T$ is not larger than 0.0003, thus negligible compared to the relative error in k ($\Delta k/k$) which is about 0.05, generally. Thus it may be assumed that

$$\Delta \ln(k/T) \simeq \Delta \ln k = \Delta k/k = 0.05$$

A point which deserves more attention is the width of the temperature range which should be employed in order to obtain activation parameters of sufficient
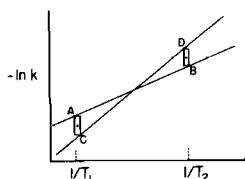


Figure 1. A modified Eyring plot showing the variation of the activation parameters (slope gives $\Delta H^{+}$ and intercept gives $\Delta S^{+}$) due to the experimental errors.

accuracy. It is obvious that the smaller is the difference between the highest and lowest temperatures studied, the higher is the uncertainty in both slope and intercept of the Eyring plot.

Using an empirical basis, let us assume that the uncertainty of the slope of an Eyring plot ($\Delta \Delta H^{+}/R$) as in Figure 1 be one-half of the difference of the slopes of the lines passing through points A and B, and C and D, respectively. It can be shown that $\Delta \Delta H^{+}/R$ is given by the formula

$$\Delta \Delta H^{+}/R = \frac{2\Delta k\, T_1 T_2}{k(T_1 - T_2 + 2\Delta T)}$$

neglecting $\Delta T(T_2 - T_1)$ compared to $T_2 T_1$. Most commonly, the temperature range employed in the kinetic studies of the reactions has a width of 20 degrees. This width plus a $\pm 0.1°$C error in temperature measurement does not justify an accuracy better than $\pm 0.5$ kcal mol$^{-1}$ for $\Delta H^{+}$ or better than $\pm 2.0$ cal mol$^{-1}$ deg$^{-1}$ for $\Delta S^{+}$.

Thus if there are no experimental reasons (for instance, analytical limitations) to constrain the study of the temperature effect to such a narrow range, this range should not be less than $30°$C.

Another important reason for adopting a wider temperature range is the need for a check of linearity in the Eyring plot. The case of a system reacting by two (or more) different parallel kinetic patterns of the same kinetic order is not infrequent. If the two paths have different activation parameters and if more than two points are obtained, the resultant Eyring plot will show curvature. The curvature may only become apparent over a significant temperature range.

Often a critical step in the calculation of $\Delta H^{+}$ involves the placement of the straight line which appears, just by inspection, to fit the experimental points of the Eyring (or Arrhenius) plot. It should be recognized that this procedure, although time saving, can seriously decrease the degree of accuracy of the activation parameters. This "subjective effect" may be larger than it is usually believed. One of us (J.O.E.) has had the occasion to test on a statistical basis the degree of uncertainty introduced by a subjective graphical method in the evaluation of activation energies. A set of experimentally derived rate constants and temperatures was given to a class of students of chemical kinetics as homework. Each of the students was asked to calculate the activation parameters at $600°$ by the usual graphical method. The data obtained from the students are presented in Figure 2–I which is a plot of $E_a$ (to the closest value of $\pm 0.1$ kcal mol$^{-1}$) against $\Delta S^{+}$ (to the closest $\pm 0.1$ cal mol$^{-1}$ deg$^{-1}$). Each circle represents the answer of one (0), two (–0), or three (–0–) students. The calculated enthalpies and entropies are linearly correlated as is to be expected when a subjective error in drawing the slope of the
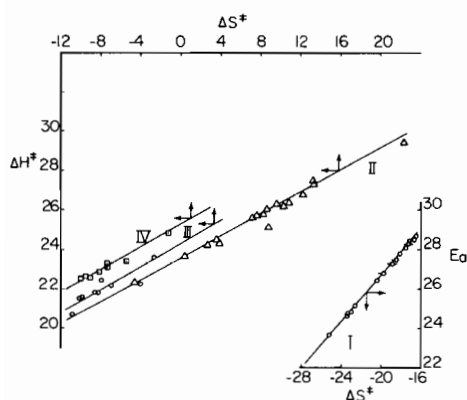
Figure 2. Four plots of $\Delta H^{\ne}$ (or $E_a$) versus $\Delta S^{\ne}$ for cases where there appears to be variability in activation parameter determination. Line I refers to the student data mentioned on page 11; lines II, III and IV refer to hydrolysis data for *trans*-Co(en)$_2$Cl$_2^+$, Cr(NH$_3$)$_5$Cl$^{2+}$ and Co(NH$_3$)$_5$Cl$^{2+}$ respectively

Arrhenius plot is made. The error in the slope then introduces an error in the calculation of $\Delta H^{\ne}$, even when the rate constant used (and thus the $\Delta G^{\ne}$ value used) is the same in every case. The slope of the resul-

tant plot of $E_a$ (or $\Delta H^{\ne}$) against $\Delta S^{\ne}$ should be equal, of course, to the temperature chosen for the calculation; the chosen temperature was 600° and the value of the slope turns out to be 607°.

Suffice it to say here that mathematical procedures such as least squares are to be preferred to more subjective procedures such as "eye-balling" the slope.

Data presented in Tables II and III concerning the aquation of the inert complexes Cr(NH$_3$)$_5$Cl$^{2+}$, Co(NH$_3$)$_5$Cl$^{2+}$ and *trans*-Co(en)$_2$Cl$_2^+$ offer some striking examples of the consequences of a "subjective linearization" of the Eyring and Arrhenius plots. These reactions have been studied by different workers under different conditions and by different techniques. While the rate constants are reasonably close to each other,* the activation enthalpies for the chloropenta-amminechromium(III) and the chloropentaammine-cobalt(III) cations span a 3 kcal mol$^{-1}$ range, and the

* As mentioned later, some of the rate constants listed were obtained by extrapolation to 25°C from data at different temperatures by using the $\Delta H^{\ne}$ value calculated by each author. Thus, in some cases, at least in part, the differences in values of k reflect the differences in values of $\Delta H^{\ne}$.

TABLE III. Activation Parameters and Reaction Conditions for Aquation of the Complexes Co(NH$_3$)$_5$Cl$^{2+}$ and *trans*-Co(en)$_2$Cl$_2^+$.

| Complex | Reaction Conds. | k | $\Delta H^{\ne}$ | $\Delta S^{\ne}$ | Ref.[a] |
|---|---|---|---|---|---|
| Co(NH$_3$)$_5$Cl$^{2+}$ | – | $1.7 \times 10^{-6}$ | 23.7 | −5.5 | q,40 |
| | 0.1$M$ HNO$_3$ | 1.7 | 22.9 | −8.1 | 85 |
| | H$_2$O | 2.1 | 24.8 | −1.3 | 86 |
| | H$_2$O | 1.7 | 23.1 | −7.4 | 87 |
| | 0.1$M$ (K,H)ClO$_4$ | 1.8 | 22.9 | −8.0 | 88 |
| | 0.002–1.0 (Na,H)NO$_3$ | 1.9 | 22.6 | −9.0 | 89 |
| | EtOH, H$_2$O (30% w) | 1.1 | 22.7 | −9.5 | 89 |
| | DXN, H$_2$O (30% w) | 1.2 | 22.6 | −10.0 | 89 |
| | ETG, H$_2$O (30% w) | 1.3 | 23.3 | −7.4 | 89 |
| *trans*-Co(en)$_2$Cl$_2^+$ | 0.1$M$ HNO$_3$ | $3.1 \times 10^{-5}$ | 27.5 | 13.1 | 161 |
| | H$_2$O | 3.8 | 29.4 | 19.9 | 162 |
| | H$_2$O, MeOH (20% w) | 2.2 | 26.4 | 8.7 | 162 |
| | MeOH, H$_2$O (39% w) | 1.5 | 24.5 | 1.6 | 162 |
| | MeOH, H$_2$O (60% w) | 0.94 | 22.3 | −6.7 | 162 |
| | EtOH, H$_2$O (18% w) | 2.4 | 26.2 | 8.2 | 162 |
| | EtOH, H$_2$O (36% w) | 1.7 | 25.7 | 5.9 | 162 |
| | EtOH, H$_2$O (54% w) | 1.6 | 25.6 | 5.4 | 162 |
| | Acetone, H$_2$O (20% w) | 2.3 | 26.8 | 10.1 | 162 |
| | Acetone, H$_2$O (40% w) | 1.6 | 25.8 | 6.1 | 162 |
| | Acetone, H$_2$O (60% w) | 1.4 | 24.5 | 1.4 | 162 |
| | DXN, H$_2$O (20% w) | 2.3 | 26.3 | 8.5 | 162 |
| | DXN, H$_2$O (40% w) | 1.9 | 24.4 | 1.7 | 162 |
| | DXN, H$_2$O (60% w) | 1.5 | 24.2 | 0.5 | 162 |
| | SUC, H$_2$O (10% w) | 4.2 | 26.3 | 9.5 | 156 |
| | ETG, H$_2$O (10% w) | – | 25.1 | 8.7 | 158 |
| | H$_2$O | 4.9 | 27.3 | 13.3 | 134 |
| | ~0.01$M$ HNO$_3$ | 3.5 | 26.1 | 8.6 | 163 |

[a] These reference numbers refer to the list entitled Data Table References.

entropies span an 8 cal $mol^{-1}$ $deg^{-1}$ range. The variations for *trans*-$Co(en)_2Cl_2^+$ are considerably larger. Such differences are not likely to be due completely to differing reaction conditions; rather they probably stem in part from arbitrary evaluation of the $\Delta H^+$ values.

These data are presented in Figure 2 which shows that $\Delta H^+$ (or $E_a$) and $\Delta S^+$ are for each complex fairly well correlated by a straight line. This situation is expected when $\Delta G^+$ is essentially constant and a random error has crept into the calculation of $\Delta H^+$, for instance, from an arbitrary choice of the slope of the plot. The error in $\Delta H^+$ must then be compensated for in the evaluation of $\Delta S^+$ from $\Delta G^+$ and $\Delta H^+$. The slopes of the lines for the three complexes are about $280°K$ (*i.e.*, reasonably near to the temperature range of the experiments).

The line from the student data is shown on Figure 2 for comparison. Although the slopes are different in the several cases ($600°K$ for the student data, and about $280°K$ for the coordination compound data), the hazard in simply putting a straight line to a series of points is clearly revealed. It is our contention that, all too often, the activation parameter data in the mechanism literature suffer from this subjective treatment of the rate data. Sadly, the errors in the resultant numbers are sufficiently large to hide interesting and real differences.

Most of the reactions of octahedral coordination compounds are carried out in aqueous solution. The reason is related to the solubility properties of the compounds; they are usually too poorly soluble in non-aqueous solvent systems to allow significant experimental investigation.

It is a fairly common practice to add along with the reagents some "inert" (in this context, non-reactive) salt, such as alkali metal nitrates or perchlorates, in order to keep the ionic strength constant. It is questionable how inert such salts are, since although the anionic component of the salt may not behave as a reactant in the ordinary sense (*e.g.*, as a ligand), it may interact with the octahedral substrate, especially when the substrate is cationic, with the formation of ionic associations having kinetic relevance. Perchlorates, which have been thought to be more safe to deal with, probably behave like the other mononegative ions.[16] The general question is, however, far from settled and should be given more attention in the future.

The criterion of "constant ionic strength" has also been criticized[17,18] for those cases where the composition of the ionic species is changed markedly. This happens often when the kinetic effect under investigation is relatively small, so that for detection of the effect a variation of the concentration over a large interval is required. Actually, when the ionic strength is higher than $0.1M$, there is little justification for

assuming the constancy of activity coefficients at constant ionic strength but changing ionic nature. Moreover it is possible that under such conditions the experimental results could conform better to simple limiting laws such as the mass action law.

Only a few systems have been studied over a sufficiently wide range of ionic conditions (*i.e.*, ionic nature and ionic strength) to allow judgment of the influence on activation parameters. In general, the variation in the parameters seems to be more random (as described above for the subjective evaluation) than rational. Nevertheless, it would be desirable that chemists working the area of coordination compound mechanisms be aware of the possibility of selecting reaction conditions which would allow ready comparison of their data with those obtained by other workers.

At present, there are two practices. One is to extrapolate rate constants (and, less often, activation parameters) to zero ionic strength. The other is to carry out experiments at a given constant ionic strength so that all of the kinetically relevant data are referred to that fixed condition. The first practice is perhaps preferable on the basis of the fundamental concepts of physical chemistry, but it necessitates a time-consuming procedure and leads to data which may not be directly comparable to those obtained at high ionic strength. The second practice is often necessary when, as we pointed out above, the concentration of a reagent must be varied over a wide range to detect a particular kinetic feature. This happens, for instance, in the study of the anation reactions of complex cations when the interchange rate constants of the ion-pairs have to be measured. In these cases, the extrapolation of the experimental data to zero ionic strength is essentially impossible since the lower practical limit of the ionic strength cannot be set much below $0.5M$.

This ionic strength value may be considered roughly the border between those conditions (of the ionic medium) chosen when an extrapolation to zero ionic strength is possible and those when the concentrations must be kept high. It would be desirable that in both cases the experimental conditions were chosen in such a manner as to allow at least an extrapolation of the relevant kinetic data to this common value ($0.5M$) of ionic strength.

## 3. Symbols and Notations

### A. General

The reactions for which data have been collected in the following tables are in order: solvolytic reactions in aqueous and non-aqueous media, acid-catalyzed aquations, base hydrolyses, isomerizations, and anations and overall second-order ligand substitutions. Most of the notations and symbols used here have obvious meanings since they are those currently em-

ployed in the literature. Some points, however, need explanation.

a) Within each reaction type, the *metals* follow the order of increasing atomic number; b) In the formula for the complex, the *last ligand on the right* is the one which is replaced or reacts and is written beginning with the donor atom; c) We have been unable to find a good general criterion for listing all the complexes. We decided to group the compounds of a given metal ion undergoing the same general type of reaction into classes according to the nature of the *five inert donor atoms*. At least three (out of the five) donor atoms are considered to identify a class. Compounds not belonging to a class as above defined, have been listed in the last part of the table.

## B. Reaction Conditions

In aqueous media, the pH (or pH range) and the ionic strength $\mu$ (or ionic strength range) are indicated. Negative pH values correspond to hydrogen ion concentrations higher than $1M$, with the defining equation being pH = $-\log[H^+]$. Also the nature of the electrolyte present in the medium is given. Often the reactions are carried out in the presence of mixed electrolytes. Whenever possible shorter notations like $(Na,H)ClO_4$ for $NaClO_4 + HClO_4$, or $(K,Ba/2,La/3)$ Cl for $KCl + BaCl_2 + LaCl_3$ have been used. When no electrolyte other than the complex itself are used, "none" appears in the column headed Medium; in these cases, the counter ion is specified within brackets, <>, under Comments. When non-electrolytes like methanol or sucrose are added to solvent water, they appear under Medium together with the added electrolytes (if any). Sometimes the amount of non-electrolyte is shown as a molar ratio, or as a weight percent (w), or as a volume ratio (v).

## C. Abbreviations

The following is a list of the less common abbreviations which have been used for compounds:

| | | |
|---|---|---|
| bn | = | Butylenediamine |
| pn | = | Propylenediamine |
| tet-me | = | (C,C,C′,C′)-tetramethyl-<br>ethylenediamine |
| Me-en | = | N-methylethylenediamine |
| Et-en | = | N-ethylethylenediamine |
| n-Pr-en | = | N-n-propylethylenediamine |
| tn | = | $NH_2(CH_2)_3NH_2$ |
| dan | = | $NH_2CH_2C(CH_3)_2CH_2NH_2$ |
| cyclam | = | 1,4,8,11-tetraazacyclo-<br>tetradecane |
| 2,3,2-tet | = | 1,4,8,11-tetraazaundecane |
| tren | = | $\beta,\beta',\beta''$-triaminotriethylamine |
| trien | = | triethylenetetramine |
| TMS | = | sulpholane |
| dien | = | diethylenetriamine |

| | | |
|---|---|---|
| tetren | = | tetraethylenepentamine |
| cytam | = | 1,3,5-triaminocyclohexane |
| tu | = | thiourea |
| tmd | = | 1,3-diaminopropane |
| DXN | = | dioxane |
| ETG | = | ethylene glycol |
| SUC | = | sucrose |
| tet-*a* | = | C-meso-5,7,7,12,14,14-hexa-<br>methyl-1,4,8,11-tetraazacyclo-<br>tetradecane |
| tet-*b* | = | C-*d,l*-5,7,7,12,16,16-hexame-<br>thyl-1,4,8,11-tetraazacyclo-<br>tetradecane |
| *trans*[14]diene | = | 5,7,7,12,14,14-hexamethyl-<br>1,4,8,11-tetraazacyclo-tetra-<br>deca-4,11-diene |

## D. Rate Constants and Activation Parameters

The rate constants given in the column designated k are at 25° C if not otherwise denoted aside.

The time unit is sec, and for the second-order constants the concentration units are mol liter$^{-1}$ ($M^{-1}$). When necessary and possible, the values of k at 25°C have been calculated by use of the enthalpy of activation and the experimental rate constant nearest to 25°C. Those cases where values of k for other temperatures are given correspond to systems studied at only one temperature and have been included either when no other kinetic data are known for the same system or to allow a comparison with data obtained in different studies. In some cases, the rate constant at 25°C has been calculated by using $\Delta H^+$, $\Delta S^+$ and the Eyring equation. These values have been listed in parentheses, ( ).

Enthalpies and entropies of activation are given as kcal mol$^{-1}$ and cal mol$^{-1}$ deg$^{-1}$ respectively. Some $\Delta H^+$ values have been obtained from measurements at only 2 temperatures and/or with a particularly narrow temperature range and so are felt to be less reliable than the others. This is indicated under the column Comments by the symbol $(2\tau)$ and/or by the width of the temperature range explored. The uncertainties in $\Delta H^+$ and $\Delta S^+$ are not given explicitly in the tables. However, when they are estimated to be higher than 1˙ kcal mol$^{-1}$ and 3 cal mol$^{-1}$ deg$^{-1}$, the numbers are underlined. The units of $\Delta V^+$ are cc mol$^{-1}$. Many entropy data have been calculated by us, since in some cases this calculation had not been carried out by the authors of the work or they had calculated it in the original article as a pre-exponential factor or equivalent.

In some cases we have found appreciable discrepancies between $\Delta S^+$ given in the literature and those calculated by us using the rate constant and the activation enthalpy given by the authors. Some of these discrepancies were due to incorrect employment of the activation energy $E_a$ (instead of the activation en-

thalpy) or to the use of the minute as time unit for k while the Planck constant was expressed on the second scale. In such cases, the $\Delta S^{\neq}$ values listed are those calculated by us. Whenever the reason for the observed discrepancy remained unexplained, the result of our calculation has been given in parentheses, together with the original value.

The rate constants $k_{-1}$ of the kinetic term $k_{-1}$ $[H^+]^{-1}$ of the aquochromium(III) complexes have been converted into the corresponding $k_{OH}$ rate constants (base hydrolysis) by setting $k_{OH} = k_{-1}/K_w$. Consequently, the activation parameters have been corrected for the standard enthalpy and entropy of the process $H_2O \rightleftarrows OH^- + H^+$, ($\Delta H = 13.3$ kcal mol$^{-1}$ and $\Delta S = -19.3$ cal mol$^{-1}$ deg$^{-1}$).

All of the calculations have been carried out with the use of an Olivetti 101 desk computer.

### E. Experimental Methods

The technique adopted for each kinetic study is indicated by a symbol under the column Method. The following is the list of symbols and corresponding technique used:

| | | |
|---|---|---|
| A | = | amperometric method |
| C | = | calorimetric method |
| Co | = | colorimetric method |
| D | = | densitometric method |
| esr | = | electron spin resonance method |
| K | = | conductometric method |
| G | = | gravimetric method |
| M | = | mass spectrometric method |
| nmr | = | nuclear magnetic resonance method |
| nmr(lb) | = | nuclear magnetic resonance line broadening method |
| P | = | polarographic method |
| pH | = | potentiometric pH measurement |
| pH stat | = | constant pH titration method |
| Pm | = | polarimetric method |
| R | = | radioactive isotope labelling technique |
| S | = | spectrophotometric method |
| $S_{fm}$ | = | spectrophotometric method (w. fast mixing) |
| $S_{sf}$ | = | spectrophotometric method (w. stopped-flow) |
| $S_{tj}$ | = | spectrophotometric method (w. T-jump) |
| T | = | titrimetric method |
| $T_f$ | = | titrimetric method (w. flow apparatus) |

### F. Remarks and Comments

In some instances (aside from the activation parameters and similar types of data in specifically designated columns) in the column headed Comments, short remarks have been included. These concern, as a rule, clarifications of some aspect of the specific system studied (such as stereochemical course or position of bond breaking), the nature of the counter ion (where given), and any further observations that we feel are useful for a better understanding of the data and mechanism. When indicating the dependence of rate parameters on reaction conditions such as reagent concentration, short notations have been adopted. The following is a specific example: $k\uparrow[H^+]\uparrow$ signifies that the rate constant increases ($\uparrow$) with increasing ($\uparrow$) hydrogen ion concentration.

Other remarks and comments are also found in the table footnotes.

The review has been put together with different sets of tables and references. The tables used to show specific points relative to textual material are placed at appropriate sites, and in many instances the relevant references are cited in the list of Text Reference presented at the end of the text. On the other hand, the tables containing the compilations of literature data are located at the end of the review and are termed Data Tables; the citations for these data are placed in Data Table References. The two types of references (*i.e.*, for text material and for data tables) are numbered separately. Although this results in some redundancy in the references, it is felt to be more flexible and to minimize the possibility of numbering errors.

### 4. Metal Oxidation State and Size

The emphasis in this review is on coordination compounds having the central metal atom in the $+3$ oxidation state. For completeness, however, we give here a brief discussion of the influence of oxidation state on the rates of ligand replacement. We consider that the effect of oxidation state is primarily electrostatic in nature (ion–ion, ion–dipole, *etc.*).

With few exceptions (*e.g.*, $Mn(CN)_6^{5-}$), rates of replacement for complexes with central metals in $+1$ oxidation state are very fast. The $+1$ hydrated cations (alkali metal cations, $Ag^+$) have water exchange rate constants in the vicinity of $10^8$ with small variation of alkali metal cation rate with size ($Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$). This is the expected pattern for rate variation, whether the mechanism be associative or dissociative, and little other data with mechanistic implications are available.

For the coordination compounds having metals in the $+2$ oxidation state, most of the complexes fall into the category termed "labile" by Taube.[2] With the newer fast reaction techniques, many ligand replacement rates have now been measured. Some relevant reviews are available.[9,10,13] The data in the review of Wilkins[13] suggest that replacement reactions in octahedral nickel(II) complexes follow an interchange mechanism not unlike that observed with complexes of cobalt(III).

The influence of oxidation state also is seen in the behavior of platinum(IV) complexes. These are so inert towards a dissociative interchange mechanism that more complicated, indirect paths for ligand replacement predominate. Catalysis by base, by Pt(III) intermediates, or by Pt(II) complexes, even though slow, carry the bulk of replacement.

The influence of central atom oxidation state can, to a significant degree in some cases, mask the effects of electronic structure. Both ligand fields and metal oxidation states are important in determining rates of ligand replacements. Their individual and combined influences on the mechanism (as contrasted to the obvious influences on overall rates) could well be the subject of an interesting review. For the present review, we shall for practical reasons restrict our attention to octahedral complexes of metals in oxidation state plus three.

If one has two metal ions having different sizes but with the same coordination number and electronic configuration (as, for example, in the complexes of cobalt(III) and rhodium(III)), an entering ligand is more readily bonded to the larger metal as the leaving group moves away. In terms of the octahedral wedge transition state, the interchanging ligands both can be less far from the "surface" of the metal at the point of a transition state. The value of $\Delta H^{+}$ will be lower and of $\Delta S^{+}$ more negative for the larger cation. The mechanistic conclusion is that one can say that the reaction may have a greater fraction of associative character as size increases.

The predicted change in $\Delta S^{+}$ value with metal ion size is seen in the data for hydrolysis of complexes having the $d^6$ low spin electronic configuration shown in Table IV. The decrease in $\Delta S^{+}$ from $-2$ for the cobalt complex to $-6$ for the rhodium complex and the further decrease to $-16$ for iridium when trifluoroacetate is the leaving group are believed to result from the increase in associative character with metal size. The changes in $\Delta H^{+}$ are barely above the level of experimental error. The predicted decrease in $\Delta H^{+}$ expected from the increase in metal size is presumably compensated for by the contribution to activation enthalpy

due to ligand field stabilization which increases in the order Co < Rh < Ir. When nitrate ion is the leaving group, the expected trend in $\Delta S^{+}$ values is again seen and no clear trend in $\Delta H^{+}$ values is apparent.

Another factor that can be important in determining the details of mechanism and that is related to metal ion size is orbital extension. The filled d orbitals of the central metal ion for low spin complexes of Co(III), Rh(III) and Ir(III) have different extensions in the space around the metal. Depending on the bonding, non-bonding, and antibonding character, orbital overlapping will influence the energy of the transition state. Since the number and importance of the several interactions possible depends on the nature of the atoms, we cannot discuss it here; suffice it to say that the influence of metal ion size and nature on the orbital length and hence on the efficiency of overlapping will have to be explored in more detailed investigations.

## 5. Acid Hydrolysis (Aquation)

As a reference point, we shall employ the aquation of cobalt(III) complexes. There are a large number of results which indicate that the mechanism involves dissociative interchange. The published[1,3,4,5,8,9,14] data (e.g., for $\Delta S^{+}$, $\Delta V^{+}$, rates with sterically-hindered ligands, lack of discrimination between incoming nucleophiles, and the linear free energy relation between leaving ligand rates and equilibria) can be satisfactorily explained on the basis of this $I_d$ model. The bond between cobalt and the leaving ligand is considerably stretched, and the new bond between metal and entering ligand (here water) is little formed. In most cases, one sees retention of geometric configuration during replacement suggesting that the entering water molecule drops into the hole which is in process of formation on departure of ligand. Concerning this mechanism, we concur with Rosseinsky[19] who – in another mechanistic context – has said "Se non è vero, è ben trovato". Roughly translated (provided, of course, that he does not object to our addition of the two accent marks), this means "Even if not the truth, it is well founded".

At first sight, there seems to be little new in the collected data on aquation reactions which leads to definitive conclusions. Some representative data for cobalt(III) and rhodium(III) are shown in Table V. The reaction in each case is replacement of ligand Y by $H_2O$. The activation enthalpies do not appear exceptional (i.e., not too high or not too low) and the entropies fall not too far from zero. Nevertheless, careful inspection of the numbers indicates that some conclusions are warranted. For example, for each of the six cases where comparison can be made, the value

TABLE IV. Activation Parameters for Hydrolysis in Acid Solution of Trifluoroacetato and Nitrato Complexes.

| Complex | $\Delta H^{+}$ | $\Delta S^{+}$ | Ref.[a] |
|---|---|---|---|
| $(NH_3)_5CoO_2C_2F_3{}^{2+}$ | 26 | $-2$ | 97 |
| $(NH_3)_5RhO_2C_2F_3{}^{2+}$ | 25 | $-6$ | 97 |
| $(NH_3)_5IrO_2C_2F_3{}^{2+}$ | 24 | $-16$ | 97 |
| $(NH_3)_5CoNO_3{}^{2+}$ | 24.3 | 1.9 | 94 |
| $(NH_3)_5RhNO_3{}^{2+}$ | 23.3 | $-3$ | 160 |
| $(NH_3)_5IrNO_3{}^{2+}$ | 26.1 | $-4$ | 160 |

[a] These reference numbers refer to the Data Table References list.

TABLE V. Rates and Activation Parameters for some Octahedral Aquation Reactions.[a]

| Rh(III) | | | | | Co(III) | | | |
|---|---|---|---|---|---|---|---|---|
| $Y^-$ | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Ref.[b] | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Ref.[b] |
| **I. For $M(NH_3)_5Y^{2+}$** | | | | | | | | |
| $NO_3^-$ | $1.2 \times 10^{-5}$ | 23.3 | $-3$ | 160 | $2.4 \times 10^{-5}$ | 24.3 | $+1.9$ | 94 |
| $SO_4^{2-}$ | $1.6 \times 10^{-6}$ | 21.4 | $-13.3$ | 102 | $8.9 \times 10^{-7}$ | 22.7 | $-10$ | 102 |
| $CF_3CO_2^-$ | $2.0 \times 10^{-7}$ | 25 | $-6$ | 97 | $1.5 \times 10^{-7}$ | 26 | $-2$ | 97 |
| $I^-$ | $6.2 \times 10^{-9}$ | 26.2 | $-7.8$ | 181 | $8.3 \times 10^{-6}$ | 19 | $-16$ | 90[c] |
| $Br^-$ | $3.4 \times 10^{-8}$ | 24.6 | $-9.9$ | 187 | $6.5 \times 10^{-6}$ | 23.9 | $-3.0$ | 85 |
| $Cl^-$ | $3.8 \times 10^{-8}$ | 24.2 | $-11.1$ | 187 | $1.7 \times 10^{-6}$ | 22.9 | $-8.1$ | 85 |
| **II. For *trans*-$M(en)_2ClY^+$** | | | | | | | | |
| $Cl^-$ | $5.4 \times 10^{-8}$ | 24.7 | $-9$ | 190 | $3.1 \times 10^{-5}$ | 27.5 | $+13.1$ | 161 |
| $Br^-$ | $8.3 \times 10^{-9}$ | 27.6 | $-3$ | 190 | $1.1 \times 10^{-4}$ | 26.0 | $+10.6$ | 136 |

[a] Rate constants have units of $sec^{-1}$ and were taken at 25°C.
[b] These reference numbers refer to the Data Table References.
[c] The data for $Co(NH_3)_5I^{2+}$ are complicated by a concurrent redox process.

of $\Delta S^{\neq}$ for the cobalt complex is more positive than for the rhodium complex.

The activation entropies for the solvolysis of complexes of the type $ML_5X^{2+}$ (where M = Cr, Rh or Ir and L = $NH_3$ or $H_2O$) are almost always lower than those for $Co(NH_3)_5X^{2+}$ which we have taken as the reference. From the direction of this difference, we can infer that there is more associative character in the replacement mechanisms for Cr, Rh and Ir than for Co. This is in agreement with conclusions in the literature based on other types of mechanistic information.[20]

As the associative character of the replacement increases, there should be a tendency towards decreased enthalpy of activation. All other things being equal, the energy of the bond being formed partially compensates for the energetic cost of bond-breaking. The activation enthalpies of the other complexes are usually lower than those for the analogous cobalt complexes, although there certainly are exceptions. The factors influencing rhodium(III) and cobalt(III) enthalpies are probably balanced, so that the previous generalization[21] $\Delta H^{\neq}_{Ir} > \Delta H^{\neq}_{Rh} > \Delta H^{\neq}_{Co}$ must now be accepted with caution even if occasionally true; once again the data in Tables IV and V are interesting in context.

The compilation of data for aquations of complexes is presented in Data Table I below.

One group of ligands (including $F^-$, $CN^-$ and $N_3^-$) appears to be exceptional in terms of activation parameters for their aquations. A case in point is $Cr(H_2O)_5 X^{2+}$. The postulated mechanism is

$Cr(H_2O)_5X^{2+} \rightleftarrows Cr(H_2O)_4(OH)(XH)^{2+}$ (fast)

$Cr(H_2O)_4(OH)(XH)^{2+} \rightarrow$
$\qquad\qquad Cr(H_2O)_4(OH)^{2+} + HX$ (rate)

$Cr(H_2O)_4(OH)^{2+} + H_3O^+ \rightarrow Cr(H_2O)_6^{3+}$ (fast)
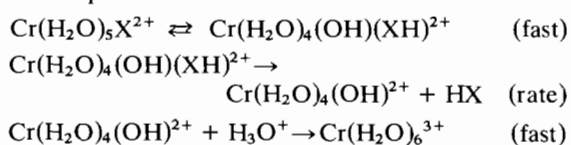
(The possibility that $H_2O$ from solvent participates directly in the rate step to form $Cr(H_2O)_5(OH)^{2+}$ cannot be excluded, however we shall ignore this possibility at this point.) The ligand XH should be a better leaving group than $X^-$ and the concurrent conversion of $H_2O$ to $OH^-$ in the coordination sphere should release electron density to the central atom making the loss of XH easier. Therefore, the overall effect of the change in proton position should be a rate enhancement. The ligands $X^-$ involved in this mechanism turn out to be the same ligands as those which undergo acid-catalyzed aquation (see below), and this is not surprising as placement of a proton on $X^-$ is an important aspect of both mechanisms. Conversion of $H_2O$ in the coordination sphere to $OH^-$ is quite analogous to the base hydrolysis mechanism discussed below.

The evidence for this type of proton tautomerism is not compelling on the basis of our activation parameter compilation, however the mechanism is a reasonable one. The aquation of $Cr(NH_3)_5F^{2+}$ does seem somewhat exceptional.

Considering aquations in general, the activation entropies are not far from zero, and this is not unreasonable for an interchange mechanism. Nevertheless, no clear trend between either $\Delta H^{\neq}$ or $\Delta S^{\neq}$ and the nature of the leaving group is apparent in this table. It is interesting to note that the values of $\Delta H^{\neq}$ are practically insensitive to the overall electrostatic charge on the complex. One can speculate that the Coulomb contribution to the metal–ligand interaction energy is hidden among other charge effects, as for example in solvation of ground state and/or transition state.

In principle, the data for aquation of similar cis and trans complexes can be employed to explore the pos-

DATA TABLE I. Aquation (Acid Hydrolysis).

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| $V(H_2O)_5NCS^{2+}$ | 1.0 | – | $(Na,H)ClO_4$ | 1.0 | 10.7 | −22.6 | $S_{SF}$ | 1 |
| $Cr(H_2O)_5(tetrenH_4)^{7+}$ | 4 | – | $HClO_4$ | $\sim 8.0\times10^{-9}$ | 28.9 | 1.4 | S | 332 |
| $Cr(H_2O)_5(trienH_3)^{6+}$ | 2.0 | – | $HClO_4$ | $1\times10^{-8}$ | 27.5 | −2.9 | S | 309 |
| $Cr(H_2O)_5(1,2,3\text{-dien}-H_2)^{5+}$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $2.8\times10^{-8}$ | 25.9 | −6.2 | S | 30 |
| $Cr(H_2O)_5NCSHg^{4+}$ | 1.0 | 0–0.85 | $(Na,H)ClO_4$ | $8.5\times10^{-5}$ | 20.4 | −8.7 | S | 2 |
| $Cr(H_2O)_5enH^{4+}$ | 3.0 | −0.52 | $HClO_4$ | $2.1\times10^{-8}$ | 24.8 | −10.5 | S | 3 |
| $Cr(H_2O)_5OH_2^{3+}$ | ~22 | – | none | $1.1\times10^{-5}$ | 30.5 | 21.1 | D; <Cl>; HCl (but not NaCl) is reported to cause the immediate exchange of two $H_2O$ molecules | 5 |
| $Cr(H_2O)_5OH_2^{3+}$ | 0.4–0.67 | 1 | $(Cr/3,H)ClO_4$ | $2.3\times10^{-5}$ | 26.1 | 7.8 | M; (2T,7°C range) | 4 |
| $Cr(H_2O)_5CNH^{3+}$ | 2.06 | ≦1.3 | $(Na,H)ClO_4$ | $3.2\times10^{-3}$ | 16.2 | −15.6 | S | 7 |
| $Cr(H_2O)_5NH_3^{3+}$ | 0.17 | 1 | $HNO_3$ | $8.7\times10^{-7}$ (40°) | – | – | S | 6 |
| $Cr(H_2O)_5py^{3+}$ | 1.0 | 0–3 | $(Na,H)ClO_4$ | $1.2\times10^{-8}$ | 27.2 | −3.5 | S | 325 |
| $\mathrm{Cr(H_2O)_5OC}$–(benzene ring)–$\mathrm{C(NH)NH_2}^{3+}$ | 1.0 | ~0 | $(Li,H)ClO_4$ | $6.5\times10^{-5}$ | 21.9 | −4.2 | S | 8 |
| $\mathrm{Cr(H_2O)_5OC}$–(benzene ring)–$\mathrm{C(NH)NH_2}^{3+}$ | 1.0 | ~0 | $(Li,H)ClO_4$ | $5.0\times10^{-5}$ | 21.8 | −5.1 | S | 8 |
| $Cr(H_2O)_5F^{2+}$ | 1.0 | 0–1.2 | $(Li,H)ClO_4$ | $6.2\times10^{-10}$ | 28.7 | −4.4 | S; $Cr(H_2O)_4(OH)(FH)^{2+}$ is suggested as the reactive species | 9 |
| $Cr(H_2O)_5Cl^{2+}$ | 1.0 | 0–1.7 | $(Li,H)ClO_4$ | $2.8\times10^{-7}$ | 24.3 | −7.0 | S | 9 |
| $Cr(H_2O)_5Br^{2+}$ | 1.0 | 0–1.3 | $(Li,H)ClO_4$ | $4.3\times10^{-6}$ | 23.8 | −3.2 | S | 10 |
| $Cr(H_2O)_5Br^{2+}$ | 2.0 | ≦0.6 | $(Na,H)ClO_4$ | $9.0\times10^{-6}$ (30°) | – | – | S | 11 |
| $Cr(H_2O)_5I^{2+}$ | 1.0 | 0–0.7 | $(Li,H)ClO_4$ | $6\times10^{-5}$ | 28.0 | 16.1 | S,C | 12 |
| $Cr(H_2O)_5I^{2+}$ | 1.07 | 0–0.6 | $(Na,H-ClO_4)$ | $1.5\times10^{-4}$ (30°) | – | – | S | 13 |
| $Cr(H_2O)_5I^{2+}$ | 1.0 | 0–1.7 | $(Li,H)ClO_4$ | $8.4\times10^{-5}$ | 23.0 | −0.2 | S | 9 |
| $Cr(H_2O)_5CN^{2+}$ | 1.0 | 0–3.1 | $(Li,H)ClO_4$ | $1.2\times10^{-5}$ | 27.9 | 12.7 | S; $Cr(H_2O)_4(OH)(HCN)^{2+}$ is suggested as the reactive species | 74 |
| $Cr(H_2O)_5CN^{2+}$ | 2.06 | ≦1.3 | $(Na,H)ClO_4$ | $9.2\times10^{-6}$ | 26.9 | 8.9 | S; $Cr(H_2O)_4(OH)(HCN)^{2+}$ is suggested as the reactive species | 7 |
| $Cr(H_2O)_5N_3^{2+}$ | 1.0 | 0.4–3.2 | $(Li,H)ClO_4$ | $4.1\times10^{-8}$ | 32.4 | 16.4 | S; $Cr(H_2O)_4(OH)(N_3H)^{2+}$ is suggested as the reactive species | 15 |

| Complex | $\mu$ | [H$^+$] | Medium | $k$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Notes | Ref |
|---|---|---|---|---|---|---|---|---|
| $Cr(H_2O)_5N_3^{2+}$ | 2.0 | $\leqq 0.6$ | $(Na,H)ClO_4$ | $6\times10^{-7}$ (40°C) | – | – | S | 16 |
| $Cr(H_2O)_5NCS^{2+}$ | 0.33 | 0.82 | $(Na,H)ClO_4$ | $9.1\times10^{-9}$ | 27.5 | –3.0 | S; $S_N2$ behavior is suggested | 17 |
| $Cr(H_2O)_5SCN^{2+}$ | 1.0 | 2 | $(Na,H)ClO_4$ | $1.7\times10^{-5}$ | 23.5 | –1.6 | S; $\Delta S^{\ddagger} = +1.0$ if the transition state is the same for both aquation and Cr–S→Cr–N isom | 18 |
| $Cr(H_2O)_5ONO_2^{2+}$ | 1.0 | 0–1.1 | $(Li,H)ClO_4$ | $7.2\times10^{-5}$ | 21.4 | –5.7 | S | 19 |
| $Cr(H_2O)_5ONO_2^{2+}$ | 1.0 | 0–1.0 | $(Li,H)ClO_4$ | $7.7\times10^{-5}$ | 21.6 | –5.1 | S | 20 |
| $Cr(H_2O)_5OClO_3^{2+}$ | 5–11 | | $HClO_4$ | $7.4\times10^{-3}$ | 14.7 | –19.0 | S (2T) | 21 |
| $Cr(H_2O)_5OCOCH_3^{2+}$ | 1.0 | 0–1.3 | $(Li,H)ClO_4$ | – | ~33 | – | S; $\Delta H^{\#}$ value refers to Cr–O cleavage | 22 |
| $Cr(H_2O)_5OSO_3^+$ | 2.0 | 0 | $(Na,H)_2SO_4$ | $1.4\times10^{-6}$ | 20.2 | –17.7 | S | 23 |
| $Cr(H_2O)_5OSO_3^+$ | 1.0 | 0–1.3 | $(Li,H)ClO_4$ | $7.5\times10^{-7}$ | 21.9 | –13 | S | 24 |
| $cis\text{-}Cr(H_2O)_4(trienH_2)^{5+}$ | 2.0 | | $HClO_4$ | $4\times10^{-7}$ | 23.6 | –9 | S | 309 |
| $Cr(H_2O)_4(1,2,3\text{-dien–H})^{4+}$ | 1.0 | $\geqq 0$ | $(Na,H)ClO_4$ | $3.1\times10^{-7}$ | 23.4 | –9.8 | S | 30 |
| $Cr(H_2O)_4en^{3+}$ | 3.0 | <0 | $HClO_4$ | $2.2\times10^{-8}$ | 27.1 | –3 | S | 3 |
| $cis\text{-}Cr(H_2O)_4Cl_2^+$ | 1.0 | | $HClO_4$ | $4.3\times10^{-5}$ | – | – | S; *cis* to *trans* isom. was not accounted for | 27 |
| $trans\text{-}Cr(H_2O)_4Cl_2^+$ | 1.0 | | HCl | $8.2\times10^{-5}$ | 25.9 | –9.3 (+9.7) | S (2T, 15°C range) | 27 |
| $trans\text{-}Cr(H_2O)_4Cl_2^+$ | 0.5 | 1–1.37 | $(Na,H)Cl$ | $8.3\times10^{-5}$ | – | – | S | 28 |
| $cis+trans\text{-}Cr(H_2O)_4(NCS)SCN^+$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $1.1\times10^{-4}$ | 19.6 | –9.8 | S | 331 |
| $Cr(H_2O)_4(tetrenH_3)^{6+}$ | 4 | –0.6 | $HClO_4$ | $3\times10^{-8}$ | 25.3 | –6 | S; substrate is a mixture of isomers. Product is $Cr(H_2O)_5(tetrenH_4)^{7+}$ | 332 |
| $Cr(H_2O)_4(NO)CNH^{3+}$ | 1.7 | – | $(Na,H)ClO_4$ | $5\times10^{-4}$ | 13.3 | –24 | esr | 25 |
| $Cr(H_2O)_4(NH_3)Cl^{2+}$ | 0.25–1.5 | <0.6 | $HClO_4$ | $4.8\times10^{-7}$ | 24.4 | –6 | S,T | 26 |
| $Cr(H_2O)_4Cl_2^+$ | – | – | – | $(8.2\times10^{-5})$ | 12.6 | –35 | – | 29 |
| $1,2,3\text{-}Cr(H_2O)_3(tetrenH_2)^{5+}$ | 4 | | $HClO_4$ | $2.7\times10^{-6}$ | 24.5 | –2 | S; product is $Cr(H_2O)_4(tetrenH_3)^{6+}$ | 332 |
| $Cr(H_2O)_3(en)NH_3^{3+}$ | 1.0 | 0–0.82 | $(Na,H)ClO_4$ | $1\times10^{-6}$ | 26.9 | 4.0 | S | 31 |
| $Cr(H_2O)_3(1,2,3\text{-dien})^{3+}$ | 1.0 | $\geqq 0$ | $(Na,H)ClO_4$ | $8.1\times10^{-7}$ | 23.7 | –6.9 | S | 30 |
| $Cr(H_2O)_3(1,2,6\text{-dien})^{3+}$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $5.3\times10^{-4}$ | 18.6 | –11 | S | 30 |
| $Cr(H_2O)_3(en)Cl^{2+}$ | 1.5 | <0.5 | $HClO_4$ | $3.0\times10^{-7}$ | 26.8 | 1.7 | S,T | 32 |
| $Cr(H_2O)_3(en)Br^{2+}$ | 3.0 | | $(Na,H)ClO_4$ | $3\times10^{-6}$ | 21.4 | –7.4 (–12) | S,T | 33 |
| $Cr(H_2O)_3(CN)(NO)(HCN)^{2+}$ | 1.7 | | $(Na,H)ClO_4$ | $2.5\times10^{-3}$ | 19.7 | –6 (–4.3) | esr | 25 |
| $cis\text{-}Cr(H_2O)_3(NH_3)Cl_2^+$ | 1.0 | 0–0.5 | $(Na,H)ClO_4$ | $2.8\times10^{-5}$ | 22.5 | –11 (–3.9) | S,T | 26 |
| $trans\text{-}Cr(H_2O)_3(NH_3)Cl_2^+$ | 1.0 | 0–0.5 | $(Na,H)ClO_4$ | $4.8\times10^{-5}$ | 19.6 | –13 | S,T | 26 |
| $1,2,3\text{-}Cr(H_2O)_3(CN)(HCN)^+$ | 2.0 | –0.2–1.0 | $(Na,H)ClO_4$ | $5.8\times10^{-4}$ | 16 | –12 | S | 279 |
| $Cr(NH_3)_5OH_2^{3+}$ | 1.7 | 1.3 | $(Na,H)ClO_4$ | $5.47\times10^{-5}$ | 22 | –4 | M; $k\uparrow$ pH$\uparrow$ | 34 |
| $Cr(NH_3)_5OH_2^{3+}$ | 0.40 | 1 | $HClO_4$ | $5.24\times10^{-5}$ | 23.2 | 0.0 | M; [complex] = 0.05$M$ | 318 |
| $Cr(NH_3)_5N_3H^{3+}$ | 8.0–10.8 | – | $H_2SO_4$ | $1.59\times10^{-4}$ | 19.1 | –11.8 | S | 35 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| $Cr(NH_3)_5ONOH^{3+}$ | 1.0 | 1.0–1.3 | $(Na,H)ClO_4$ | $3.70 \times 10^{-1}$ | 21.3 | 10.8 | $S_{SF}$ | 36 |
| $Cr(NH_3)_5F^{2+}$ | 0.1 | 7 | $NaNO_3$ | $9.7 \times 10^{-8}$ | 26.0 | $-3.4$ | T | 38 |
| $Cr(NH_3)_5F^{2+}$ | 0.1 | 1–10.5 | $(Na,H)(ClO_4,OH)$ | $2.54 \times 10^{-7}$ | 24.4 | $-4.6$ $(-6.8)$ | P;S | 39 |
| $Cr(NH_3)_5Cl^{2+}$ | – | – | – | $8.0 \times 10^{-6}$ | 21.8 | $-8.7$ | – | q 40 |
| $Cr(NH_3)_5Cl^{2+}$ | 1.0 | – | $HClO_4$ | $7.35 \times 10^{-6}$ | 23.6 | $-2.8$ | S | 37 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.5 | 1–4 | $(Na,H)ClO_4$ | $6.8 \times 10^{-6}$ | 22.2 | $-8$ | S; k indep. of pH but dep. on $\mu$ | 43 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.1 | 1–10 | $(Na,H)(ClO_4,OH)$ | $9.3 \times 10^{-6}$ | 21.8 | $-8.4$ | P | 41 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.2 | 1–2 | $(Na,D)ClO_4,(D_2O)$ | $5.6 \times 10^{-6}$ | 22.4 | $-7.5$ | P | 44 |
| $Cr(NH_3)_5Cl^{2+}$ | 1.0 | 0.4 | $(Na,H)ClO_4$ | $3.9 \times 10^{-6}$ | 22.3 | $-8.5$ | S; k↑[H⁺]↓ (base cat.) | 42 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.106 | 1.3 | $(Na,H)ClO_4$ | $6.8 \times 10^{-6}$ | 20.7 | $-12.7$ | S | 34 |
| $Cr(NH_3)_5Cl^{2+}$ | – | – | $MeOH:H_2O$ 1:4.5 (m) | $6.0 \times 10^{-6}$ | 21.5 | $-10.3$ | T | 45 |
| $Cr(NH_3)_5Cl^{2+}$ | – | – | $EtOH:H_2O$ 1:4.5 (m) | $6.0 \times 10^{-6}$ | 21.6 | $-10.0$ | T | 45 |
| $Cr(NH_3)_5Br^{2+}$ | – | – | – | $5 \times 10^{-5}$ | 22 | $-4.4$ | – | q 40 |
| $Cr(NH_3)_5Br^{2+}$ | 1.0 | – | $HClO_4$ | $6.8 \times 10^{-5}$ | 23.9 | 2.6 | S | 37 |
| $Cr(NH_3)_5Br^{2+}$ | 0.1 | 1–10.0 | $(Na,H)(ClO_4,OH)$ | $1.0 \times 10^{-4}$ | 20.9 | $-6.7$ | P | 41 |
| $Cr(NH_3)_5Br^{2+}$ | 0.2 | 1–2 | $(Na,D)ClO_4,(D_2O)$ | $9.8 \times 10^{-5}$ | 22.3 | $-2.1$ | P | 44 |
| $Cr(NH_3)_5I^{2+}$ | 1.0 | – | $HClO_4$ | $7.8 \times 10^{-3}$ (26 °C) | – | – | S; Difficulties from solubility problems | 37 |
| $Cr(NH_3)_5I^{2+}$ | 0.1 | 1–10 | $(Na,H)(ClO_4,OH)$ | $1.0 \times 10^{-3}$ | 20.8 | $-2.5$ | P | 41 |
| $Cr(NH_3)_5I^{2+}$ | 0.2 | 1–2 | $(Na,H)ClO_4,(D_2O)$ | $1.5 \times 10^{-3}$ | 22.4 | 3.7 | P | 44 |
| $Cr(NH_3)_5N_3^{2+}$ | 0.1–0.2 | 1.2–2 | $(Na,H)ClO_4$ | $3.6 \times 10^{-8}$ | 26.3 | $-4.9$ | S; (10 °C range) | 326 |
| $Cr(NH_3)_5NCS^{2+}$ | 0.06 | 2.5 | $HClO_4$ | $9.3 \times 10^{-8}$ | 24.9 | $-7.2$ | S | 40 |
| $Cr(NH_3)_5NCS^{2+}$ | 0.2 | 1–2 | $(Na,D)ClO_4,(D_2O)$ | $4.0 \times 10^{-8}$ | 24.6 | $-9.8$ | P | 44 |
| $Cr(NH_3)_5NCS^{2+}$ | 0.07 | 1.5 | $HClO_4$ | $8.7 \times 10^{-8}$ | 24.7 | $-8.0$ | S,T: $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are given for $\mu$ ext. to O | 46 |
| $Cr(NH_3)_5NCS^{2+}$ | 0.106 | 1.3 | $(Na,H)ClO_4$ | $4.1 \times 10^{-7}$ | 29.6 | 11 | S; Note the large discrepancy relative to other data on the same complex | 34 |
| $Cr(NH_3)_5ONO^{2+}$ | 1.0 | slightly acidic | $\begin{cases} KNO_3 \\ (Na,H)OCOCH_3 \end{cases}$ | $3.2 \times 10^{-5}$ | 34.4 | 36.3 | S | 213 |
| $Cr(NH_3)_5ONO_2^{2+}$ | 0.010 | | $HClO_4$ | $7.0 \times 10^{-4}$ | 21.0 | $-3$ | S | 48 |
| $Cr(NH_3)_5OCOCF_3^{2+}$ | 0.10 | 1.03–1.72 | $(Li,H)ClO_4$ | $8.7 \times 10^{-6}$ | 20.2 | $-25$ $(-13.9)$ | S | 49 |
| $Cr(NH_3)_5OCOCCl_3^{2+}$ | 0.13 | 1–2 | $(Na,H)ClO_4$ | $3.6 \times 10^{-6}$ | 21.5 | $-11.3$ | S | 320 |
| $Cr(NH_3)_5OSO_3^{+}$ | 0 (ext.) | – | – | $1.2 \times 10^{-6}$ | – | | S | 50 |
| $Cr(Me-NH_2)_5Cl^{2+}$ | 1.0 | 0.4 | $(Na,H)ClO_4$ | $(7.0 \times 10^{-7})$ | (22) | $(-13)$ | T; k↑[H⁺]↓ (base cat.) | 42 |

| Complex | | | Medium | | | | Remarks | Ref. |
|---|---|---|---|---|---|---|---|---|
| Cr(Et-NH₂)₅Cl²⁺ | 1.0 | 0.4 | (Na,H)ClO₄ | $3.3 \times 10^{-7}$ | 26.0 | − 1.0 | T; k↑[H⁺]↓ (base cat.) | 42 |
| Cr(Ali-NH₂)₅Cl²⁺ | 1.0 | 0.4 | (Na,H)ClO₄ | $2.9 \times 10^{-7}$ | 26.0 | − 1.2 | T; k↑[H⁺]↓ (base cat.) | 42 |
| cis-Cr(NH₃)₄(H₂O)Cl²⁺ | 1.0 | 1.0 | (Na,H)ClO₄ | $2.0 \times 10^{-4}$ | 21.4 | − 3.7 | S; ≥95% cis prod. | 51 |
| cis-Cr(NH₃)₄(H₂O)Cl²⁺ | 1.0 | 1.0 | HClO₄ | $5.4 \times 10^{-6}$ | 21.3 | −18 (−11) | — | q 352 |
| cis-Cr(NH₃)₄(H₂O)Br²⁺ | 1.0 | 1/[H⁺] ext.to 0 | (Na,H)ClO₄ | $8.0 \times 10^{-5}$ | 20.2 | − 9.5 | S | 352 |
| cis-Cr(NH₃)₄(H₂O)I²⁺ | 1.0 | 0-1.78 1/[H⁺] ext.to 0 | (Na,H)ClO₄ | $1.1 \times 10^{-3}$ | 19.7 | − 6 | S | 327 |
| cis-Cr(NH₃)₄(H₂O)I²⁺ | 1.0 | | (Na,H)ClO₄ | $8.5 \times 10^{-4}$ | 20.2 | − 4.9 | S | 352 |
| cis-Cr(NH₃)₄(OH)I⁺ | 1.0 | 12-14 | Na(ClO₄,OH) | 6.3 | 17.0 | 2 | S | 327 |
| trans-Cr(NH₃)₄(H₂O)Cl²⁺ | 1.0 | | HClO₄ | $8.6 \times 10^{-7}$ | 23.4 | − 7.8 | S,T; ≥90% trans prod. | 51 |
| trans-Cr(NH₃)₄(H₂O)Cl²⁺ | 1.0 | 1/[H⁺] ext. to 0 | HClO₄ | $6.5 \times 10^{-7}$ | 23.3 | − 9.5 | — | q 352 |
| trans-Cr(NH₃)₄(H₂O)Br²⁺ | 1.0 | | (Na,H)ClO₄ | $1.0 \times 10^{-5}$ | 21.6 | − 9.4 (−4.4) | S | 352 |
| trans-Cr(NH₃)₄(H₂O)I²⁺ | 1.0 | 0-1.78 1/[H⁺] ext. to 0 | (Na,H)ClO₄ | $7.4 \times 10^{-5}$ | 21.4 | − 5 | S | 327 |
| trans-Cr(NH₃)₄(H₂O)I²⁺ | 1.0 | | (Na,H)ClO₄ | $9.5 \times 10^{-5}$ | 20.9 | − 6.7 | S | 352 |
| trans-Cr(NH₃)₄Cl₂⁺ | 1.0 | 0-0.7 | (Na,H)ClO₄ | $4.9 \times 10^{-5}$ | 21.0 | − 7.8 | S; ≧92% trans prod. | 51 |
| trans-Cr(NH₃)₄ClBr⁺ | 1.0 | 0-0.7 | (Na,H)ClO₄ | $3.1 \times 10^{-4}$ | 20.2 | − 6.8 | S; ≧95% trans prod. | 51 |
| trans-Cr(NH₃)₄ClI⁺ | 1.0 | 0-1 | (Na,H)ClO₄ | $3.3 \times 10^{-4}$ | 18.0 | − 9 | S | 327 |
| trans-Cr(NH₃)₄BrCl⁺ | 1.0 | 0-0.7 | (Na,H)ClO₄ | $2.9 \times 10^{-4}$ | 19.5 | − 9.3 | S; 100% trans prod. | 51 |
| trans-Cr(NH₃)₄(OH)I⁺ | 1.0 | 12-14 | Na(ClO₄,OH) | 2.1 | 18.7 | 5.5 | S | 327 |
| Cr(NH₃)₄(NCS)NH₃²⁺ | ~0 | — | NaOH | $3.9 \times 10^{-7}$ | 28.5 | 11.9 (7.8) | S | 213 |
| trans(?)-Cr(en)(NH₃)(H₂O)₂Br²⁺ | 1.0 | 0-0.8 | (Na,H)ClO₄ | $4 \times 10^{-6}$ | 22.6 | − 7.0 | S,T; probable config. for Br⁻ and a H₂O molecule | 31 |
| trans(?)-Cr(en)(H₂O)₂Br₂⁺ | 2.0 | ≦0.5 | (Na,H)ClO₄ | $4.0 \times 10^{-4}$ | 19.2 | − 9.2 | S,T; probable config. refers to the Br's | 33 |
| trans(?)-Cr(en)(NH₃)(H₂O)Br₂⁺ | 0.3 | 0.5-1 | (Na,H)ClO₄ | $4.1 \times 10^{-4}$ | 20.1 | − 7.0 | S,T; probable config. refers to the Br's | 31 |
| Cr(en)(H₂O)₂Cl₂⁺ | 0.1 | 1-2 | (Na,H)ClO₄ | $3.1 \times 10^{-5}$ | 24.7 | 3.8 | S,T | 32 |
| trans-Cr(en)F₂(en)⁺ | 1.0 | 0.24-1.36 | (Na,H)ClO₄ | $1.2 \times 10^{-5}$ | 24.1 | − 0.3 | S; the prod. is trans-CrF₂(en)(enH) ΔH⁺ ↓μ↓; ΔS⁺ ↓μ↓ | 328 |
| trans-Cr(en)(NCS)₂en⁺ | 0.010 | | HNO₃ | $3.5 \times 10^{-6}$ | 23.8 | − 3.6 | S | 63 |
| cis-Cr(en)₂(H₂O)Cl²⁺ | 0.10 | | HNO₃ | $2.8 \times 10^{-5}$ | (35.3) | (39.1) | T; (2T), 100% cis prod. | 52 |
| cis-Cr(en)₂(H₂O)Br²⁺ | 0.06-0.14 | | HClO₄ | $1.8 \times 10^{-4}$ | — | — | S | 53 |
| cis-Cr(en)₂(H₂O)NCS²⁺ | 0.75 | | HClO₄ | $1.5 \times 10^{-6}$ | — | — | S | 54 |
| cis-Cr(en)₂Cl₂⁺ | 0.10 | | HNO₃ | $3.3 \times 10^{-5}$ | 20.5 | 5.7 | T; 100% cis prod. | 52 |
| cis-Cr(en)₂Cl₂⁺ | 0.10 | | HNO₃ | $3.5 \times 10^{-4}$ | — | — | T | 55 |
| cis-Cr(en)₂Cl₂⁺ | — | | none | $3.8 \times 10^{-4}$ | _17.3_ | _−15.3_ | T; <Cl⁻> | 56 |
| cis-Cr(en)₂Br₂⁺ | 0.1 | 1-2 | (Li,H)ClO₄ | $2.8 \times 10^{-3}$ | — | — | S; 97% cis prod. | 53 |
| cis-Cr(en)₂(N₃)₂⁺ | 0.4 | 2.12 | (Na,H)ClO₄ | $1.4 \times 10^{-6}$ | 23.4 | − 6.9 | S | 58 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| cis-Cr(en)₂(OH)Cl⁺ | 0.1 | 10.1–10.7 | { en / LiClO₄ } | $3.3 \times 10^{-3}$ | – | – | S; 96% *cis* prod. | 57 |
| cis-Cr(en)₂(NCS)Cl⁺ | 0.1–1.0 | | LiClO₄ | $8.1 \times 10^{-5}$ | 19.6 | –11.5 | S,T; 98% *cis* prod. | 54 |
| trans-Cr(en)₂(H₂O)Br²⁺ | 1.4 | | HNO₃ | $3.0 \times 10^{-6}$ | – | – | S | 53 |
| trans-Cr(en)₂Cl₂⁺ | 0.1 | | HNO₃ | $3.9 \times 10^{-5}$ | – | – | S | 55 |
| trans-Cr(en)₂Cl₂⁺ | 0.1 | 1.0–2.9 | (Li,H)NO₃ | $2.2 \times 10^{-5}$ | 22.6 | –4.0 | T | 59 |
| trans-Cr(en)₂Cl₂⁺ | – | 3.7 | – | $2.3 \times 10^{-5}$ | 22.6 | –3.8 | T; <Cl⁻> | 60 |
| trans-Cr(en)₂Br₂⁺ | 0.1 | | HNO₃ | $3.3 \times 10^{-4}$ | 21.8 | –1.4 | S,T | 61 |
| trans-Cr(en)₂Br₂⁺ | 0.1 | 1–2 | (Li,H)ClO₄ | $3.2 \times 10^{-4}$ | – | – | S; 4% *trans* prod. | 53 |
| trans-Cr(en)₂(OH)Cl⁺ | 0.1 | 9.8–10.8 | { en / LiClO₄ } | $4.6 \times 10^{-3}$ | – | – | S; 87% *trans* prod. | 57 |
| trans-Cr(en)₂(NCS)₂⁺ | 0.1 | | HNO₃ | $8.8 \times 10^{-6}$ (55°) | – | – | T | 62 |
| cis-Cr(dipy)₂Cl₂⁺ | 0.5 | 1.0 | (Na,H)Cl | $2.9 \times 10^{-7}$ | 22.8 | –11.9 | S | 356 |
| trans-Cr(dipy)₂Cl₂⁺ | – | 3.3–3.9 | HNO₃ | $1.9 \times 10^{-7}$ | 23.8 | –10 | T | 353 |
| trans-Cr(tmd)₂(H₂O)Cl²⁺ | 1.0 | | HNO₃ | $2.9 \times 10^{-6}$ | 21.1 | –13.1 | T | 321 |
| trans-Cr(tmd)₂(H₂O)Br²⁺ | 1.0 | | HNO₃ | $1.0 \times 10^{-5}$ | 23.6 | –2.2 | T | 321 |
| trans-Cr(tmd)₂Cl₂⁺ | 0.1 | | HNO₃ | $2.1 \times 10^{-5}$ | 23.9 | 0.1 | T,S | 321 |
| trans-Cr(tmd)₂Br₂⁺ | 0.3 | | HNO₃ | $3.6 \times 10^{-4}$ | 22.3 | 0.5 | T,S | 321 |
| cis,α-Cr(trien)Cl₂⁺ | 0.1 | 1–3 | (Na,H)ClO₄ | $1.9 \times 10^{-4}$ | 20.6 | –6.4 | T,S | 64 |
| Cr(H₂O)(tetrenH)⁴⁺ | 4 | | HClO₄ | $3.5 \times 10^{-4}$ | 22.5 | 1 | S; prod. is 1,2,3-Cr(H₂O)₃(tetrenH₂)⁵⁺ | 332 |
| Cr(H₂O)(tetren)³⁺ | 4 | | HClO₄ | $1.4 \times 10^{-4}$ | 20.1 | –9 | S; prod. is Cr(H₂O)₂(tetrenH)⁴⁺ | 332 |
| cis-Cr(ox)(α-trienH)²⁺ | 1.9 | ≦1 | (Li,H)NO₃ | $2.9 \times 10^{-4}$ | 19.9 | –8.1 | S | 67 |
| CrCl₃(H₂O)₂tu | 12 | | HCl | $2.4 \times 10^{-4}$ | 14.5 | –26.4 | S | 65 |
| CrCl₃(H₂O)tu₂ | 12 | | HCl | $2.6 \times 10^{-3}$ | 15.0 | –20.1 | S | 65 |
| CrCl₃tu₃ | 12 | | HCl | $6.9 \times 10^{-3}$ | 15.1 | –17.8 | S | 65 |
| Cr(acac)₃ | 2 | | HClO₄ | $8.0 \times 10^{-6}$ | 29.3 | 16.4 | S | 66 |
| trans-Cr(NH₃)₂(NCS)₄⁻ | – | | none | $1.9 \times 10^{-6}$ | 26.6 | 4.6 | Co; <K⁺> | 71 |
| trans-Cr(NH₃)₂(NCS)₄⁻ | – | | MeOH:H₂O (3:1 by V) | $1.2 \times 10^{-6}$ | 27.9 | 8.0 | Co; <K⁺> | 71 |
| Cr(NCS)₆³⁻ | – | | – | $6.1 \times 10^{-7}$ | 28.1 | 7 | R | 47 |
| cis-Cr(ox)₂(H₂O)DMSO⁻ | ≦0.1 | 1–4 | HClO₄ | $3.0 \times 10^{-4}$ | 17.0 | –17.6 | S | 68 |
| cis-Cr(ox)₂(DMSO)₂⁻ | ≦0.1 | 1–4 | HClO₄ | $1.2 \times 10^{-3}$ | 12.3 | –30.6 | S | 68 |
| cis-Cr(ox)₂(H₂O)(oxH₂)⁻ | 2.0 | – | (Na,H)ClO₄ | $1.5 \times 10^{-5}$ | 28.5 | 14.7 | S | 69 |
| cis-Cr(ox)₂(H₂O)NCS²⁻ | 1.0 | 3–4 | NaNO₃ | $1.6 \times 10^{-5}$ | 20.1 | –13.1 | S; 100% *cis* prod. | 330 |
| cis-Cr(ox)₂(H₂O)(oxH)²⁻ | 2.0 | | (Na,H)ClO₄ | $1.6 \times 10^{-5}$ | 21.6 | –8.4 | S | 69 |
| trans-Cr(ox)₂py₂⁻ | 0.1–2 | 1–3 | (Na,H)ClO₄ | $1.7 \times 10^{-5}$ | 27.7 | 12.6 | S | 70 |
| trans-Cr(ox)₂(H₂O)OCOCH₃²⁻ | 0.1–2 | 2–5 | (Na,H)ClO₄ | $6.2 \times 10^{-4}$ | 16.3 | –18.8 | S | 70 |
| trans-Cr(ox)₂(OH)OCOCH₃²⁻ | 0.1–2 | 9–12 | Na(ClO₄,OH) | $2.7 \times 10^{-2}$ | 8.4 | –38 | S | 70 |

| Complex | | | Medium | $k$ | | | Notes | Ref |
|---|---|---|---|---|---|---|---|---|
| Cr(Me-mal)₃³⁻ | 1.0 | 0–1.0 | (Na,H)ClO₄ | $9.7 \times 10^{-5}$ | – | – | S | 369 |
| Mn(CN)₆³⁻ | 0.18–1.2 | 9–10.8 | K(NO₃,CN) | $4.4 \times 10^{-4}$ | ~8 | –47 | R | 72 |
| Fe(H₂O)₅Cl²⁺ | 3.0 | 0–0.6 | (Mg/2,H)ClO₄ | 1.1 | – | – | $S_{SF}$ | 73 |
| Fe(H₂O)₅Br²⁺ | 1.0 | – | HClO₄ | $1.5 \times 10^{+12}$ | 18.3 | 12.8 | $S_{SF}$; 2T; 14° C range | 74 |
| Fe(H₂O)₅N₃²⁺ | 1.0 | 0–0.35 | (Li,H)ClO₄ | $2.0 \times 10^{+1}$ | 14.7 | – 3.2 | $S_{SF}$ | 75 |
| Fe(H₂O)₅NCS²⁺ | 0.40 | 0.7–1.5 | (Na,H)ClO₄ | $8.8 \times 10^{-1}$ | 14.5 | – 9.6 | $S_{SF}$; ΔS‡ is calcd. from ΔS° and ΔS‡ of the reverse reaction | 76 |
| Fe(H₂O)₅NCS²⁺ | 3.0 | –0.25 | (Mg/2,H)ClO₄ | $6.8 \times 10^{-1}$ | – | – | $S_{SF}$ | 77 |
| Fe(H₂O)₅SO₃⁺ | 1.0 | 0.3–1.7 | (Na,H)ClO₄ | 1.1 | 8.4 | –30 | $S_{SF}$; SO₃²⁻ probably S-bonded | 280 |
| Fe(H₂O)₂(NCS)₄⁻ | 8.0 | – | KNCS | $1.0 \times 10^{+5}$ | 10.3 | – 1.5 | nmr(1b); most likely Fe–N bonded | 78 |
| Fe(CN)₅SCN³⁻ | 1.0 | 1.0–1.7 | (Na,H)(ClO₄,NCS) | $8 \times 10^{-5}$ | – | – | S | 332 |
| Co(NH₃)₅OPO₃H₄⁴⁺ | 10.4 | – | HClO₄ | – | 22.9 | – | R | 79 |
| Co(NH₃)₅OH₂³⁺ | 0.6 | 2.0–2.2 | HClO₄ | $5.9 \times 10^{-6}$ | 26.6 | 6.7 | M; <ClO₄>, [complex] = 0.1 | 80 |
| Co(NH₃)₅N₃H³⁺ | 7.2–12.4 | | H₂SO₄ | $1.1 \times 10^{-4}$ | 24.1 | 4.2 | S | 35 |
| Co(NH₃)₅OP(OH)₃³⁺ | 0.8–4.1 | | HClO₄ | $1.4 \times 10^{-6}$ | 25.6 | – 7.4 | R | 79 |
| Co(NH₃)₅OP(OCH₃)₃³⁺ | 0.5 | 0.4–1.0 | (Na,H)ClO₄ | $2.0 \times 10^{-4}$ | – | (0.6) | S; k is corrected for 80% Co–O rupture | 81 |
| Co(NH₃)₅OCOCH₂NH₃³⁺ | 0.1 | 0.3–2.0 | (Na,H)ClO₄ | $5.9 \times 10^{-9}$ | 29.0 | 1 | S; k↑μ↓(ΔH‡ and ΔS‡ are 22.0 and –20 at μ = 1.0, resp.) | 82 |
| Co(NH₃)₅F²⁺ | – | – | none | $8.7 \times 10^{-8}$ | 20.7 | –21.4 | T; <NO₃⁻> | 83 |
| Co(NH₃)₅F²⁺ | 0.12 | 5.13 | LiClO₄ | $8.7 \times 10^{-8}$ | 24.4 | – 8.4 | T; pH given is initial pH | 84 |
| Co(NH₃)₅Cl²⁺ | – | – | – | $1.7 \times 10^{-6}$ | 23.7 | – 5.5 | | q 40 |
| Co(NH₃)₅Cl²⁺ | 0.1 | – | HNO₃ | $1.7 \times 10^{-6}$ | 22.9 | – 8.1 | S | 85 |
| Co(NH₃)₅Cl²⁺ | – | – | none | $2.1 \times 10^{-6}$ | 24.8 | – 1.3 | K; <Cl⁻> | 86 |
| Co(NH₃)₅Cl²⁺ | – | – | none | $1.7 \times 10^{-6}$ | 23.12 | – 7.4 | T { <ClO₄⁻>, activ. param. at 25° C dΔH‡/dT = 50 cal/mole × °K } | 87 |
| Co(NH₃)₅Cl²⁺ | 0.002–1.0 | 6.9–1.0 | (Na,H)NO₃ | $1.9 \times 10^{-6}$ | 22.6 | – 9.0 | T, [2], <NO₃⁻> | 89 |
| Co(NH₃)₅Cl²⁺ | – | – | EtOH 30% (w) | $1.1 \times 10^{-6}$ | 22.7 | – 9.5 | T, [2]; k↓D↓ (at diff. [EtOH]),<NO₃⁻> | 89 |
| Co(NH₃)₅Cl²⁺ | – | – | DXN 30% (w) | $1.2 \times 10^{-6}$ | 22.6 | –10.0 | T, [2] Rate constant depends on [H₂O], <NO₃⁻> | 89 |
| Co(NH₃)₅Cl²⁺ | – | – | ETG 30% (w) | $1.3 \times 10^{-6}$ | 23.3 | – 7.4 | T, [2]; k↓D↓ (at diff. [ETG]) <NO₃⁻> | 89 |
| Co(NH₃)₅Cl²⁺ | 0.1 | 2 | (K,H)ClO₄ | $1.8 \times 10^{-6}$ | 22.9 | – 8.1 | S; (2T, 10° range) | 88 |
| Co(NH₃)₅Cl²⁺ | 0.01 | – | HNO₃ | $4.0 \times 10^{-6}$ | 22.9 | – 6.4 | S | 350 |
| Co(NH₃)₅Br²⁺ | – | – | – | $6.3 \times 10^{-6}$ | 24.0 | – 1.8 | | q 40 |
| Co(NH₃)₅Br²⁺ | 0.1 | – | HNO₃ | $6.5 \times 10^{-6}$ | 23.9 | – 3.0 | S | 85 |
| Co(NH₃)₅Br²⁺ | 0.002–0.8 | 1.0–6.5 | (Na,H)NO₃ | $7.4 \times 10^{-6}$ | 21.8 | – 8.9 | T, [2] <NO₃⁻> | 89 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| Co(NH₃)₅Br²⁺ | — | — | MeOH 50% (w) | $1.9 \times 10^{-6}$ | 23.1 | −7.1 | T, [2]; $S_N2$; k depends on [H₂O] <NO₃⁻> | 89 |
| Co(NH₃)₅Br²⁺ | — | — | DXN 50% (w) | $2.6 \times 10^{-6}$ | 22.6 | −8.5 | T, [2]; k depends on [H₂O]; <NO₃⁻> | 89 |
| Co(NH₃)₅Br²⁺ | — | — | ETG 50% (w) | $3.9 \times 10^{-6}$ | 21.9 | −9.9 | T, [2]; k↓D↓; <NO₃⁻> | 89 |
| Co(NH₃)₅I²⁺ | 1.0 | 3 | (NH₄,H)ClO₄ | $8.3 \times 10^{-6}$ | 19 | −16 | S | 90 |
| Co(NH₃)₅N₃²⁺ | 0.064–0.164 | 1.85 | (Na,H)ClO₄ | $2.1 \times 10^{-9}$ | 33.1 | 12.8 | S | 91 |
| Co(NH₃)₅NCS²⁺ | 0.05 | 2.5 | HClO₄ | $2.8 \times 10^{-9}$ | 26.8 | −7.8 | S; k = a + b[NCS⁻] <ClO₄⁻> | 40 |
| Co(NH₃)₅NCS²⁺ | 0.002–0.1 | 1–2.7 | HClO₄ | $3.6 \times 10^{-10}$ | 30.1 | −0.7 | S,T; (80≤T≤97°C) | 46 |
| Co(NH₃)₅NO₂²⁺ | 0.12 | 0.2–7 | HClO₄ | $1.2 \times 10^{-8}$ | 29.6 | 4.5 | S | 92 |
| Co(NH₃)₅NO₂²⁺ | 1.0 | acid | (K,H)NO₃ | $8.2 \times 10^{-8}$ | 23.9 | −11.1 | S; The reaction was carried out under conditions where k may be separated from a concomitant redox process | 93 |
| Co(NH₃)₅ONO₂²⁺ | 0.12 | 2 | (Li,H)ClO₄ | $2.4 \times 10^{-5}$ | 24.3 | 1.9 | S; d$\Delta H^{\ddagger}$/dT = −20 cal/mol⁻¹ deg⁻¹ | 94 |
| Co(NH₃)₅NH₂SO₃²⁺ | 1.0 | | LiClO₄ | $3 \times 10^{-5}$ | — | | S | 99 |
| Co(NH₃)₅OPO₃H₂²⁺ | 1.0 | 2.0–2.7 | (Na,H)NaHPO₄ / NaClO₄ | $2.2 \times 10^{-7}$ | 23.3 | −11.2 | R | 95 |
| Co(NH₃)₅OCOCH₃²⁺ | 0.1 | 1–2 | (Na,H)ClO₄ | $2.7 \times 10^{-8}$ | 25 | −8 | S | 97 |
| Co(NH₃)₅OCOCH₂Cl²⁺ | — | — | — | $1.3 \times 10^{-7}$ | 26.3 | −1.6 | — | q 98 |
| Co(NH₃)₅OCOCHCl₂²⁺ | — | — | — | $4 \times 10^{-8}$ | 26.4 | −3.5 | — | q 98 |
| Co(NH₃)₅OCOCF₃²⁺ | 0.1 | 1.0–2.0 | (Na,H)ClO₄ | $1.5 \times 10^{-7}$ | 26 | −2 | S | 97 |
| Co(NH₃)₅OCOCCl₃²⁺ | — | — | — | $1.6 \times 10^{-7}$ | 25.7 | −3.0 | — | q 98 |
| Co(NH₃)₅OCOC(CH₃)₃²⁺ | 0.1 | 1.0–2.0 | (Na,H)ClO₄ | $4.6 \times 10^{-9}$ | 32 | 10.7 | S | 97 |
| Co(NH₃)₅oxH²⁺ | 1.0 | 0–7 | (Na,H)ClO₄ | $2.2 \times 10^{-8}$ | 28.4 | 1 | S | 96 |
| Co(NH₃)₅OSO₃⁺ | ~0.2 | 2 | Na₂SO₄ / HClO₄ | $1.2 \times 10^{-6}$ | 18.7 | −24 | S; (2T, 13°C range) | 100 |
| Co(NH₃)₅OSO₃⁺ | — | — | Na₂SO₄ | $7.0 \times 10^{-7}$ | 24.4 | −4.9 | R; [2] | 101 |
| Co(NH₃)₅OSO₃⁺ | 1.0 | 0–2 | (Na,H)ClO₄ | $8.9 \times 10^{-7}$ | 22.7 | −10 | S | 102 |
| Co(NH₃)₅OS₂O₂⁺ | 1.0 | | (K, Ba/2, La/3)Cl | $1.6 \times 10^{-7}$ | 19.3 | −24.8 | T | 103 |
| Co(NH₃)₅ox⁺ | 1.0 | 1–7 | (Na,H)ClO₄ | $1.5 \times 10^{-8}$ | 26.2 | −5 | S | 96 |
| Co(NH₃)₅OPO₃H⁺ | 1.0 | 5–6 | (Na,H)NaHPO₄ / NaClO₄ | $7.9 \times 10^{-9}$ | 26.8 | −6.6 | R | 95 |
| Co(NH₃)₅OPO₃ | 1.0 | | NaClO₄ | $1.5 \times 10^{-9}$ | 39.6 | 34 | R | 95 |
| Co(Me-NH₂)₅Cl²⁺ | 0.01–0.1 | | HClO₄ | $3.7 \times 10^{-5}$ | 22.0 | 5.1 | T | 105 |
| Co(Me-NH₂)₅Cl²⁺ | 0.01 | | HNO₃ | $3.3 \times 10^{-5}$ | 22.6 | 3.2 | S | 350 |
| Co(Et-NH₂)₅Cl²⁺ | 0.01 | | HNO₃ | $1.6 \times 10^{-4}$ | 21.3 | −4.4 | S | 350 |

| Complex | μ | pH | Medium | k | | | Notes | Ref |
|---|---|---|---|---|---|---|---|---|
| Co(n Pr NH₂)₅Cl²⁺ | 0 01 | | HNO₃ | $1\ 9\times10^{-4}$ | 20 9 | $-5\ 5$ | S | 350 |
| Co(n Bu NH₂)₅Cl²⁺ | 0 01 | | HNO₃ | $2\ 0\times10^{-4}$ | 20 8 | $-5\ 6$ | S | 350 |
| Co(t Bu NH₂)₅Cl²⁺ | 0 01 | | HNO₃ | $3\ 7\times10^{-4}$ | 16 1 | $-18\ 3$ | S | 350 |
| cis Co(NH₃)₄(H₂O)OPO₃H₄⁴⁺ | 10 8 | | HClO₄ | $1\ 1\times10^{-6}$ | 24 4 | $-4\ 0$ | R | 79 |
| cis Co(NH₃)₄(H₂O)OPO₃H₃³⁺ | 0 66–5 7 | | HClO₄ | $3\ 6\times10^{-6}$ | 24 9 | $-7\ 8$ (0 1) | R | 79 |
| | | | | | | | | |
| trans Co(NH₃)₄Cl₂⁺ | 0 1 | | HNO₃ | $1\ 8\times10^{-3}$ | – | – | S | 130 |
| trans Co(NH₃)₄Cl₂⁺ | 10 | | HClO₄ | $1\ 5\times10^{-3}$ | 22 0 | 2 4 | T S 45 ± 10% trans prod | 154 |
| trans Co(NH₃)₄(NCS)Cl⁺ | 0 5 | | HNO₃ | $3\ 6\times10^{-6}$ | 25 7 | 3 | S | 346 |
| trans Co(NH₃)₄(NO₂)Cl⁺ | 0 1 | | HNO₃ | $2\ 7\times10^{-2}$ | 17 6 | $-6\ 7$ | S 100% trans prod | 333 |
| trans Co(NH₃)₄(NO₂)Br⁺ | 0 1 | | HNO₃ | $7\ 2\times10^{-2}$ | 19 2 | 1 | S 100% trans prod | 333 |
| Co(NH₃)₃(NO₂)₂NCS | – | | – | $8\ 2\times10^{-5}$ | 25 8 | 9 3 | – | 174 |
| Co(NH₃)₂(ONO)₄⁻ | 2 5 | | HClO₄ | $1\ 7\times10^{-4}$ | 16 0 | $-22\ 1$ | S | 176 |
| trans Co(py)₄(H₂O)Cl²⁺ | – | | none | – | 25 4 | – | K S <Cl⁻> | 155 |
| trans Co(py)₄Cl₂⁺ | – | | SUC 10% (w) | $9\ 8\times10^{-6}$ | 31 7 | 24 9 | T [2] k↓[SUC]↑but ΔH‡ and ΔS‡ are essentially constnt up to 40% SUC <Cl⁻> | 156 |
| | | | | | | | | |
| trans Co(py)₄Cl₂⁺ | – | | ETG 10–70% (w) | $(9\ 5\times10^{-6})$ | 30 4 | 20 5 | T [2] | 158 |
| | | | | | | | | |
| trans Co(py)₄Cl₂⁺ | – | 1–9 2 | – | $8\ 4\times10^{-6}$ | – | – | T | 159 |
| trans Co(β pic)₄Cl₂⁺ | – | 1–9 2 | – | $2\ 5\times10^{-5}$ | – | – | T | 159 |
| trans Co(γ pic)₄Cl₂⁺ | – | 1–9 2 | – | $1\ 5\times10^{-5}$ | – | – | T | 159 |
| Co(en)(NH₃)(NO₂)NCS | – | – | – | $2\ 9\times10^{-5}$ | 22 3 | $-4\ 8$ | – | 174 |
| cis Co(en)(NH₃)₂Cl₂⁺ | 0 1 | | HNO₃ | $2\ 3\times10^{-4}$ | – | – | S | 130 |
| trans Co(en)(NH₃)₂Cl₂⁺ | 0 1 | | HNO₃ | $2\ 2\times10^{-4}$ | – | – | S | 130 |
| cis Co(en)₂(OH₂)₂³⁺ | 0 8 | | (Na H)ClO₄ | $7\ 5\times10^{-6}$ | 28 8 | 15 | M | 125 |
| cis Co(en)₂(NH₃)(OH₂)³⁺ | 0 01 | | HClO₄ | $1\ 1\times10^{-6}$ | – | – | M | 106 |
| cis Co(en)₂(H₂O)OPO₃H₃³⁺ | 4 0 | | HClO₄ | $5\times10^{-8}$ | 24 9 | $-8\ 3$ | R | 79 |
| cis Co(en)₂(NH₃)OPO₃H₃³⁺ | 3 7 | | HClO₄ | $3\ 6\times10^{-7}$ | 27 1 | $-2\ 8$ | R 100% cis prod | 302 |
| cis Co(en)₂(H₂O)Cl²⁺ | – | 2–3 | HNO₃ | $1\ 6\times10^{-6}$ | – | – | T <SO₄²⁻> | 127 |
| cis Co(en)₂(NH₃)Cl²⁺ | – | | none | $3\ 7\times10^{-7}$ | 24 9 | $-4\ 3$ | T <ClO₄⁻> | 87 |
| cis Co(en)₂(NH₃)Cl²⁺ | indep of μ | 0 3–2 | (Na H)(NO₃ ClO₄) | $(7\ 0\times10^{-9})$ | 23 2 | $-18$ | – [2] act param indep of μ pH presence of EtOH GLC ETG | 108 |
| | | | | | | | | |
| cis Co(en)₂(NH₃)Cl²⁺ | – | | – | $5\ 5\times10^{-7}$ | 22 6 | $-11\ 4$ | T | q 107 |
| l cis Co(en)₂(NH₃)Br²⁺ | 0 17 | | HClO₄ | $1\ 6\times10^{-6}$ | 22 5 | $-9\ 6$ | S (2T) | 109 |
| d l cis Co(en)₂(NH₃)ONO₂²⁺ | 0 17 | | HClO₄ | $9\ 4\times10^{-6}$ | 23 5 | $-2\ 7$ | S (2T) | 109 |
| cis Co(en)₂(NH₂OH)Cl²⁺ | 0 50 | | HClO₄ | $5\ 0\times10^{-6}$ | 19 7 | $-16\ 7$ | T <NO₃⁻> | 119 |
| cis Co(en)₂(NH₂OH)Br²⁺ | 0 50 | | HClO₄ | $2\ 1\times10^{-5}$ | 19 6 | $-14\ 2$ | T <NO₃⁻> | 111 |
| cis Co(en)₂(MeNH₂)Cl²⁺ | | | none | $2\ 3\times10^{-7}$ | 24 4 | $-7\ 1$ | T <NO₃⁻> | 107 |
| cis Co(en)₂(MeNH₂)Cl²⁺ | 0 1 | | HNO₃ | $3\ 5\times10^{-7}$ | 23 9 | $-8$ | T [2] k ΔH‡ and ΔS‡ are not sensitive to added ETG up to 40% by w | 110 |
| | | | | | | | | |
| cis Co(en)(MeNH₂)Br²⁺ | | | none | $4\ 6\times10^{-7}$ | 26 3 | 0 7 | T <NO₃⁻> | 111 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| cis(?)-Co(en)₂(EtNH₂)Cl²⁺ | 0.1 | 4.7–5.7 | {(Na,H)OCOCH₃ / (Na,H)OCOH | $5.0 \times 10^{-7}$ | 22.6 | –11 | T; [2] | 112 |
| cis-Co(en)₂(EtNH₂)Cl²⁺ | | | none | $1.5 \times 10^{-7}$ | 26.1 | – 2.2 | T; <NO₃⁻> | 107 |
| cis(?)-Co(en)₂(EtNH₂)Cl²⁺ | | 3 | HNO₃ | $3.4 \times 10^{-7}$ | 24.3 | – 6.5 | T; $\Delta H^{\ddagger}$ is insensitive to →40% w DXN and →60% ETG; $\Delta S^{\ddagger}$↓ by a factor of ~2 in both cases | 113 |
| cis-Co(en)₂(EtNH₂)Br²⁺ | – | – | none | $2.9 \times 10^{-7}$ | 27.5 | 3.8 | T; <NO₃⁻> | 111 |
| cis-Co(en)₂(n-PrNH₂)Cl²⁺ | – | – | none | $3.2 \times 10^{-7}$ | 24.6 | – 5.7 | S; <NO₃⁻> | 114 |
| cis-Co(en)₂(n-PrNH₂)Br²⁺ | – | – | none | $1.8 \times 10^{-6}$ | 22.9 | – 8.0 | T; <NO₃⁻> | 111 |
| cis-Co(en)₂(i-PrNH₂)Cl²⁺ | – | – | none | $1.2 \times 10^{-6}$ | 24.3 | – 4.1 | T; <NO₃⁻> | 114 |
| cis-Co(en)₂(i-PrNH₂)Br²⁺ | – | – | none | $7.3 \times 10^{-6}$ | 22.9 | – 5.2 | T; <NO₃⁻> | 111 |
| cis-Co(en)₂(AllNH₂)Cl²⁺ | – | – | none | $2.0 \times 10^{-7}$ | 25.4 | – 4.0 | T; <NO₃⁻> | 115 |
| cis-Co(en)₂(AllNH₂)Cl²⁺ | 0.1 | 1 | HNO₃ | $3.3 \times 10^{-7}$ | 23.3 | –18 (–10) | T; [2]; Act. par. are unaffected by →40% (w) ETG and →20% (w) DXN | 110 |
| cis-Co(en)₂(AllNH₂)Br²⁺ | – | – | none | $5.6 \times 10^{-7}$ | 26.8 | 2.8 | T; <NO₃⁻> | 111 |
| cis-Co(en)₂(Pr-2-ynylNH₂)Cl²⁺ | – | – | none | $1.2 \times 10^{-7}$ | 25.4 | – 5.0 | T; <NO₃⁻> | 115 |
| cis-Co(en)₂(Pr-2-ynylNH₂)Br²⁺ | | | none | $3.1 \times 10^{-7}$ | 26.6 | 0.9 | T; <ClO₄⁻> | 111 |
| cis-Co(en)₂(CH₂OHCH₂NH₂)Cl²⁺ | | | none | $1.7 \times 10^{-6}$ | 21.8 | –11.8 | T; 100% cis prod.; <NO₃⁻> | 116 |
| cis-Co(cn)₂(CH₂ClCH₂NH₂)Cl²⁺ | 0.1 | | HClO₄ | $8.1 \times 10^{-8}$ | 25.5 | – 5 | T | 117 |
| cis-Co(en)₂(CH₂ClCH₂NH₂)Br²⁺ | 0.1 | | HClO₄ | $4.2 \times 10^{-7}$ | 25.5 | – 2.1 | T | 117 |
| cis-Co(en)₂(CH₂BrCH₂NH₂)Br²⁺ | 0.1 | | HClO₄ | $7.3 \times 10^{-7}$ | 25.7 | – 0.4 | T | 117 |
| cis-Co(en)₂(CH₃OCH₂CH₂NH₂)Cl²⁺ | | | none | $5.6 \times 10^{-7}$ | 22.5 | –11.7 | T; <NO₃⁻> | 118 |
| cis-Co(en)₂(CH₃CHOHCH₂NH₂)Cl²⁺ | | | none | $1.3 \times 10^{-6}$ | 22.2 | –11.0 | T; 100% cis prod.; <NO₃⁻> | 116 |
| cis-Co(en)₂(CH₂OHCH₂CH₂CH₂NH₂)Cl²⁺ | | | none | $3.5 \times 10^{-7}$ | 23.4 | – 9.6 | T; 100% cis prod.; <NO₃⁻> | 116 |
| cis-Co(en)₂(CH₃OCH₂CH₂CH₂NH₂)Cl²⁺ | | | none | $6.5 \times 10^{-7}$ | 22.2 | –12.4 | T; <NO₃⁻> | 118 |
| cis-Co(en)₂(CH₃CHClCH₂NH₂)Cl²⁺ | 0.1 | | HClO₄ | $9.8 \times 10^{-8}$ | 25.5 | – 5.1 | T | 117 |
| cis-Co(en)₂(CH₂ClCH₂NH₂)Cl²⁺ | 0.1 | | HClO₄ | $1.3 \times 10^{-7}$ | 25.8 | – 3.6 | T | 117 |
| cis-Co(en)₂(CH₂OH(CH₂)₃NH₂)Cl²⁺ | | | none | $3.7 \times 10^{-7}$ | 23.7 | – 8.5 | S,T; <NO₃⁻> | 347 |
| cis-Co(en)₂(CH₂OH(CH₂)₄NH₂)Cl²⁺ | | | none | $4.8 \times 10^{-7}$ | 23.4 | – 9.0 | S,T; <NO₃⁻> | 347 |
| cis-Co(en)₂(CH₂OH(CH₂)₅NH₂)Cl²⁺ | | | none | $4.8 \times 10^{-7}$ | 23.4 | – 9.0 | S,T; <NO₃⁻> | 347 |
| cis-Co(en)₂(Φ-CH₂NH₂)Cl²⁺ | 0.05 | | HNO₃ | $1.8 \times 10^{-7}$ | 24.5 | –15 (–7.2) | T; [2]; Act. par. are unchanged by addition of ETG (40% by w.) and DXN (20% by w.) | 110 |

| Complex | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| cis-Co(en)₂(py)Cl²⁺ | 0.1 | | HNO₃ | $2.6\times10^{-7}$ | 25.4 | −11 (−3.4) | T; [2]; Act. par. are unchanged by addition of ETG (40% by w.) and DXN (20% by w.) | 110 |
| cis-Co(en)₂(py)Cl²⁺ | 0.1 | 2 | (Na,H)ClO₄ / (Na,H)NO₃ | $6.2\times10^{-7}$ | 23.8 | −5.0 (−7.1) | T | 120 |
| cis-Co(en)₂(py)Br²⁺ | 0.1 | 3 | (Na,H)NO₃ | $(1.7\times10^{-6})$ | 23.8 | −5.1 | T | 120 |
| cis-Co(en)₂(β-pic)Cl²⁺ | 0.1 | 2 | (Na,H)ClO₄ / (Na,H)NO₃ | $5.2\times10^{-7}$ | 23.8 | −5.0 (−7.4) | T | 120 |
| cis-Co(en)₂(β-pic)Br²⁺ | – | – | – | $(1.9\times10^{-6})$ | 23.6 | −5.5 | – | 358 |
| cis-Co(en)₂(γ-pic)Cl²⁺ | 0.1 | 2 | (Na,H)ClO₄ / (Na,H)NO₃ | $(2.4\times10^{-6})$ | 23.2 | −6.4 | – | 358 |
| cis-Co(en)₂Cl(DMA)²⁺ | 0.0125 | | HClO₄ | $9.5\times10^{-4}$ | 22.9 | 4.7 | S | 126 |
| cis-Co(en)₂Cl(DMSO)²⁺ | 0.0125 | | HClO₄ | $1.5\times10^{-5}$ | 24.6 | 1.5 | S | 126 |
| cis-Co(en)₂Cl(DMF)²⁺ | 0.0125 | | HClO₄ | $7.2\times10^{-6}$ | 24.6 | 0.5 (2.5) | S | 126 |
| cis-Co(en)₂(DMA)Cl²⁺ | 0.0125 | 0–2 | HClO₄ | $2.3\times10^{-5}$ | 11.0 | −43 | S | 126 |
| cis-Co(en)₂(CH₃COO)(CH₃COOH)²⁺ | 2.0 | | (Na,H)ClO₄ | $8.9\times10^{-2}$ | 15.4 | −13 | S,S_SF; 100% *cis* prod. | 329 |
| d-cis-Co(en)₂F₂⁺ | – | – | none | $3.0\times10^{-6}$ | – | – | T; <NO₃⁻> | 128 |
| cis-Co(en)₂(OH)F⁺ | – | – | none | $2.8\times10^{-4}$ | 21.5 | −2.7 | T | 129 |
| cis-Co(en)₂Cl₂⁺ | 0.1 | | HNO₃ | $2.5\times10^{-4}$ | – | – | S | 130 |
| cis-Co(en)₂Cl₂⁺ | 0.012 | | HNO₃ | $1.2\times10^{-3}$ | 21.6 | −4.0 | S,T; 100% *cis* prod. | q 52 |
| cis-Co(en)₂Cl₂⁺ | 0.01 | | HNO₃ | $2.4\times10^{-4}$ | – | – | S; Very accurate k | 131 |
| cis-Co(en)₂Cl₂⁺ | 0.1 | | HNO₃ | $1.40\times10^{-4}$ | – | – | | 132 |
| cis-Co(en)₂Cl₂⁺ | – | | none | $2.4\times10^{-4}$ | 27.5 | 17.1 | T, [2]; <Cl⁻> | 134 |
| cis-Co(en)₂Cl₂⁺ | 0.01 | | HNO₃ | $2.4\times10^{-4}$ | – | – | T | 133 |
| cis-Co(en)₂Cl₂⁺ | – | | SUC | $(1.4\times10^{-4})$ | 20.6 | −7 | – | 135 |
| cis-Co(en)₂Cl₂⁺ | – | | 10–40% (w) | $(1.3\times10^{-5})$ | 22.0 | −7 | – | 135 |
| cis-Co(en)₂BrCl⁺ | 0.01 | 2.0 | HNO₃ | $1.4\times10^{-4}$ | 22.5 | −0.7 | S,T; >95% *cis* prod. | 136 |
| cis-Co(en)₂(OH)Cl⁺ | – | | none | $1.2\times10^{-2}$ | 22.5 | 7.9 | K,T; 100% *cis* prod. <SO₄²⁻> | 131 |
| cis-Co(en)₂(OH)Cl⁺ | 0.01 | 7.0–8.7 | HClO₄ | $1.3\times10^{-2}$ | – | – | T | 137 |
| cis-Co(en)₂(N₃)Cl⁺ | 0.01 | | HClO₄ | $2.4\times10^{-4}$ | 21.1 | −4.3 | S,T; 100% *cis* prod. | 138 |
| cis-Co(en)₂(NCS)Cl⁺ | 0.004 | | HClO₄ | $1.1\times10^{-5}$ | 20.2 | −13.5 | S,T; 100% *cis* prod. | 139 |
| cis-Co(en)₂(NCS)Cl⁺ | 0.1~0 | | NaClO₄ / NaNO₃ / NaCl / Na₂SO₄ | $7.8\times10^{-6}$ | 21.7 | −9 | T, [2]; lg k↓(1/D)↑ *(see below)* | 140 |
| cis-Co(en)₂(NCS)Cl⁺ | – | | Acetone 40% (w) | $2.7\times10^{-6}$ | 21.8 | −10 | T, [2]; D = 48.5 | 140 |
| cis-Co(en)₂(NCS)Cl⁺ | – | | MeOH 40% (w) | $2.8\times10^{-6}$ | 23.4 | −5 | T, [2]; D = 52.2 | 140 |
| cis-Co(en)₂(NCS)Cl⁺ | – | | ETG 40% (w) | $5.1\times10^{-6}$ | 21.8 | −9 | T, [2]; D = 58.5 | 140 |
| cis-Co(en)₂(NCS)Cl⁺ | – | | SUC 40% (w) | $5.6\times10^{-6}$ | 21.1 | −11 | T, [2]; D = 59.8 | 140 |
| cis-Co(en)₂(NO₂)Cl⁺ | 2.1–5.1 | | HClO₄ | $1.2\times10^{-4}$ | 21.8 | −3.4 | S; 100% *cis* prod. | 141 |
| cis-Co(en)₂(NO₂)Cl⁺ | – | | none | $1.2\times10^{-4}$ | – | – | T; 100% *cis* prod.; <Cl⁻> | 133 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| *cis*-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | – | $1.1 \times 10^{-4}$ | 20.6 | $-7.8$ | –; lgk increases linearly with (1/D) | 142 |
| *cis*-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | SUC 40% (w) | $5.3 \times 10^{-5}$ | 21.1 | $-7.3$ | – | 142 |
| *cis*-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | MeOH 40% (w) | $2.7 \times 10^{-5}$ | 21.2 | $-8.4$ | | 142 |
| *cis*-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | ETG 40% (w) | $4.8 \times 10^{-5}$ | 20.9 | $-8.4$ | | 142 |
| *cis*-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | Acetone 40% (w) | $1.8 \times 10^{-5}$ | 21.9 | $-6.9$ | – | 142 |
| *cis*-Co(en)$_2$ClBr$^+$ | 0.01 | | HNO$_3$ | $5.7 \times 10^{-4}$ | 23.3 | 4.8 | S,T; >95% *cis* prod. | 136 |
| *cis*-Co(en)$_2$Br$_2^+$ | 0.1 | | HNO$_3$ | $1.1 \times 10^{-3}$ | 23.2 | 5.6 | S,T | 143 |
| *cis*-Co(en)$_2$Br$_2^+$ | 0.1 | 1–2 | HNO$_3$ or HClO$_4$ | $9.3 \times 10^{-4}$ | 21.3 | $-1$ | S; 72% *cis* prod. | 334 |
| *cis*-Co(en)$_2$(OH)Br$^+$ | 0.01 | | HNO$_3$ | $5.9 \times 10^{-2}$ | 22.7 | 12.1 | S,T; 96 ± 4% *cis* prod. | 136 |
| *cis*-Co(en)$_2$(NCS)Br$^+$ | 0.004 | | HClO$_4$ | $2.3 \times 10^{-5}$ | 22.5 | $-4.3$ | S,T; 100% *cis* prod. | 139 |
| *cis*-Co(en)$_2$(NCS)Br$^+$ | 0.01 | | HNO$_3$ EtOH 40% (w) | $9.8 \times 10^{-6}$ | 21.4 | $-10$ | T | 144 |
| *cis*-Co(en)$_2$(NCS)Br$^+$ | 0.01 | | HNO$_3$ Acetone 40% (w) | $9.4 \times 10^{-6}$ | 20.6 | $-12$ | T; lgk decreases linearly with (1/D) | 144 |
| *cis*-Co(en)$_2$(NCS)Br$^+$ | 0.01 | | HNO$_3$ ETG 40% (w) | $1.6 \times 10^{-5}$ | 21.5 | $-9$ ($-8.4$) | T; lgk decreases linearly with (1/D) | 144 |
| *cis*-Co(en)$_2$(OH)$_2^+$ | 0.8 | 13.5–13.9 | Na(ClO$_4$,OH) | $3.0 \times 10^{-5}$ | 27.4 | 13 | M | 125 |
| *cis*-Co(en)$_2$(OCOH)$_2^+$ | 0.1 | 1–4 | (Na,H)ClO$_4$ | $4.1 \times 10^{-6}$ | 22 | $-9$ | S | 359 |
| *cis*-Co(en)$_2$(OCOCH$_3$)$_2^+$ | 0.1 | 1–4 | (Na,H)ClO$_4$ | $9.3 \times 10^{-6}$ | 22 | $-8$ | S | 359 |
| *cis*-Co(en)$_2$(OCOCH$_2$C(CH$_3$)$_3$)$_2^+$ | 0.1 | 1–4 | (Na,H)ClO$_4$ | $3.8 \times 10^{-5}$ | 21 | $-8.3$ | S | 359 |
| *cis*-Co(en)$_2$(OCOCCl$_3$)$_2^+$ | 0.1 | 1–4 | (Na,H)ClO$_4$ | $4.2 \times 10^{-6}$ | – | $-15$ | S | 359 |
| *cis*-Co(en)$_2$(OCO-Ph)$_2^+$ | 0.1 | 1–4 | (Na,H)ClO$_4$ | $7.5 \times 10^{-6}$ | 20 | $-15$ | S | 359 |
| *cis*-Co(en)$_2$CO$_3^+$ | 1.0 | | NaClO$_4$ | $4.6 \times 10^{-5}$ | 21.4 | $-6.6$ | S; Possibly CO since $k_{oh}/k_{aq}$ is unusually low (60) | 145 |
| *cis*-Co(en)$_2$SO$_4^+$ | 0.023 | | KNO$_3$ | $7.7 \times 10^{-5}$ | 19.9 | $-10$ | S; 100% *cis*-Co(en)$_2$ (H$_2$O)OSO$_3^+$ prod. | 146 |
| *trans*-Co(en)$_2$(OH$_2$)$_2^{3+}$ | 0.8 | 0.1–0.5 | (Na,H)ClO$_4$ | $1.1 \times 10^{-5}$ | 30.6 | 21.5 | M | 125 |
| *trans*-Co(en)$_2$(H$_2$O)(NH$_2$Ph)$^{3+}$ | – | – | none | $3.0 \times 10^{-7}$ | 29.5 | 10.5 | A; <Cl⁻> | 122 |
| *trans*-Co(en)$_2$(H$_2$O)Cl$^{2+}$ | – | 2–3 | HNO$_3$ | $2.5 \times 10^{-6}$ | – | – | T | 127 |
| *trans*-Co(en)$_2$(NH$_3$)(OH$_2$)$^{3+}$ | 0.05 | | HClO$_4$ | $4.5 \times 10^{-6}$ (30°) | – | – | M; 99% *trans* prod. | 106 |
| *trans*-Co(en)$_2$(NH$_3$)OPO$_3$H$_3^{3+}$ | 3.7 | | HClO$_4$ | $3.6 \times 10^{-7}$ | 27.0 | $-2.6$ | R; 100% *trans* prod. | 302 |
| *trans*-Co(en)$_2$(NH$_3$)Cl$^{2+}$ | 0.17 | | HClO$_4$ | $3.7 \times 10^{-7}$ | 23.0 | $-10.8$ | S; (2T), 84% *trans* prod. | 109 |
| *trans*-Co(en)$_2$(NH$_3$)Cl$^{2+}$ | 0.1–0.17 | | HClO$_4$ | $2.9 \times 10^{-7}$ | 23 | $-11.3$ | S; 100% *trans* prod. | 121 |
| *trans*-Co(en)$_2$(NH$_3$)Cl$^{2+}$ | – | 0.3–2 | HNO$_3$ | $6 \times 10^{-9}$ | 23.6 | $-17$ | – | 108 |
| *trans*-Co(en)$_2$(NH$_3$)Br$^{2+}$ | 0.1–0.17 | | HClO$_4$ | $1.2 \times 10^{-6}$ | 24 | $-5.1$ | S; 100% *trans* prod. | 121 |
| *trans*-Co(en)$_2$(NH$_3$)ONO$_2^{2+}$ | 0.1 | | HClO$_4$ | $6.9 \times 10^{-6}$ | 24.9 | 1.4 | S; 100% *trans* prod. | 121 |
| *trans*-Co(en)$_2$(Ph-NH$_2$)Cl$^{2+}$ | – | – | none | $2.4 \times 10^{-5}$ | 26.2 | 8.2 | K; <Cl⁻> | 122 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| *trans*-$Co(en)_2F_2^+$ | 0.1–2 | — | KNO$_3$ | $1 \times 10^{-6}$ | — | — | C | 128 |
| *trans*-$Co(en)_2Cl_2^+$ | 0.1 | | HNO$_3$ | $3.1 \times 10^{-5}$ | 27.5 | 13.1 | S,T | 161 |
| *trans*-$Co(en)_2Cl_2^+$ | 0.01 | — | HNO$_3$ | $3.5 \times 10^{-5}$ | — | — | S,T; 65% *trans* prod. | 131 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | — | — | 23.6 | — | — | q 131 |
| *trans*-$Co(en)_2Cl_2^+$ | 0.01 | | HNO$_3$ | $2.70 \times 10^{-5}$ | — | — | S; very accurate k | 132 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | none | $3.8 \times 10^{-5}$ | 29.4 | 19.9 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | none | $4.9 \times 10^{-5}$ | 27.3 | 13.3 | T; [2] <Cl$^-$> | 134 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | MeOH 20% (w) | $2.2 \times 10^{-5}$ | 26.4 | 8.7 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | MeOH 39% (w) | $1.5 \times 10^{-5}$ | 24.5 | 1.6 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | — | | MeOH 60% (w) | $9.4 \times 10^{-6}$ | 22.3 | -6.7 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | EtOH 18% (w) | $2.4 \times 10^{-5}$ | 26.2 | 8.2 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | EtOH 36% (w) | $1.7 \times 10^{-5}$ | 25.7 | 5.9 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | EtOH 54% (w) | $1.6 \times 10^{-5}$ | 25.6 | 5.4 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | Acetone 20% (w) | $2.3 \times 10^{-5}$ | 26.8 | 10.1 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | 0.005 | | Acetone 40% (w) | $1.6 \times 10^{-5}$ | 25.8 | 6.1 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | HNO$_3$ | $3.6 \times 10^{-5}$ | — | — | S; ≧80% *cis* prod. | 170 |
| *trans*-$Co(en)_2Cl_2^+$ | | | Acetone 60% (w) | $1.4 \times 10^{-5}$ | 24.5 | 1.4 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | DXN 20% (w) | $2.3 \times 10^{-5}$ | 26.3 | 8.5 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | DXN 40% (w) | $1.9 \times 10^{-5}$ | 24.4 | 1.7 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | 0.005 | | DXN 60% (w) | $1.5 \times 10^{-5}$ | 24.2 | 0.5 | S; <Cl$^-$> | 162 |
| *trans*-$Co(en)_2Cl_2^+$ | | | HNO$_3$ | $3.6 \times 10^{-5}$ | — | — | S; ≧80% *cis* prod. | 170 |
| *trans*-$Co(en)_2Cl_2^+$ | | | SUC 10% (w) | $4.2 \times 10^{-5}$ | 26.3 | 9.5 | T, [2]; k↓[SUC]↑ but $\Delta H^\ddagger$ and $\Delta S^\ddagger$ remain essentially const. →40% SUC (w) | 156 |
| *trans*-$Co(en)_2Cl_2^+$ | | 7.0–8.7 | ETG 10% (w) | $(2.0 \times 10^{-4})$ | 25.1 | 8.7 | T, [2]; k↓[ETG]↑ but $\Delta H^\ddagger$ and $\Delta S^\ddagger$ remain essentially constant | 158 |
| *trans*-$Co(en)_2Cl_2^+$ | ~0.01 | — | HNO$_3$ | $3.5 \times 10^{-5}$ | 26.1 | — | T; mixt. *cis* + *trans* prod. | 133 |
| *trans*-$Co(en)_2Cl_2^+$ | ~0.01 | — | HNO$_3$ | $3.5 \times 10^{-5}$ | 26.0 | 8.6 | T | 163 |
| *trans*-$Co(en)_2ClBr^+$ | 0.01 | — | HNO$_3$ | $1.1 \times 10^{-4}$ | 24.6 | 10.6 | S,T; 80±5% *trans* prod. | 136 |
| *trans*-$Co(en)_2BrCl^+$ | ~0.01 | — | HNO$_3$ | $4.5 \times 10^{-5}$ | 25.5 | 4.1 | S,T; 50±5% *trans* prod. | 136 |
| *trans*-$Co(en)_2Br_2^+$ | 0.1 | — | HNO$_3$ | $1.4 \times 10^{-4}$ | 25.0 | 9.4 | S,T | 128 |
| *trans*-$Co(en)_2Br_2^+$ | 0.01 | — | HNO$_3$ | $1.4 \times 10^{-4}$ | 24.8 | 7.8 | S,T; 70±2% *trans* prod. | 136 |
| *trans*-$Co(en)_2(OH)F^+$ | | | none | $4.0 \times 10^{-5}$ | — | 4.6 | T; <ClO$_4^-$> | 129 |
| *trans*-$Co(en)_2(OH)Cl^+$ | | 7.0–8.7 | | $1.4 \times 10^{-3}$ | — | — | T | 137 |
| *trans*-$Co(en)_2(OH)Cl^+$ | | — | | $1.6 \times 10^{-3}$ | 25.6 | 14.6 | K,T | 131 |
| *trans*-$Co(en)_2(OH)Br^+$ | | — | | $9.5 \times 10^{-3}$ | 24.4 | 14.1 | S,T; 27±2% *trans* prod. | 136 |
| *trans*-$Co(en)_2(CN)Cl^+$ | | — | none | $7.8 \times 10^{-5}$ | 22.0 | -3.4 | T; 100% *trans* prod.; <NO$_3^-$> | 164 |
| *trans*-$Co(en)_2(CN)Br^+$ | | — | none | $4.7 \times 10^{-4}$ | 23.4 | 4.7 | T; 100% *trans* prod.; <Br$^-$> | 166 |
| *trans*-$Co(en)_2(N_3)Cl^+$ | 0.010 | | HClO$_4$ | $2.2 \times 10^{-4}$ | 23.1 | 2.2 | S,T; 80% *trans* prod. | 138 |
| *trans*-$Co(en)_2(N_3)Cl^+$ | 0.010 | | HClO$_4$ | $2.6 \times 10^{-4}$ | 20.7 | -6 | S; 100% *trans* prod. | 149 |
| *trans*-$Co(en)_2(N_3)Br^+$ | 0.010 | — | HClO$_4$ | $8.5 \times 10^{-4}$ | 20.0 | -6 | S; 100% *trans* prod. | 149 |
| *trans*-$Co(en)_2(NO_2)Cl^+$ | | 5.0 | | $9.8 \times 10^{-4}$ | 20.9 | -2.2 | S; 100% *trans* prod. | 141 |
| *trans*-$Co(en)_2(NO_2)Cl^+$ | | — | none | $1.0 \times 10^{-3}$ | — | — | T; 100% *trans* prod., <NO$_3^-$> | 133 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^\ddagger$ | $\Delta S^\ddagger$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | – | $8.9 \times 10^{-4}$ | 19.6 | –6.7 | – | 142 |
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | SUC 40% (w) | $4.9 \times 10^{-4}$ | 19.3 | –8.9 | – | 142 |
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | ETG 40% (w) | $4.4 \times 10^{-4}$ | 19.0 | –10.1 | – | 142 |
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | MeOH (30% by w.) | $4.5 \times 10^{-4}$ | 18.7 | –11.1 | k is a function of [H$_2$O] but not of D. / – | 142 |
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.1 | – | Acetone 30% (w) | $4.4 \times 10^{-4}$ | 18.8 | –10.8 | – | 142 |
| trans-Co(en)$_2$(NO$_2$)Br$^+$ | – | – | – | $5.1 \times 10^{-3}$ | 21.4 | –1 | – | q 167 |
| trans-Co(en)$_2$(NCS)Cl$^+$ | 0.007 | – | – | $4.5 \times 10^{-8}$ | 29.8 | 7.8 | S | 165 |
| trans-Co(en)$_2$(NCS)Cl$^+$ | | | ETG 40% (w) | $2.4 \times 10^{-8}$ | 29.4 | 5 | T; [2] logk decreases | 140 |
| trans-Co(en)$_2$(NCS)Cl$^+$ | | | SUC 40% (w) | $2.6 \times 10^{-8}$ | 29.5 | 6 | T; [2] linearly with | 140 |
| trans-Co(en)$_2$(NCS)Cl$^+$ | | | GLC 40% (w) | $2.3 \times 10^{-8}$ | 29.4 | 5 | T; [2] (1/D) and is | 140 |
| trans-Co(en)$_2$(NCS)Cl$^+$ | | | EtOH 30% (w) | $1.6 \times 10^{-8}$ | 29.1 | 3 | T; [2] insensitive to the nature of the organic component | 140 |
| trans-Co(en)$_2$(NCS)Br$^+$ | 0.007 | – | HClO$_4$ | $2.4 \times 10^{-7}$ | 29.5 | 10.1 | S; 55% trans prod. | 139 |
| trans-Co(en)$_2$(NCS)Br$^+$ | 0.01 | – | {HNO$_3$, EtOH 40% (w)} | $1.4 \times 10^{-7}$ | 28.0 | 4 | T; [2], logk decreases linearly with (1/D) | 144 |
| trans-Co(en)$_2$(NCS)Br$^+$ | 0.01 | – | {HNO$_3$, ETG 40% (w)} | $1.8 \times 10^{-7}$ | 27.7 | 4 | T; [2], logk decreases linearly with (1/D) | 144 |
| trans-Co(en)$_2$(NCS)Br$^+$ | 0.01 | – | {HNO$_3$ GLC 40% (w)} | $1.6 \times 10^{-7}$ | 28.5 | 6 | T; [2] | 144 |
| trans-Co(en)$_2$(OH)$_2^+$ | 0.8 | 13.5–13.9 | Na(ClO$_4$,OH) | $2.3 \times 10^{-6}$ | 30.4 | 20 (18) | M | 125 |
| trans-Co(en)$_2$(CH$_3$COO)(OHCOCH$_3$)$^{2+}$ | 2.0 | –0.3–1 | (Na,H)ClO$_4$ | $1.6 \times 10^{-4}$ | 23.0 | 1 | S,Ssf; 75% trans prod. | 329 |
| trans-Co(en)$_2$(CH$_3$COO)Cl$^+$ | 0.012 | – | HClO$_4$ | $3.1 \times 10^{-6}$ | 26.8 | 6.7 | S,T; 80% cis prod. | 323 |
| trans-Co(en)$_2$($\Phi$-COO)Cl$^+$ | 0.012 | – | HClO$_4$ | $1.2 \times 10^{-6}$ | 29.3 | 13.2 | S,T | 323 |
| Co(en)$_2$(H$_2$O)Cl$^{2+}$ | 0.1 | 4.7 | {(Na,H)OCOCH$_3$ (Na,H)OCOH} | $2.7 \times 10^{-5}$ | 26.9 | 11 | T; [2], k↑ pH↑ | 112 |
| trans-Co(Me-en)$_2$Cl$_2^+$ | 0.1 | – | HNO$_3$ | $1.6 \times 10^{-5}$ | 26.5 | 8.4 | S,T | 161 |
| trans-Co(Et-en)$_2$Cl$_2^+$ | 0.1 | – | HNO$_3$ | $9.6 \times 10^{-5}$ | 27.5 | 15.4 | S,T | 161 |
| trans-Co(en)(tn)Cl$_2^+$ | 0.10 | – | HNO$_3$ | $4.3 \times 10^{-4}$ | 25.5 | 11.6 | S | 161 |
| trans-Co(n-Pr-en)$_2$Cl$_2^+$ | 0.10 | – | HNO$_3$ | $1.2 \times 10^{-4}$ | 26.5 | 12.4 | T | 161 |
| trans-Co(pn)$_2$Cl$_2^+$ | 0.10 | – | HNO$_3$ | $6.1 \times 10^{-5}$ | 27.5 | 14.6 | T | 161 |
| trans-Co(pn)$_2$(OH)Cl$^+$ | | 7–8.7 | NaOH | $1.3 \times 10^{-3}$ | – | – | T | 136 |
| trans-Co(d,l-bn)$_2$Cl$_2^+$ | 0.1 | – | HNO$_3$ | $1.5 \times 10^{-4}$ | 25.5 | 9.5 | S,T | 161 |
| trans-Co(m-bn)$_2$Cl$_2^+$ | 0.0025 | – | HNO$_3$ | $4.2 \times 10^{-3}$ | 23.5 | 9.4 | S | 161 |
| trans-Co(i-bn)$_2$Cl$_2^+$ | 0.10 | – | HNO$_3$ | $2.2 \times 10^{-3}$ | 25.5 | 14.8 | S | 161 |
| Co(i-bn)$_2$(cytam)Cl$^{2+}$ | 0.01 | – | HClO$_4$ | $1.2 \times 10^{-4}$ | 23.4 | –0.5 (2.0) | S | 123 |
| cis-Co(phen)$_2$Cl$_2^+$ | – | – | none | $6.8 \times 10^{-5}$ | 23.1 | 0 | T, <Cl$^-$> | 153 |

| Complex | | | Medium | $k$ | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| *trans*-Co(dipy)₂(NO₂)₂⁺ | 2.5 | ≤1 | (Na,H)NO₃ | $1.3\times10^{-7}$ | 23.5 | −11.2 | S; <H⁺> | 169 |
| *trans*-Co(DH)₂Cl₂⁻ | – | – | none | $2.7\times10^{-4}$ | 23.3 | 3.6 | P; <H⁺> | 171 |
| *trans*-Co(DH)₂Br₂⁻ | – | – | none | $3.8\times10^{-4}$ | 23.9 | 6.0 | P; (2T), <H⁺> | 171 |
| *trans*-Co(DH)₂(NCS)₂⁻ | – | – | – | $1.2\times10^{-8}$ | 31.6 | 12.9 | C,G,T; <H⁺> | 173 |
| *trans*-Co(DH)₂(SO₃)Cl²⁻ | – | – | – | $(6.0\times10^{-7})$ | 23.5 | −8.3 | **K**, pH, T | 172 |
| *trans*-Co(DH)₂(SO₃)Br²⁻ | – | – | – | $(8.4\times10^{-7})$ | 21.5 | −14.2 | **K**, pH, T | 172 |
| *trans*-Co(DH)₂(SO₃)I²⁻ | – | – | none | $(9.8\times10^{-7})$ | 19.5 | −20.6 | **K**, pH, T | 172 |
| Co(acac)₂(H₂O)ONO | 0.5 | – | NaClO₄ | $1.4\times10^{-4}$ | 26.2 | 12.5 | S | 175 |
| Co(CpdoxH)(CpdoxH₂)(NO₂)(NO₂H)⁺ | 1.0 | – | (Na,H)(ClO₄,NO₃) | $3.6\times10^{-4}$ | 18.8 | −10.9 | C; colorim. | 345 |
| Co(CpdoxH)(CpdoxH₂)(NO₂)₂ | 1.0 | – | (Na,H)(ClO₄,NO₃) | $1.1\times10^{-6}$ | 25.4 | −0.2 | C; colorim. | 345 |
| Co(dien)(NO₂)₂NCS | – | – | – | $3.1\times10^{-6}$ | 26.9 | 6.5 | – | 174 |
| ε-Co(dien)(en)Cl²⁺ | 0.01 | | HClO₄ | $3.3\times10^{-7}$ | 24.4 | −5 | S | 123 |
| ω-Co(dien)(en)Cl²⁺ | 0.01 | | HClO₄ | $1.9\times10^{-7}$ | 23.4 | −9 | S | 123 |
| ω-Co(dien)(en)Br²⁺ | 0.01 | | HClO₄ | $2.4\times10^{-7}$ | 25.4 | −2 | S | 123 |
| ω-Co(dien)(en)I²⁺ | 0.01 | | HClO₄ | $1.8\times10^{-7}$ | 28.4 | 7 | S | 123 |
| *trans*-Co(dan)Cl₂⁺ | 0.10 | | HNO₃ | $3\times10^{-3}$ | 23.5 | 8.8 | S | 161 |
| *cis*-Co(tren)(H₂O)Cl²⁺ | 1.0 | | HClO₄ | $2.4\times10^{-6}$ | 21.6 | −11 | S,K | 295 |
| *cis*-Co(tren)(H₂O)Br²⁺ | 0.1 | | HClO₄ | $1.6\times10^{-6}$ | – | | S,K | 150 |
| *cis*-Co(tren)F₂⁺ | – | – | none | $9.0\times10^{-6}$ | 22.3 | −6.5 | S; <ClO₄⁻> | 277 |
| *cis*-Co(tren)Cl₂⁺ | 0.1 | | HClO₄ | $3.0\times10^{-3}$ | 17.3 | −10.4 | S,K | 355 |
| *cis*-Co(tren)Br₂⁺ | 0.1 | | HClO₄ | $2.8\times10^{-2}$ | 15.1 | −15.0 | S,K | 150 |
| D,α-*cis*-Co(trien)(H₂O)Cl²⁺ | 0.1 | 1–3 | (Na,H)ClO₄ | $5.2\times10^{-7}$ | 23.5 | −8.4 | S,K,Pₘ⁻ } Retent of *cis* | 147 |
| β-*cis*-Co(trien)(H₂O)Cl²⁺ (slow isomer) | 0.1 | 1–3 | (Na,H)ClO₄ | $2.0\times10^{-6}$ | 26.4 | 3.9 | S,K,Pₘ⁻ } conf. and opt. act. | 147 |
| β-*cis*-Co(trien)(H₂O)Cl²⁺ (fast isomer) | 0.1 | 1–3 | (Na,H)ClO₄ | $8.2\times10^{-5}$ | – | – | S,K,Pₘ⁻ | 147 |
| β-*cis*-Co(trien)(H₂O)Cl²⁺ | 0.01 | | HClO₄ | $2.4\times10^{-6}$ | – | – | S,K | 148 |
| *cis*-Co(trien)(NH₃)Cl²⁺ | – | – | none | $1.7\times10^{-7}$ | 24.9 | −5.8 | T; [3], <ClO₄⁻> | 87 |
| α-*cis*-Co(trien)Cl₂⁺ | 0.01 | | HClO₄ | $1.5\times10^{-4}$ | – | – | S,K | 148 |
| D-α-*cis*-Co(trien)Cl₂⁺ | 0.001–1.0 | | HClO₄ | $1.6\times10^{-4}$ | 20.9 | −5.8 | S,K,Pₘ | 147 |
| *cis*-Co(trien)Cl₂⁺ | 0.1 | | HNO₃ | $1.5\times10^{-4}$ | – | – | S | 130 |
| β-*cis*-Co(trien)Cl₂⁺ | 0.01 | | HClO₄ | $1.5\times10^{-3}$ | – | – | S,K | 148 |
| D-β-*cis*-Co(trien)Cl₂⁺ | 0.002–1 | 0–3 | (Na,H)ClO₄ | $1.5\times10^{-3}$ | 20.5 | 2.7 | S,K,Pₘ | 147 |
| D-α-*cis*-Co(trien)(OH)Cl⁺ | 0.1 | 1–3 | (Na,H)ClO₄ | $3.8\times10^{-3}$ | 18.8 | 6.5 | S,K,Pₘ | 147 |
| *trans*-Co(trien)(H₂O)Cl²⁺ | 0.1 | | HClO₄ | $2.0\times10^{-6}$ | 26.4 | 3.9 | S,K | 147 |
| *trans*-SS-Co(trien)Cl₂⁺ | 0.1 | | HClO₄ | $3.2\times10^{-3}$ | 25.4 | 15.3 | S,K | 147 |
| β-*cis*-(RR,SS)-Co(2,3,2-tet)Cl₂⁺ | 0.005–1 | | HNO₃ | $1.1\times10^{-3}$ | 22.3 | 2 (3) | S; β (RR,SS) conf. presumed | 152 |
| *trans*-R,S-Co(2,3,2-tet)Cl₂⁺ | 0.016 | | HNO₃ | $1.5\times10^{-5}$ | 24.3 | −1 | S; 100% *trans*-R,S prod. | 152 |
| *trans*-RR,SS-Co(2,3,2-tet)Cl₂⁺ | 0.014 | | HClO₄ | $2.9\times10^{-4}$ | 25.9 | 12 | S; 50±20% *trans*-RR,SS prod. | 152 |
| *cis*-Co(cyclam)Cl₂⁺ | 0.51 | 2.0 | {Na(NO₃Cl) / HClO₄} | $1.6\times10^{-2}$ | 18.3 | −5.4 | S; 100% *cis* prod. | 151 |
| *trans*-Co(cyclam)Cl₂⁺ | 0.01 | | HNO₃ | $1.1\times10^{-6}$ | 24.3 | −4.3 | S; 100% *trans* prod. | 168 |
| *trans*-Co(cyclam)(OH)Cl⁺ | 0.10 | 7.0–11.8 | buffers | $1.2\times10^{-2}$ | 18.8 | −4.2 | S; 100% *trans* prod. | 168 |
| *trans*-Co(cyclam)(NC)Cl⁺ | 0.010 | | HNO₃ | $4.8\times10^{-7}$ | 23.5 | −9 | S; 100% *trans* prod. | 252 |
| *trans*-Co(cyclam)(NO₂)Cl⁺ | 0.010 | | HNO₃ | $4.3\times10^{-5}$ | 20.6 | −9 | S; 100% *trans* prod. | 252 |

DATA TABLE I. (Cont.)

| Complex | $\mu(m)$ | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| trans-Co(cyclam)(NO₂)Br⁺ | 0.010 | | HNO₃ | $5.5 \times 10^{-4}$ | (21.0) | $-3$ | S | 348 |
| trans-Co(cyclam)(NCS)Cl⁺ | 0.010 | | HNO₃ | $3.2 \times 10^{-8}$ | 24.2 | $-11$ | S | 346 |
| trans-Co(rac-L′)(H₂O)Cl²⁺ | 0.010 | | HNO₃ | $3.4 \times 10^{-4}$ | 39.5 | $\underline{58}$ | S,T | 360 |
| trans-Co(rac-L′)Cl₂⁺ | 0.010 | | HNO₃ | $4.2 \times 10^{-3}$ | 28.3 | $\underline{25}$ | S,T | 360 |
| trans-Co(L)Cl₂⁺ | 0.010 | | HNO₃ | $9.3 \times 10^{-4}$ | 25.6 | 13 | S,T | 360 |
| α-Co(tetren)Cl²⁺ | 1.0 | | HClO₄ | $4.6 \times 10^{-8}$ | 26.4 | $-5$ | S,T | 124 |
| Co(CN)₅OH₂²⁻ | 1.0 | 6.4 | NaClO₄ | $1.3 \times 10^{-3}$ (40°) | $-$ | $-$ | M | 177 |
| Co(CN)₅I³⁻ | 1.0 | $-$ | NaClO₄ | $6.2 \times 10^{-7}$ | 29.7 | 12.5 | S | 178 |
| Co(CN)₅N₃³⁻ | 1.0 | 6.0–13.0 | Na(ClO₄,OH) | $5.4 \times 10^{-8}$ | 27.3 | $-0.6$ | S; (2T) | 177 |
| Co(CN)₅NCS³⁻ | 1.0 | 13 | Na(ClO₄,OH) | $2.8 \times 10^{-8}$ | 31.1 | 11.5 | S; (2T) | 177 |
| Co(CN)₅OS₂O₂⁴⁻ | 1.0 | 13.7–14.0 | K(NO₃,OH) | $2.6 \times 10^{-8}$ | 21.6 | $-21.1$ | S | 179 |
| Mo(NCS)₆³⁻ | $-$ | $-$ | NCS⁻ | $3.5 \times 10^{-6}$ | 21.3 | $-11.8$ | R | 47 |
| MoCl₆³⁻ | $-$ | 3.2–4.5 | { KH Phthalate / H₂SO₄ or KOH | $1.3 \times 10^{-4}$ (0°) | $-$ | $-$ | S | 354 |
| Ru(NH₃)₅Cl²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $7.1 \times 10^{-7}$ | 22.6 | $-10.8$ | S | 180 |
| Ru(NH₃)₅Br²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $8.7 \times 10^{-7}$ | 22.6 | $-10.5$ | S | 181 |
| Ru(NH₃)₅I²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $2.5 \times 10^{-7}$ | 23.9 | $-8.5$ | S | 181 |
| cis-Ru(NH₃)₄Cl₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $7.8 \times 10^{-6}$ | 21.8 | $-8.8$ | S | 181 |
| cis-Ru(en)₂(H₂O)Cl²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $1.7 \times 10^{-5}$ | 20.1 | $-13.0$ | S | 181 |
| cis-Ru(en)₂(H₂O)Br²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $1.4 \times 10^{-5}$ | 21.8 | $-7.7$ | S | 181 |
| cis-Ru(en)₂(H₂O)I²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $2.7 \times 10^{-5}$ | 24.4 | 2.4 | S | 181 |
| cis-Ru(en)₂Cl₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $3.8 \times 10^{-5}$ | 19.9 | $-12.0$ | S | 181 |
| cis-Ru(en)₂Br₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $3.2 \times 10^{-5}$ | 20.5 | $-10.3$ | S | 181 |
| cis-Ru(en)₂I₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $1.0 \times 10^{-5}$ | 22.1 | $-7.2$ | S | 181 |
| cis-Ru(-pn)₂Cl₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $3.8 \times 10^{-5}$ | 18.2 | $-17.8$ | S | 181 |
| cis-Ru(α-trien)(H₂O)Cl²⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $2.0 \times 10^{-4}$ | $-$ | $-$ | | 181 |
| cis-Ru(α-trien)Cl₂⁺ | 0.1 | | CH₃–⟨O⟩–SO₃H | $5.85 \times 10^{-4}$ | 18.1 | $-12.6$ | S | 181 |
| Ru(H₂O)Cl₅²⁻ | $-$ | $-$ | $-$ | $(3.5 \times 10^{-3})$ | 21.4 | 2 | | q 182 |
| RuCl₆³⁻ | 1.0 | | HCl | $6.7 \times 10^{-2}$ | $-$ | $-$ | R | q 187 |
| RuCl₆³⁻ | 6.0 | | HCl | $\underline{1.8 \times 10^{-3}}$ | $\underline{24.6}$ | $\underline{12}$ | R | 182 |

| Complex | | $\mu$ | Added salt | $k$ | $\frac{27}{33}$ | $\frac{27}{18}$ | | $q$ |
|---|---|---|---|---|---|---|---|---|
| $RuCl_6^{3-}$ | — | — | — | $(8\times10^{-2})$ | | | | 182 |
| $Rh(H_2O)_6^{3+}$ | 12 | ≥0.7 | $(Al/3,H)ClO_4$ | $3.2\times10^{-8}$ | 23.9 | −1 | M | 183 |
| $Rh(NH_3)_5OH_2^{3+}$ | 0.5 | 2.0–1.3 | $(Na,H)ClO_4$ | $1.0\times10^{-5}$ | 24.6 | 0.8 | M | 184 |
| $Rh(NH_3)_5OH_2^{3+}$ | 0.25 | 2 | $HClO_4$ | $8.4\times10^{-6}$ | 26.7 | 5.0 | M; [compl.] = 0.040M | 318 |
| $Rh(NH_3)_5N_3H^{3+}$ | 8.1–9.2 | | $H_2SO_4$ | $2.0\times10^{-6}$ | 20.4 | −21.4 | S | 35 |
| $Rh(NH_3)_5Cl^{2+}$ | 0.01–0.025 | | none | $1.42\times10^{-7}$ | 23.8 | −12.2 | R; <$Cl^-$> | 188 |
| $Rh(NH_3)_5Cl^{2+}$ | 0.1 | | $HClO_4$ | $4.83\times10^{-8}$ | 22.2 | −15.3 | S | 185 |
| $Rh(NH_3)_5Cl^{2+}$ | 0.2 | | $NaClO_4$ | $1.5\times10^{-7}$ | 24.2 | −11.1 | T | 186 |
| $Rh(NH_3)_5Cl^{2+}$ | | | $NH_4Br$ | $3.8\times10^{-8}$ | 23.5 | −13.3 | S | 187 |
| $Rh(NH_3)_5Br^{2+}$ | 0.1 | | none | $4.87\times10^{-8}$ | 24.4 | −9.6 | R; <$Br^-$> | 189 |
| $Rh(NH_3)_5Br^{2+}$ | 0.2 | | $NaClO_4$ | $6.30\times10^{-8}$ | 24.6 | −9.9 | T | 186 |
| $Rh(NH_3)_5Br^{2+}$ | | | $NH_4Cl$ | $3.40\times10^{-8}$ | 25.4 | −10.3 | S | 187 |
| $Rh(NH_3)_5I^{2+}$ | 0.1 | | none | $8.31\times10^{-9}$ | 26.7 | −4.2 | R; <$I^-$> | 188 |
| $Rh(NH_3)_5I^{2+}$ | 0.2 | | $NaClO_4$ | $1.95\times10^{-8}$ | 26.2 | −7.8 | T | 186 |
| $Rh(NH_3)_5I^{2+}$ | | | $NH_4Cl$ | $6.2\times10^{-9}$ | 23.3 | −3 | S | 187 |
| $Rh(NH_3)_5ONO_2^{2+}$ | 1.0 | 2 | $(Na,H)ClO_4$ | $1.2\times10^{-5}$ | 25 | −6 | S | 160 |
| $Rh(NH_3)_5OCOCF_3^{2+}$ | 0.1 | 2–1 | $(Na,H)ClO_4$ | $2.0\times10^{-7}$ | 21.4 | −13.3 | S | 97 |
| $Rh(NH_3)_5OSO_3^{+}$ | 1.0 | 0–2 | $(Na,H)ClO_4$ | $1.6\times10^{-6}$ | 24.1 | −9.2 | S | 102 |
| $trans\text{-}Rh(NH_3)_4Cl_2^{+}$ | 0.05–0.1 | — | $NaBr$ or $NaI$ | $1.3\times10^{-7}$ | 23.8 | −13 | S | 336 |
| $trans\text{-}Rh(en)_2Cl_2^{+}$ | — | — | — | $6.4\times10^{-8}$ | 24.5 | | R | 191 |
| $trans\text{-}Rh(en)_2Cl_2^{+}$ | | | none | — | | | S; 100% *trans* prod.; k insensitive to $\mu$ | 192 |
| $trans\text{-}Rh(en)_2Cl_2^{+}$ | 0.1 | | $NaI$ | $5.4\times10^{-8}$ | 24.7 | −9 | S; 100% *trans* prod.; k insensitive to $\mu$ | 190 |
| $trans\text{-}Rh(en)_2BrCl^{+}$ | 0.20 | | $NaBr$ | $1.7\times10^{-7}$ | 23.2 | −11.7 | S; 100% *trans* prod.; k insensitive to $\mu$ | 190 |
| $trans\text{-}Rh(en)_2ICl^{+}$ | — | — | — | $1.0\times10^{-4}$ | 14.0 | −31.8 | S; 100% *trans* prod.; k insensitive to $\mu$ | 191 |
| $trans\text{-}Rh(en)_2ICl^{+}$ | 0.20 | | $NaI$ | $4.8\times10^{-5}$ | 21.1 | −7.5 | S | 190 |
| $trans\text{-}Rh(en)_2ClBr^{+}$ | 0.20 | | $NaCl$ | $8.3\times10^{-9}$ | 27.6 | −3 | S; 100% *trans* prod.; k insensitive to $\mu$ | 190 |
| $trans\text{-}Rh(en)_2Br_2^{+}$ | — | — | — | $5.6\times10^{-7}$ | 20.0 | −22.0 | S; 100% *trans* prod.; k insensitive to $\mu$ | 191 |
| $trans\text{-}Rh(en)_2Br_2^{+}$ | 0.1–0.5 | | $NaI$ | $1.8\times10^{-7}$ | 25.2 | −5 | S | 190 |
| $trans\text{-}Rh(en)_2IBr^{+}$ | — | | — | $4.6\times10^{-5}$ | 16.1 | −26.3 (−24.3) | S; 100% *trans* prod.; k insensitive to $\mu$ | 191 |
| $trans\text{-}Rh(en)_2IBr^{+}$ | 0.20 | | $NaBr$ | $2.1\times10^{-5}$ | 23.1 | −3 | S | 190 |
| $trans\text{-}Rh(en)_2I_2^{+}$ | — | | — | $3.5\times10^{-6}$ | 26.2 | 4.4 | S; 100% *trans* prod.; k insensitive to $\mu$ | 191 |
| $trans\text{-}Rh(en)_2I_2^{+}$ | 0.20 | | $NaCl$ or $NaBr$ or $NaCN$ | $4.3\times10^{-6}$ | 25.1 | 1 | S | 190 |
| $Rh(DH)_2(SO_3H)Br^{+}$ | 0.05 | | $HNO_3$ | $1.2\times10^{-5}$ | 13.7 | −35.1 | T | 349 |
| $Rh(DH)_2(SO_3H)I^{+}$ | 0.05 | | $HNO_3$ | $3.0\times10^{-5}$ | 12.2 | −38.3 | T | 349 |
| $Rh(H_2O)Cl_5^{2-}$ | 4.0 | | $H(ClO_4,Cl)$ | $3.9\times10^{-5}$ | 25.2 | 5.8 | S | 193 |
| $RhCl_6^{3-}$ | 4.0 | | $H(ClO_4,Cl)$ | $1.8\times10^{-3}$ | 24.5 | 11.1 | S | 194 |
| $Ir(NH_3)_5OH_2^{3+}$ | 0.96 | 0.3–2.0 | $(Na,H)ClO_4$ | $6.5\times10^{-8}$ | 28.2 | 3.0 | M | 195 |
| $Ir(NH_3)_5Cl^{2+}$ | | | none | $1.1\times10^{-9}$ | 22.4 | −24.3 | R; <$Cl^-$> | 188 |
| $Ir(NH_3)_5Br^{2+}$ | | | none | $1.1\times10^{-9}$ | 22.5 | −24.1 | R; <$Br^-$> | 192 |

DATA TABLE I. (Cont.)

| Complex | $\mu$(m) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comment | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| Ir(NH$_3$)$_5$I$^{2+}$ | | | none | $1.9 \times 10^{-10}$ | 25.6 | $-17.3$ | R; $<$I$^-$$>$ | 188 |
| Ir(NH$_3$)$_5$ONO$_2{}^{2+}$ | 1.0 | 2 | (Na,H)ClO$_4$ | $6.9 \times 10^{-8}$ | 26.1 | $- 4$ | S | 160 |
| Ir(NH$_3$)$_5$OCOCF$_3{}^{2+}$ | 0.1 | 1–2 | (Na,H)ClO$_4$ | $5.1 \times 10^{-9}$ | 24 | $-16$ | S | 97 |
| trans-Ir(en)$_2$Cl$_2{}^+$ | 0.5 | | Na(ClO$_4$,X) | $1.4 \times 10^{-10}$ | 29.2 | $- 6$ | S,T; X$^-$ = I$^-$, N$_3{}^-$, Br$^-$ | 196 |
| trans-Ir(en)$_2$BrCl$^+$ | 0.5 | | Na(ClO$_4$,Br) | $4.4 \times 10^{-10}$ | 27.1 | $- 9$ ($-10.4$) | S,T | 196 |
| trans-Ir(en)$_2$ICl$^+$ | 0.5 | | Na(ClO$_4$,X) | $1.5 \times 10^{-8}$ | 25.3 | $- 4$ ($-9.4$) | S,T; X$^-$ = I$^-$, Br$^-$ | 196 |
| trans-Ir(en)$_2$Br$_2{}^+$ | 0.5 | | Na(ClO$_4$,X) | $8.5 \times 10^{-10}$ | 27.2 | $- 9$ | S,T; X$^-$ = I$^-$, N$_3{}^-$ | 196 |
| trans-Ir(en)$_2$IBr$^+$ | 0.5 | | Na(ClO$_4$,X) | $6.3 \times 10^{-9}$ | 27.1 | $- 5$ | S,T; X$^-$ = I$^-$, Cl$^-$ | 196 |
| trans-Ir(en)$_2$I$_2{}^+$ | 0.5 | | Na(ClO$_4$,X) | $2.0 \times 10^{-9}$ | 28.7 | $- 3$ ($-2.1$) | S,T; X$^-$ = Cl$^-$, Br$^-$ | 196 |
| Ir(H$_2$O)$_3$Cl$_3$ | – | ~3 | H$_2$SO$_4$ | $(4.7 \times 10^{-9})$ | 28.9 | 0.3 | R | 197 |
| Ir(H$_2$O)$_3$Br$_3$ | – | ~3 | H$_2$SO$_4$ | $(7.3 \times 10^{-11})$ | 33.0 | 5.8 | R | 197 |
| trans-Ir(H$_2$O)$_2$Cl$_4{}^-$ | 3.8 | $\leqq$0 | (Na,H)ClO$_4$ | $8 \times 10^{-9}$ | 29.9 | 4.7 | S | 198 |
| Ir(H$_2$O)$_2$Cl$_4{}^-$ | – | ~3 | H$_2$SO$_4$ | $(1.4 \times 10^{-8})$ | 30.1 | 6.5 | R | 197 |
| Ir(H$_2$O)$_2$Br$_4{}^-$ | – | ~3 | H$_2$SO$_4$ | $(6.1 \times 10^{-8})$ | 28.8 | 5.1 | R | 197 |
| Ir(H$_2$O)Cl$_5{}^{2-}$ | 3.75 | <0 | (Na,H)ClO$_4$ | $2.9 \times 10^{-7}$ | 28.8 | 8.2 | S,T | 199 |
| Ir(H$_2$O)Cl$_5{}^{2-}$ | – | ~3 | H$_2$SO$_4$ | $(2.5 \times 10^{-7})$ | 28.8 | 7.9 | R | 197 |
| IrCl$_6{}^{3-}$ | – | ~3 | H$_2$SO$_4$ | $(4.0 \times 10^{-5})$ | 24.9 | 4.9 | R | 197 |
| IrCl$_6{}^{3-}$ | 1.0 | | HClO$_4$ | $2.5 \times 10^{-5}$ | 27.4 | 12.3 | R | 200 |
| IrCl$_6{}^{3-}$ | 2.2 | 0 | (Na,H)ClO$_4$ | $1.0 \times 10^{-5}$ | 29.8 | 18.6 | S | 201 |

DATA TABLE II. Solvolysis (non-aqueous solvents).

| Complex | $\mu$(M) | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| V(DMSO)$_5$(SSA)$^{3+}$ | – | – | DMSO | $1.7 \times 10^{-3}$ | – | – | S. | 202 |
| V(DMSO)$_5$(NCS)$^{2+}$ | 0.15 | – | DMSO NaClO$_4$ | 1.5 | – | – | S$_{SF}$ | 202 |

| Complex | | Solvent | Rate | | | Method | Ref |
|---|---|---|---|---|---|---|---|
| V(DMSO)4(dipy)3+ | — | DMSO | $3.6 \times 10^{-3}$ | — | — | S | 202 |
| Cr(NH3)6^3+ | — | liq NH3 | $4.1 \times 10^{-6}$ | 32 | 24.2 | nmr | 203 |
| cis-Cr(ox)2(OH2)2^- | — | DMSO | $2.0 \times 10^{-4}$ | 28.5 | 20.2 | S | 68 |
| cis-Cr(ox)2(DMSO)(OH2)^- | — | DMSO | $6.5 \times 10^{-5}$ | 29.7 | 21.9 | S | 68 |
| Cr(NH3)2(NCS)4^- | — | MeOH | $1.6 \times 10^{-6}$ | 27.7 | 7.9 | C0 | 71 |
| Cr(NH3)2(NCS)4^- | — | MeOH:MeNO2 1:1(v) | $2.1 \times 10^{-7}$ | 30.4 | 12.9 | C0 | 71 |
| Cr(NCS)6^3- | 0.1 | MeOH NaClO4 | $(1.8 \times 10^{-5})$ | 26.4 | 8.3 | S | 204 |
| cis-Cr(en)2Br2^+ | — | DMSO | $(2.7 \times 10^{-5})$ | 21 | − 9 | S | 366 |
| cis-Cr(en)2(DMSO)Br2^+ | — | DMSO | $(1.0 \times 10^{-4})$ | 19 | −13 | S | 366 |
| trans-Cr(en)2Br2^+ | — | DMSO | $(3.7 \times 10^{-5})$ | 22 | − 5 | S | 366 |
| cis-Co(en)2Cl2^+ | — | DMF | $2.8 \times 10^{-5}$ | *18.2* | *−18.3* | S | 207 |
| cis-Co(en)2ClBr^+ | — | DMF | $2.1 \times 10^{-5}$ | 19.6 | −14.2 | S | 207 |
| cis-Co(en)2Cl(DMF)^2+ | ~0 | DMSO | $1.2 \times 10^{-5}$ | 24.0 | + 0.6 | nmr | 205 |
| cis-Co(en)2Cl(DMF)^2+ | ~0 | DMA | $6.0 \times 10^{-6}$ | 26.8 | 12(7.5) | S | 205 |
| cis-Co(en)2Cl(DMSO)^2+ | ~0 | DMA | $9.6 \times 10^{-6}$ | 25.9 | 9.9(5.4) | S | 205 |
| cis-Co(en)2Cl(DMSO-d6)^2+ | — | DMF | $1.2 \times 10^{-5}$ | 24.0 | 0.6 | nmr | 206 |
| cis-Co(en)2Cl(DMA)^2+ | ~0 | DMSO | $1.4 \times 10^{-3}$ | 21.7 | 1.3 | S; 16.6% *trans* prod | 205 |
| cis-Co(en)2Cl(DMA)^2+ | ~0 | DMF | $1.9 \times 10^{-3}$ | 30.0 | 29.5 | S; 16.6% *trans* prod | 205 |
| cis-Co(tren)Br2^+ | — | FA | $2.7 \times 10^{-2}$ | 10.1 | −31.8 | S; K; k ↑D↑ | 208 |
| cis-Co(tren)Br2^+ | — | DMSO | $7.7 \times 10^{-4}$ | 17.9 | −12.7 | S; K; k ↑D↑ | 208 |
| cis-Co(tren)Br2^+ | — | DMF | $4.3 \times 10^{-4}$ | 22.1 | 0.2 | S; K; k ↑D↑ | 208 |
| cis-Co(tren)Br2^+ | — | NMF | $2.5 \times 10^{-1}$ | — | — | S; K; k ↑D↑ | 208 |
| trans-Co(en)2Cl2^+ | — | DMF | $8.5 \times 10^{-7}$ | 21.2 | −15.2 | S | 207 |
| trans-Co(en)2Cl2^+ | 0.1 | DMF KNCS | $1.6 \times 10^{-6}$ | 23.5 | − 6.3 | S | 167 |
| trans-Co(en)2(Cl)(OH2)^2+ | ~0 | DMSO | $2.7 \times 10^{-4}$ | 26.3 | 13.4 | S; 16.6% *trans* prod | 205 |
| trans-Co(en)2(Cl)(OH2)^2+ | ~0 | DMF | $1.1 \times 10^{-4}$ | 23.2 | 1.2 | S | 205 |
| trans-Co(en)2(Cl)DMF^2+ | ~0 | DMF | $1.4 \times 10^{-4}$ | 23.6 | 3.0 | nmr | 205 |
| trans-Co(en)2(NO2)Cl^+ | — | FA | $4.1 \times 10^{-5}$ | 22.3 | − 3.8 | S | 209 |
| trans-Co(en)2(NO2)Cl^+ | 0–1.5 | TMS KCNS | $8.0 \times 10^{-4}$ | 21.5 | − 0.6 | S; prod. is Co(en)2(NO2)NCS^+ | 209 |
| trans-Co(en)2(NO2)Cl^+ | 0.1 | DMF KNCS | $1.5 \times 10^{-5}$ | 22.9 | − 3.8 | S | 167 |
| trans-Co(en)2(NO2)Br^+ | 0.1 | DMF KNCS | $2.8 \times 10^{-4}$ | 19.9 | − 8.0 | S | 167 |
| trans-Co(en)2(OCOC6H5)2^+ | — | CH3COOH | $1.2 \times 10^{-4}$ (84.5°) | — | — | S | 364 |
| trans-Co(en)2(OCOC6H4-2-CH3)2 | — | CH3COOH | $4.6 \times 10^{-4}$ (84.5°) | — | — | S | 364 |
| trans-Co(en)2(OCOC6H4-3-CH3)2 | — | CH3COOH | $2.3 \times 10^{-4}$ (84.5°) | — | — | S | 364 |
| trans-Co(en)2(OCOC6H4-4-CH3)2 | — | CH3COOH | $2.6 \times 10^{-4}$ (84.5°) | — | — | S | 364 |

TABLE VI. Activation Parameters for Aquation of Isomeric Complexes of Type $Co(en)_2AX^{n+}$ [a, b, c, d]

| A | X | cis | | trans | | | |
|---|---|---|---|---|---|---|---|
| | | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\delta\Delta H^{\ddagger}$ | $\delta\Delta S^{\ddagger}$ |
| Cl | Cl | 21.6 | − 4.0 | 27.5 | 13.1 | +5.9 | +17.1 |
| Br | Cl | 22.5 | − 0.7 | 24.6 | 4.1 | +2.1 | + 4.8 |
| OH | Cl | 22.5 | 7.9 | 25.6 | 14.6 | +3.1 | + 6.7 |
| $N_3$ | Cl | 21.1 | − 4.3 | 23.1 | 2.2 | +2.0 | + 6.5 |
| NCS | Cl | 20.2 | −13.5 | 29.8 | 7.8 | +9.6 | +21.3 |
| $NO_2$ | Cl | 21.8 | − 3.4 | 20.9 | −2.2 | −0.9 | + 1.2 |
| $NH_3$ | Cl | 24.9 | − 4.3 | 23 | −11 | −1.9 | − 6.7 |
| Cl | Br | 23.3 | 4.8 | 26.0 | 10.6 | −2.7 | + 5.8 |
| Br | Br | 23.2 | 5.6 | 25.5 | 9.4 | +2.3 | + 3.8 |
| OH | Br | 22.7 | 12.1 | 24.4 | 14.1 | +1.7 | + 2.0 |
| NCS | Br | 22.5 | − 4.3 | 29.5 | 10 | +7.0 | +14.4 |
| $NH_3$ | Br | 22.5 | − 9.6 | 24 | −5.1 | +1.5 | + 4.5 |

[a] The reaction is $Co(en)_2AZ^{n+} + H_2O \rightarrow Co(en)_2AH_2O^{n+1} + X^-$.

[b] The quantity $\delta\Delta H^{\ddagger}$ is defined as $\Delta H^{\ddagger}$ (*trans*) less $\Delta H^{\ddagger}$ (*cis*); $\delta\Delta S^{\ddagger}$ is defined similarly.

[c] Units of $\Delta H^{\ddagger}$ are kcal $mol^{-1}$, and of $\Delta S^{\ddagger}$ are cal $mol^{-1}$ $deg^{-1}$.

[d] Data taken from Data Table References 52, 131, 136, 138, 139, 141, 87, 143, 109, 121, 128, 161 and 165.

sibility of a *trans*-effect in octahedral systems. In practice, this is not easy. For example, in the isomeric systems *cis* and *trans* $Co(en)_2AX^{n+}$ where A is a monodentate, non-leaving ligand and $X^-$ is the leaving group, one is not simply looking at the *trans*-effect of A. Rather, one is comparing the effect of A with that effect due to one end of an ethylenediamine ligand. Some data are given in Table VI. It is clear that the values of $\Delta S^{\ddagger}$ for the *trans* complexes are generally more positive than those for *cis* complexes; a similar trend is seen in the values of $\Delta H^{\ddagger}$. The values of $\delta\Delta H^{\ddagger}$ decrease for ligand A in the order

$$NCS^- > Cl^- > OH^- > Br^- \simeq N_3^- > NO_2^- > NH_3$$

and those for $\delta\Delta S^{\ddagger}$ in the order

$$NCS^- > Cl^- > OH^- \simeq N_3^- > Br^- > NO_2^- > NH_3$$

Our knowledge of the *trans*-effect in octahedral systems is limited, and it seems possible that the magnitude of the *trans*-effect will depend on the nature of the leaving group. Roughly, however, what we see in the above orders is that the values of the δ are in opposite order to those of the *trans*-effect, *at least for the anions*. For the anions, Poë and Vuik[22a] report the order

$$Cl^- \simeq OH^- < Br^- < I^-$$

and it has been suggested[22b] that $I^- \simeq NO_2^-$ for the *trans*-effect. Making the assumption that $NH_3$ and one end of ethylenediamine have about the same *trans*-effect, we may conclude that the *trans*-effect decreases the value of $\Delta H^{\ddagger}$ (still considering anionic ligands) while lowering the value of $\Delta S^{\ddagger}$. This is explicable if

the *trans*-effect moves the mechanism toward a more associative nature; however, neither the assumption nor the conclusion can be considered definite, particularly in view of the anomalous position of ammonia (which is a neutral ligand rather than anionic). Experiments relevant to these points would be welcomed.

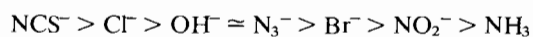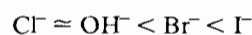It should be stressed here that, as suggested by Poë, the observed kinetic *trans*-effect should be corrected for the thermodynamic *trans*-effect and this correction might change somewhat the sequence. Also the recent review of Byrd and Wilmarth[23d] makes a strong case for a D mechanism for octahedra having a strong *trans*-effect ligand.

The problem of the octahedral *trans*-effect is important, and we list here references bearing on this question that we have found during the course of our literature survey.[22, 23]

## 6. Solvolysis

Data on formation rates of solvo-complexes (other than aquo, of course) are given in Data Table II. One sees immediately that the amount of data in non-aqueous solvent systems is very much less than in water, and further that the variety of systems studied is such that generalization is almost impossible. The activation parameters cover a wide range, and the values of $\Delta S^{\ddagger}$ are seen to be both positive and negative. Whether this is due to experimental uncertainties or to variable nature of the complex-solvent interaction is not known.

## 7. Acid-catalyzed Aquation

The cleavage of a metal–ligand bond can be facilitated by protonation of the leaving group. Using Co $(en)_2F_2^+$ as the substrate example, the postulated mechanism is

$$Co(en)_2F_2^+ + H^+ \rightleftarrows Co(en)_2F(FH)^{2+} \quad \text{(fast)}$$

$$Co(en)_2F(FH)^{2+} + H_2O \rightarrow$$
$$Co(en)_2F(H_2O)^{2+} + HF \quad \text{(rate)}$$

with the rate-determining step involving the cleavage of the Co–FH bond. The rate has been found to be faster in $D_2O$ than in $H_2O$. Since $D_3O^+$ in $D_2O$ is a stronger acid than $H_3O^+$ in $H_2O$, the isotope experiment indicates that proton transfer occurs in a rapid equilibrium prior to the rate step. Acid catalysis is observed when the leaving ligand is basic towards protons; some such ligands are $N_3^-$, $CN^-$, $F^-$, $NO_2^-$, $SO_4^{2-}$, $HPO_4^{2-}$, $SO_3^{2-}$, $ox^{2-}$, $mal^{2-}$, $CO_3^{2-}$ and various acetates. This much seems certain, but the extent of participation by water in this step is not known.

Comparison of the activation parameters in Data Table III with those for the analogous complexes in Data Table I (aquation reactions) shows no consistent difference. We expected that the acid-catalyzed path would be related to the aquation path in some non-complicated way. For instance, were the mechanism essentially dissociative in both cases, the $\delta \Delta S^{\ddagger}$ values would be expected to be near the difference between the protonated ligand and the ligand itself in water solution. Unfortunately although in some instances this situation seems to occur, the lack of entropy data for many leaving groups prevents a complete analysis.

Some data which compare rates and activation parameters for acid-catalyzed and normal aquations are present in Table VII. Not even the ratio $k_h/k_a$

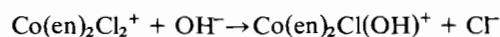which ranges from $3.1 \times 10^{-2}$ to $1.3 \times 10^3$ shows a distinct trend. Since $\delta \Delta G^{\ddagger}$ varies by seven kcal mol⁻¹, we should see some changes in the enthalpy and entropy of activation terms. However no clear trend is observed, and any trend must be covered by other factors. It is, therefore, interesting to see the ubiquitous $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ compensation effect showing up in the values. A plot of $\delta \Delta H^{\ddagger}$ values against $\delta \Delta S^{\ddagger}$ values forms a rough straight line with slope of $340°K$ which is uncomfortably close to the $25°C$ ($298°K$) of the data.

## 8. Base Hydrolysis

The dispute over the mechanism for the rapid base hydrolysis such as for example

$$Co(en)_2Cl_2^+ + OH^- \rightarrow Co(en)_2Cl(OH)^+ + Cl^-$$

centered about the mode of action for hydroxide ion. The rate law is first-order in base. A direct displacement such as obtains for base hydrolysis in many organic compounds was favored by some research groups. The alternative mechanism invoked the unimolecular heterolytic scission of the conjugate base of the complex. Now, there is quite general agreement that this conjugate base mechanism is the preferred one.

We believe, however, that this is a particularly clear example of a reaction whose progress exhibited activation parameters giving a definitive clue as to the actual mechanism, and for the purpose of demonstrating the importance of these parameters, we shall discuss some of the arguments here. Some recent reviews concerning this mechanism are available;[1,3,4,10,14,24] details of

TABLE VII. Comparison of Activation Parameters for Acid-Catalyzed and Normal Aquations.[a]

| Complex | $k_h$ | $k_a$ | $k_h/k_a$ | $\Delta H^{\ddagger}_h$ | $\Delta H^{\ddagger}_a$ | $\delta \Delta H^{\ddagger}$ | $\Delta S^{\ddagger}_h$ | $\Delta S^{\ddagger}_a$ | $\delta \Delta S^{\ddagger}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Fe(H_2O)_5N_3^{2+}$ | 5.1 | 20. | 0.26 | 19.6 | 14.7 | 4.9 | 10.5 | − 3.2 | 13.7 |
| $Cr(H_2O)_5F^{2+}$ | $1.4 \times 10^{-8}$ | $6.2 \times 10^{-10}$ | 23 | 24.5 | 28.7 | − 4.2 | −12.4 | − 4.4 | − 8.0 |
| $Cr(H_2O)_5CN^{2+}$ | $5.2 \times 10^{-4}$ | $1.2 \times 10^{-5}$ | 43 | 17.0 | 27.9 | −10.9 | −16.4 | +12.7 | −29.1 |
| $Cr(H_2O)_5N_3^{2+}$ | $2.3 \times 10^{-7}$ | $4.1 \times 10^{-8}$ | 21 | 23.2 | 32.4 | − 9.2 | − 8.3 | +16.4 | −24.7 |
| $Cr(H_2O)_5SO_4^{+}$ | $2.3 \times 10^{-8}$ | $7.5 \times 10^{-7}$ | 0.031 | 26.5 | 21.9 | + 4.6 | − 1.3 | − 1.3 | +11.7 |
| $Co(NH_3)_5F^{2+}$ | $1.1 \times 10^{-4}$ | $8.7 \times 10^{-8}$ | $1.3 \times 10^3$ | 29.6 | 20.7 | 8.9 | 22.6 | −21.4 | 44.0 |
| $Co(NH_3)_5NO_2^{2+}$ | $2.6 \times 10^{-6}$ | $8.2 \times 10^{-8}$ | 32 | 18.4 | 23.9 | − 5.5 | −22.7 | −11.1 | −11.6 |
| $Co(NH_3)_5OCOCH_3^{2+}$ | $3.2 \times 10^{-6}$ | $2.7 \times 10^{-8}$ | $1.2 \times 10^2$ | 25 | 25 | 0 | 2 | − 8 | +10 |
| $Co(NH_3)_5OxH^{2+}$ | $2.0 \times 10^{-7}$ | $2.2 \times 10^{-8}$ | 9.1 | 22.7 | 28.4 | − 5.7 | −14 | + 1 | −15 |
| $Co(NH_3)_5SO_4^{+}$ | $9.5 \times 10^{-7}$ | $8.9 \times 10^{-7}$ | 1.1 | 28.4 | 22.7 | 5.7 | 9.2 | −10 | +19.2 |
| $Rh(NH_3)_5SO_4^{+}$ | $1.1 \times 10^{-6}$ | $1.6 \times 10^{-6}$ | 0.69 | 28.5 | 21.4 | 7.1 | 9.9 | −13.3 | +23.2 |

[a] The following are the definitions for symbols in the table: $k_h$ = rate for acid-catalyzed aquation; $k_a$ = rate for normal aquation; $\Delta H^{\ddagger}_h$ = enthalpy of activation for acid-catalyzed aquation; $\Delta H^{\ddagger}_a$ = enthalpy of activation for normal aquation; $\delta \Delta H^{\ddagger}$ = difference in activation enthalpies $(\Delta H^{\ddagger}_h - \Delta H^{\ddagger}_a)$; $\Delta S^{\ddagger}_h$ = entropy of activation for acid-catalyzed aquation; $\Delta S^{\ddagger}_a$ = entropy of activation for normal aquation; and $\delta \Delta S^{\ddagger}$ = difference in activation entropies $(\Delta S^{\ddagger}_h - \Delta S^{\ddagger}_a)$.
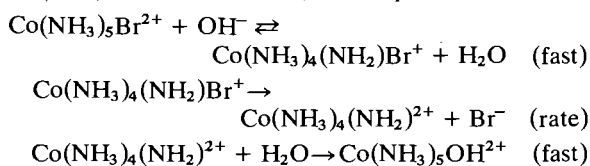
DATA TABLE III. Acid-Catalyzed Aquation.

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| $Fe(H_2O)_5N_3^{2+}$ | 1.0 | <0.3 | $(Li,H)ClO_4$ | 5.1 | 19.6 | 10.5 | $S_{SF}$ | 75 |
| $Fe(H_2O)_5SO_3^+$ | 1.0 | 0.3–1.7 | $(Na,H)ClO_4$ | 3.7 | 10.4 | −21 | $S_{SF}$; probably S-bonded | 280 |
| $Cr(H_2O)_5F^{2+}$ | 1.0 | 0–1.15 | $(Li,H)ClO_4$ | $1.4 \times 10^{-8}$ | 24.5 | −12.4 | S | 9 |
| $Cr(H_2O)_5CN^{2+}$ | 1.0 | 0–3.1 | $(Li,H)ClO_4$ | $5.2 \times 10^{-4}$ | 17.0 | −16.4 | S | 14 |
| $Cr(H_2O)_5N_3^{2+}$ | 1.0 | 0.6–3.15 | $(Na,H)ClO_4$ | $2.3 \times 10^{-7}$ | 23.2 | −8.3 | S | 15 |
| $Cr(H_2O)_5ONO^{2+}$ | 1.0 | 0–2 | $(Na,H)ClO_4$ | $3.2 \times 10^{-1}$ | 19.8 | 9(5.6) | $S_{SF}$ | 210 |
| $Cr(H_2O)_5OPO_2H_2^{2+}$ | 1.0 | 0–1.1 | $(Li,H)ClO_4$ | $1.7 \times 10^{-6}$ | 18.1 | −24.2 | S | 211 |
| $Cr(H_2O)_5OSO_3^+$ | 1.0 | 0–1.3 | $(Li,H)ClO_4$ | $2.3 \times 10^{-8}$ | 26.5 | −1.3 | S | 24 |
| $cis\text{-}Cr(H_2O)_4(CN)_2^+$ | 2.0 | – | $(Na,H)ClO_4$ | $8.3 \times 10^{-4}$ | 19.9 | −5.9 | S | 212 |
| $Cr(NH_3)_5F^{2+}$ | 1.0 | 0 | $HClO_4$ | $1.5 \times 10^{-7}$ | 28 | 4 | S | 37 |
| $Cr(NH_3)_5(ONO)^{2+}$ | 1.0 | – | $HClO_4$ | $5.1 \times 10^{-2}$ | 11.9 | −24.8 | S | 213 |
| $Cr(NH_3)_5(OCOCCl_3)^{2+}$ | 0.13 | 1–2 | $KNO_3$ | $2 \times 10^{-3}$ | 21.6 | 1.6 | S | 320 |
| $cis\text{-}Cr(en)_2F_2^+$ | 0.01–0.15 | 0.8–2 | $HClO_4$ | $5.3 \times 10^{-5}$ | 23 | 0.9 | T | 214 |
| $cis\text{-}Cr(en)_2F(ONO)^+$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $1.6 \times 10^{-2}$ | 20.9 | 3.4 | S; 100% cis product | 278 |
| $cis\text{-}Cr(en)_2(H_2O)(ONO)^{2+}$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $1.3 \times 10^{-1}$ | 20.1 | +4.9 | S; 100% cis product | 278 |
| $cis\text{-}Cr(en)_2(ONO)_2^+$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $5.0 \times 10^{-1}$ | 22 | 18 | S; 100% cis product | 278 |
| $trans\text{-}Cr(en)_2Cl(ONO)^+$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $2.8 \times 10^{-2}$ | 21.0 | 4.9 | S; 100% trans product | 278 |
| $trans\text{-}Cr(en)_2Br(ONO)^+$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $3.6 \times 10^{-2}$ | 20.3 | 3.0 | S; 100% trans product | 278 |
| $trans\text{-}Cr(en)_2(H_2O)(ONO)^{2+}$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $9.6 \times 10^{-2}$ | 19.8 | 3.2 | S; 100% trans product | q 278 |
| $trans\text{-}Cr(en)_2(ONO)_2^+$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $6.5 \times 10^{-2}$ | 24.3 | 17.6 | S; 100% trans product | 278 |
| $trans\text{-}Cr(en)_2(DMSO)(ONO)^{2+}$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $8.0 \times 10^{-2}$ | – | – | S; 100% trans product | 278 |
| $trans\text{-}Cr(en)_2(DMF)(ONO)^{2+}$ | 0.15 | ≥0.82 | $(Na,H)ClO_4$ | $7.6 \times 10^{-2}$ | 20.1 | 3.8 | S; 100% trans product | 278 |
| $Cr(mal)_3^{3-}$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $3.6 \times 10^{-4}$ | 23.4 | 4.2 | S; one $mal^{2-}$ is lost | 217 |
| $Cr(Me\text{-}mal)_3^{3-}$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $5.9 \times 10^{-4}$ | – | – | S; the product is $trans\text{-}Cr(me\text{-}mal)_2(OH_2)_2^-$ | 305 |
| $cis\text{-}Cr(H_2O)_2(ox)_2^-$ | 2.0 | 2–3 | $(Na,H)ClO_4$ | $2.3 \times 10^{-6}$ | 23.9 | −4.5 | S; one $ox^{2-}$ is lost | 215 |
| $cis\text{-}Cr(H_2O)_2(mal)_2^-$ | 2.0 | 0.3–1 | $(Na,H)ClO_4$ | $2.3 \times 10^{-3}$ | – | – | S; one $mal^{2-}$ is lost | 216 |
| $cis\text{-}Cr(H_2O)_2(mal)_2^-$ | – | – | – | $6.5 \times 10^{-5}$ | 21.8 | −4.7 | S | 157 |
| $trans\text{-}Cr(H_2O)_2(mal)_2^-$ | 1.0 | 0 | $HClO_4$ | $1.1 \times 10^{-5}$ | 24.3 | 0.4 | S | 157 |
| $Co(NH_3)_5F^{2+}$ | 0.112 | 1–1.7 | $(K,H)NO_3$ | $1.1 \times 10^{-4}$ | 29.6 | 22.6 | T | 83 |
| $Co(NH_3)_5(NO_2)^{2+}$ | →0 | – | $HClO_4$ | $4.0 \times 10^{-9}$ | 38.2 | 31.2 | S | 92 |
| $Co(NH_3)_5(NO_2)^{2+}$ | 1.0 | – | $(K,H)NO_3$ and urea | $2.6 \times 10^{-6}$ | 18.4 | −22.7 | S | 93 |
| $Co(NH_3)_5(OCOCH_3)^{2+}$ | 0.1 | 1–2 | $(Na,H)ClO_4$ | $3.2 \times 10^{-6}$ | 25 | 2 | S | 97 |
| $Co(NH_3)_5(OCOC(CH_3)_3)^{2+}$ | 0.1 | 1–2 | $(Na,H)ClO_4$ | $6.2 \times 10^{-7}$ | 26 | 6(3) | S | 97 |
| $Co(NH_3)_5(OCOCH_2NH_3)^{3+}$ | 0.1 | 0.3–2 | $(Na,H)ClO_4$ | $5.9 \times 10^{-9}$ | 29 | 1 | S; when $\mu = 1.0$, $\Delta H^{\neq} = 22$, $\Delta S^{\neq} = -20$ | 82 |
| $Co(NH_3)_5(oxH)^{2+}$ | 1.0 | 7.0 | – | $2.0 \times 10^{-7}$ | 22.7 | −14 | S | 96 |
| $Co(NH_3)_5(OSO_3)^+$ | 1.0 | 0–2.3 | $(Na,H)ClO_4$ | $9.5 \times 10^{-7}$ | 28.4 | 9.2 | S | 102 |
| $cis\text{-}Co(en)_2(NO_2)_2^+$ | 3.5 | <0 | $(Na,H)ClO_4$ | $1.4 \times 10^{-5}$ | 25.0 | 3.1 | S | 218 |
| $cis\text{-}Co(en)_2(N_3)_2^+$ | – | – | – | $2.4 \times 10^{-4}$ | 26.1 | 12.5 | S | 218 |

the experimental results plus other references are summarized in these articles.

Let us first consider the direct displacement mechanism. The mechanism requires both particles in the transition state with a fair degree of reagent orientation. It is expected from known entropies of activation for associative processes that a value of about $-15$ cal mol$^{-1}$ deg$^{-1}$ for $\Delta S^{\ddagger}$ would be found.[25]

The alternative mechanism, designated $S_N1CB$ (for substitution, nucleophilic, unimolecular, conjugate base), is postulated to be made up of three steps. With $Co(NH_3)_5Br^{2+}$ as substrate, the steps are as follows:

$$Co(NH_3)_5Br^{2+} + OH^- \rightleftharpoons$$
$$Co(NH_3)_4(NH_2)Br^+ + H_2O \quad \text{(fast)}$$
$$Co(NH_3)_4(NH_2)Br^+ \rightarrow$$
$$Co(NH_3)_4(NH_2)^{2+} + Br^- \quad \text{(rate)}$$
$$Co(NH_3)_4(NH_2)^{2+} + H_2O \rightarrow Co(NH_3)_5OH^{2+} \quad \text{(fast)}$$

The first step is a rapid equilibrium (somewhat akin to neutralization of a weak acid). The second step is rate-determining, and it is the unimolecular scission of the intermediate formed in the first step.

A positive $\Delta S^{\ddagger}$ value is predicted for the $S_N1CB$ mechanism. The first step

$$NH-M-X^{n+} + OH^- \rightleftharpoons H_2O + N-M-X^{(n-1)+}$$
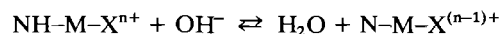
is closely similar to known "neutralization" reactions in the literature; some of these are given in Table VIII along with the estimated values of $\Delta S^{\circ}_{neu}$. These are positive and large because of the considerable charge neutralization. The second step, which involves some charge separation concurrent with formation of two particles from one, is expected to have a $\Delta S^{\ddagger}_2$ near to zero as is the case for aquation of $Co(NH_3)_5X^{2+}$ where $X^-$ is a large leaving group. Using the two values $\Delta S^{\circ}_{neu} = 34$ (average value from Table VIII) and $\Delta S^{\ddagger}_2 \cong 0$, we obtain for $\Delta S^{\ddagger}$ an estimated value of $+34$ cal mol$^{-1}$ deg$^{-1}$.

The bulk of the experimental values for $\Delta S^{\ddagger}$ in Data Table IV lie between $+20$ and $+40$, and there is

| Complex | $\mu$ | range | Medium | $k$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Notes | Ref |
|---|---|---|---|---|---|---|---|---|
| *cis*-Co(en)₂(OCOH)₂⁺ | 0.1 | 1-4 | (Na,H)ClO₄ | $4.4 \times 10^{-3}$ | 13 | $-27$ | S | 359 |
| *cis*-Co(en)₂(OCOCH₃)₂⁺ | 0.1 | 1-4 | (Na,H)ClO₄ | $1.2 \times 10^{-1}$ | — | — | — | 359 |
| *cis*-Co(en)₂(OCOCH₂C(CH₃)₃)₂⁺ | 0.1 | 1-4 | (Na,H)ClO₄ | $9.6 \times 10^{-2}$ | 17 | 7 | S | 359 |
| *cis*-Co(en)₂(OCOC₆H₅)₂⁺ | 0.1 | 1-4 | (Na,H)ClO₄ | $2.5 \times 10^{-3}$ | 13 | $-24$ | S | 359 |
| *cis*-Co(en)₂(OCOCCl₃)₂⁺ | 0.1 | 1-4 | (Na,H)ClO₄ | $1.1 \times 10^{-3}$ | — | — | S | 359 |
| *cis*-Co(phen)₂CO₃⁺ | 1.0 | ~0—1.2 | (Na,H)Cl | $1.5 \times 10^{-4}$ | *20.4* | *8.6* | S; ring opening with CoO | 343 |
| *cis*-Co(bipy)₂CO₃⁺ | 1.0 | ~0—1.2 | (Na,H)Cl | $2.2 \times 10^{-4}$ | *22.3* | *1.5* | S; ring opening with CoO | 343 |
| *cis*-Co(tren)F₂⁺ | 0.5 | 0.35-1.35 | (Na,H)ClO₄ | $3.5 \times 10^{-3}$ | 21.0 | 2.3 | S; 100% *trans* product | 277 |
| *trans*-Co(en)₂(NO₂)₂⁺ | 3.5 | <0 | (Na,H)ClO₄ | $3.0 \times 10^{-5}$ | 24.3 | 2.3 | S | 218 |
| *trans*-Co(en)₂(NO₂)₂⁺ | 2.5 | <0 | (Na,H)ClO₄ | $3.5 \times 10^{-5}$ | 25.6 | 7.1 | S | 219 |
| *trans*-Co(dipy)₂(NO₂)₂⁺ | 2.5 | ≲1 | (Na,H)NO₃ | $2.2 \times 10^{-7}$ | 27.4 | 3.0 | S | 169 |
| Co(CN)₅(OSO₂)⁴⁻ | 1.0 | — | NaClO₄ | 2.5 | — | — | — | 220 |
| Rh(NH₃)₅(OCOCH₃)²⁺ | 0.1 | 1-2 | (Na,H)ClO₄ | $5.8 \times 10^{-6}$ | 23 | 4 | S | 97 |
| Rh(NH₃)₅(OCOC(CH₃)₃)²⁺ | 0.1 | 1-2 | (Na,H)ClO₄ | $2.0 \times 10^{-6}$ | 23 | 6 | S | 97 |
| Rh(NH₃)₅(OSO₃)⁺ | 1.0 | 0.2-2 | (Na,H)ClO₄ | $1.1 \times 10^{-6}$ | 28.5 | 9.9 | S | 102 |
| Ir(NH₃)₅(OCOCH₃)²⁺ | 0.1 | 1-2 | (Na,H)ClO₄ | $9.1 \times 10^{-8}$ | 25 | $-8$ | S | 97 |
| Ir(NH₃)₅(OCOCF₃)²⁺ | 0.1 | 1-2 | (Na,H)ClO₄ | $3.7 \times 10^{-6}$ | 14 | $-36$ | S | 97 |

TABLE VIII. Some Entropies of Neutralization of Aquo-complexes.[a,b,c]

| Complex | $K_a$ | $\Delta H^{\circ}_{ion}$ | $\Delta S^{\circ}_{ion}$ | $\Delta S^{\circ}_{neu}$ |
|---|---|---|---|---|
| V(H₂O)₆³⁺ | $2 \times 10^{-3}$ | 10 | 20 | 39 |
| Cr(H₂O)₆³⁺ | $2 \times 10^{-4}$ | 9.4 | 14 | 33 |
| Mn(H₂O)₆³⁺ | $9 \times 10^{-1}$ | 4.8 | 15.7 | 35 |
| Fe(H₂O)₆³⁺ | $6 \times 10^{-3}$ | 12.3 | 31 | 50 |
| Co(H₂O)₆³⁺ | $2 \times 10^{-2}$ | 10 | 25 | 44 |
| Rh(H₂O)₆³⁺ | $4 \times 10^{-4}$ | 4.3 | $-1$ | 18 |
| Rh(NH₃)₅OH₂³⁺ | $4 \times 10^{-7}$ | 6 | $-9$ | 10 |

[a] $K_a$, $\Delta H^{\circ}_{ion}$, and $\Delta S^{\circ}_{ion}$ are for the process $H_2O-M-X_5^{n+} \rightleftharpoons HO-M-X_5^{n-1} + H^+$
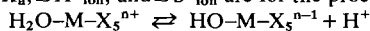
[b] $\Delta S^{\circ}_{neu}$ is for the process $H_2O-M-X_5^n + OH^- \rightleftharpoons HO-M-X_5^{n-1} + H_2O$.
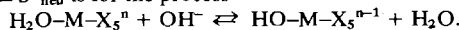
[c] Data from text ref. 25.

DATA TABLE IV. Base Hydrolysis.

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| $Cr(H_2O)_5py^{3+}$ | 1.0 | 0–3 | $(Na,H)ClO_4$ | $9.9 \times 10^3$ | 22.3 | 34.5 | S | 325 |
| $Cr(H_2O)_5Cl^{2+}$ | 1.0 | 0–1.7 | $(Li,H)ClO_4$ | $2.8 \times 10^6$ | 16.1 | 25.0 | S; see below* | 9 |
| $Cr(H_2O)_5Br^{2+}$ | 1.0 | 0–1.3 | $(Li,H)ClO_4$ | $9.2 \times 10^7$ | 13.8 | 24.0 | T; see below* | 10 |
| $Cr(H_2O)_5Br^{2+}$ | 2.0 | – | – | $1.1 \times 10^8$ (30°C) | – | – | S; see below* | 11 |
| $Cr(H_2O)_5I^{2+}$ | 1.0 | 0–0.7 | $(Li,H)ClO_4$ | $(4.0 \times 10^9)$ | 7.3 | 9.9 | S,T; see below* | 12 |
| $Cr(H_2O)_5I^{2+}$ | 1.07 | 0–0.6 | $(Na,H)ClO_4$ | $8.2 \times 10^9$ (30°C) | – | – | S; see below* | 13 |
| $Cr(H_2O)_5I^{2+}$ | 1.0 | 0–1.7 | $(Li,H)ClO_4$ | $3.4 \times 10^9$ | 15.6 | 37.2 | S; see below* | 9 |
| $Cr(H_2O)_5SCN^{2+}$ | 1.0 | 2 | $(Na,H)ClO_4$ | $2.7 \times 10^8$ | 14.5 | 31.0(28.7) | S; see below* | 18 |
| $Cr(H_2O)_5N_3^{2+}$ | 1.0 | 0.4–2.15 | $(Li,H)ClO_4$ | $2.1 \times 10^3$ | 23.9 | 36.6 | S; see below* | 15 |
| $Cr(H_2O)_5ONO_2^{2+}$ | 1.0 | 0–1.1 | $(Li,H)ClO_4$ | $1.0 \times 10^8$ | 11.6 | 17.1 | S; see below* | 20 |
| $Cr(H_2O)_5ONO_2^{2+}$ | 1.0 | 0–1.1 | $(Li,H)ClO_4$ | $1.4 \times 10^7$ | – | – | S; see below* | 19 |
| $Cr(H_2O)_5OSO_3^{+}$ | 1.0 | 0–1.3 | $LiClO_4$ | $3.2 \times 10^5$ | 14.4 | 14.9 | S; see below* | 24 |
| $cis + trans\text{-}Cr(H_2O)_4(NCS)SCN^{+}$ | 1.0 | 0–1 | $(Na,H)ClO_4$ | $7.3 \times 10^8$ | 11.6 | 21.9 | S | 331 |
| $trans(?)\text{-}Cr(H_2O)_4Cl_2^{+}$ | 0.5 | 10–3.7 | $(Na,H)Cl$ | $2.6 \times 10^7$ | – | – | S | 28 |
| $Cr(NH_3)_5F^{2+}$ | 0.1 | – | $Na(NO_3,OH)$ | $2.7 \times 10^{-6}$ | 23.2 | -6.2 | T | 38 |
| $Cr(NH_3)_5F^{2+}$ | 0.1 | 13 | $NaOH$ | $3.2 \times 10^{-7}$ | 32.4 | 20.6 | P | 338 |
| $Cr(NH_3)_5F^{2+}$ | 0.11 | – | $EtOH–H_2O$ 1:4.5 | $6.3 \times 10^{-6}$ | 25.5 | 3.2 | T | 45 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.1 | 11.5–13 | $Na(ClO_4,OH)$ | $1.8 \times 10^{-3}$ | 26.1 | 16.5 | P | 41 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.11 | – | $MeOH–H_2O$ 1:4.5 | $2.5 \times 10^{-3}$ | 27.7 | 22.5 | T | 45 |
| $Cr(NH_3)_5Cl^{2+}$ | 0.11 | – | $EtOH–H_2O$ 1:4.5 | $5.2 \times 10^{-3}$ | 27.6 | 23.6 | T | 45 |
| $Cr(NH_3)_5Br^{2+}$ | 0.1 | 11.5–13 | $Na(ClO_4,OH)$ | $7.2 \times 10^{-2}$ | 25.7 | 22.5 | P | 41 |
| $Cr(NH_3)_5I^{2+}$ | 0.1 | ≧11.5 | $Na(ClO_4,OH)$ | 3.7 | 26.2 | 26.8 | P | 41 |
| $Cr(NH_3)_5N_3^{2+}$ | 0.2 | 0.7–1.3 | $Na(ClO_4,OH)$ | $1.8 \times 10^{-5}$ | 24.9 | 2.9 | S, (10° range) | 326 |
| $Cr(NH_3)_5NCS^{2+}$ | 0 | – | – | $8.1 \times 10^{-6}$ | 35.0 | 35.6 | S,T | 46 |
| $Cr(NH_3)_5NCS^{2+}$ | 0–0.5 | 7–13.7 | $NaOH$ | $2.3 \times 10^{-6}$ | 31.4 | 21 | S | 213 |
| $cis\text{-}Cr(en)_2F_2^{+}$ | 0.010 | 7.9 | Buffer $B(OH)_4^{-}/H_3BO_3$ | 210(40.5°C) | – | – | T | 214 |
| $cis\text{-}Cr(en)_2Cl_2^{+}$ | 0.10 | 11.3–14 | $Na(NO_3,OH)$ | $2.7 \times 10^{-2}$ | – | – | T | 55 |
| $cis\text{-}Cr(en)_2OHCl^{+}$ | 0.10 | 10.1–10.7 | $Na(ClO_4,OH)$ | 2.2 | – | – | S; 96% cis prod | 57 |
| $trans\text{-}Cr(en)_2Cl_2^{+}$ | 0.10 | 11.3–14 | $Na(NO_3,OH)$ | $3.7 \times 10^{-2}$ | – | – | T | 55 |
| $trans\text{-}Cr(en)_2OHCl^{+}$ | 0.10 | 9.8–10.8 | $Na(ClO_4,OH)$ | $<3 \times 10^{-3}$ | – | – | S; 87% trans product | 57 |
| $Fe(OH_2)_5Cl^{2+}$ | 3.0 | <0.6 | $Na(ClO_4,OH)$ | $3.4 \times 10^{14}$ | – | – | S; note unusual k | 73 |
| $Co(NH_3)_5F^{2+}$ | 0(ext) | – | – | $1.3 \times 10^{-2}$ | 26.1 | 20.4 | T | 222 |

\* Original results given by rate law $k = k_1[H^{+}]^{-1}$. Activation parameters and rate constants are corrected for the $k_w$, $\Delta H^{\circ}$ and $\Delta S^{\circ}$ of the process $H_2O \rightleftarrows H^{+} + OH^{-}$, $k_w = 1.0 \times 10^{-14}$, $\Delta H^{\circ} = 13.3$, $\Delta S^{\circ} = -19.3$.

| Complex | | pH | Medium | $k$ | | | Method | Ref. |
|---|---|---|---|---|---|---|---|---|
| $Co(NH_3)_5F^{2+}$ | 0.11 | — | MeOH–H₂O 1:4.5 | $1.0 \times 10^{-2}$ | 26.4 | 20.9 | T | 45 |
| $Co(NH_3)_5F^{2+}$ | 0.11 | — | EtOH–H₂O 1:4.5 | $2.1 \times 10^{-2}$ | 26.5 | 22.7 | T | 45 |
| $Co(NH_3)_5Cl^{2+}$ | 0(ext) | — | — | 1.5 | 27.6 | 30.7(34.8) | T | 222 |
| $Co(MH_3)_5Cl^{2+}$ | 0.1 | 12–14 | Na(ClO₄,OH) | 0.61 | — | — | $S_{SF}$ | 223 |
| $Co(NH_3)_5Cl^{2+}$ | 0.05–0.005 | 11.7–12.7 | NaOH | 0.81 | 28.7 | 37 | S | 85 |
| $Co(NH_3)_5Cl^{2+}$ | 0(ext) | — | NaOH | 1.6 | 26.6 | 31.6 | S; (13.4° range) | 224 |
| $Co(NH_3)_5Br^{2+}$ | 0(ext) | — | — | 6.2 | 27.6 | 37.7 | T | 222 |
| $Co(NH_3)_5Br^{2+}$ | 1.0 | 12.0–13.4 | Na(ClO₄,OH) | 1.4 | — | — | $S_{SF}$ | 223 |
| $Co(NH_3)_5Br^{2+}$ | 0.05–0.005 | 11.7–12.7 | NaOH | 6.0 | 23.5 | 23 | S | 85 |
| $Co(NH_3)_5Br^{2+}$ | 0(ext) | — | NaOH | 8.9 | 27.0 | 36.4 | S | 225 |
| $Co(NH_3)_5Br^{2+}$ | variable | 10 | NaOH | 5.2 | — | — | S | 226 |
| $Co(NH_3)_5Br^{2+}$ | 0(ext) | (initial) | NaOH | 10 (30°C) | — | — | S | 227 |
| $Co(NH_3)_5I^{2+}$ | 0.1 | — | Na(ClO₄,OH) | 6.3 | 27.2 | 36.4 | pH stat | 228 |
| $Co(NH_3)_5I^{2+}$ | 0(ext) | — | — | 17.4 | 27.2 | 38.4 | S | 229 |
| $Co(NH_3)_5I^{2+}$ | 1.0 | — | NH₄ClO₄, NH₃ | 3.70 | 21 | 19(14.5) | S | 90 |
| $Co(NH_3)_5I^{2+}$ | 0(ext) | — | — | 23 | 28.3 | 42.6 | T | 222 |
| $Co(NH_3)_5NO_2^{2+}$ | 0(ext) | — | — | $4.2 \times 10^{-6}$ | 37.4 | 42.4 | S,T | 230 |
| $Co(NH_3)_5N_3^{2+}$ | 0(ext) | — | — | $3.0 \times 10^{-4}$ | 32.6 | 34.7 | S,T | 91 |
| $Co(NH_3)_5NCS^{2+}$ | 0(ext) | — | — | $5.0 \times 10^{-4}$ | 34.0 | 40.4 | S,T | 46 |
| $Co(NH_3)_5NCS^{2+}$ | 0.007 | 11.3 | NaOH | $1.4 \times 10^{-3}$ | 21.6 | 1.9 | K | 231 |
| $Co(NH_3)_5ONO^{2+}$ | 0.1 | — | NaClO₄ | 15 | 28.1 | 41.0 | pH stat | 228 |
| $Co(NH_3)_5ONO^{2+}$ | 0.12 | — | LiClO₄,NaOH | 12 | 28.8 | 43 | S | 94 |
| $Co(NH_3)_5(NH_2SO_3)^{2+}$ | 1.0 | — | NaClO₄ | $1.0 \times 10^{2}$ | 32 | 58 | S | 99 |
| $Co(NH_3)_5(NHSO_3)^{+}$ | 1.0 | 13.5–14.0 | Na(ClO₄,OH) | $2.5 \times 10^{-7}$ | 41.2 | 46 | S | 99 |
| $Co(NH_3)_5OCOCHCl_2^{2+}$ | 1.0 | 13.0–13.1 | Na(Cl,OH) | $5.8 \times 10^{-3}$ | 28.9 | 28.8 | S | 98 |
| $Co(NH_3)_5OCOCCl_3^{2+}$ | 1.0 | 12.8–13.5 | Na(Cl,OH) | $2.2 \times 10^{-2}$ | 23.3 | 12.5 | S | 98 |
| $Co(NH_3)_5OCOCF_3^{2+}$ | 1.0 | — | Na(Cl,OH) | $2.1 \times 10^{-2}$ | 22.7 | 10 | S | 232 |
| $Co(NH_3)_5OCOCF_3^{2+}$ | 1.0 | — | Na(Cl,OH) | $1.6 \times 10^{-2}$ | 27 | 24 | – CoO | 233 |
| $Co(NH_3)_5OCO_2^{+}$ | 1.0 | 12.3–14.0 | Na(NO₃,OH) | $3.3 \times 10^{-6}$ | 30.0 | 18 | S | 234 |
| $Co(NH_3)_5(ox)^{+}$ | 1.0 | 13.0–14.0 | Na(Cl,OH) | $2.5 \times 10^{-4}$ | 31.7 | 32.2 | S | 235 |
| $Co(NH_3)_5(mal)^{+}$ | 1.0 | 13.6–14.0 | Na(Cl,OH) | $2.8 \times 10^{-5}$ | 28.0 | 14.4 | S | 235 |
| $Co(NH_3)_5(fumarate)^{+}$ | 1.0 | 13.6–14.0 | Na(Cl,OH) | $8.0 \times 10^{-5}$ | 28.5 | 18.3 | S | 235 |
| $Co(NH_3)_5OSO_3^{+}$ | 1.0 | 13.3–12.7 | Na(ClO₄,OH) | $4.9 \times 10^{-2}$ | 26.3 | 24.0 | S | 99 |
| $Co(NH_3)_5OS_2O_2^{+}$ | 1.0 | 12.6–13.3 | NaOH,NH₄NO₃ | $6 \times 10^{-5}$ | 27.6 | 14.4 | T | 103 |
| $Co(NH_3)_5OS_2O_2^{+}$ | 0(ext) | — | — | $1.1 \times 10^{-4}$ | 30.4 | 25.7 | – | 337 |
| $Co(NH_3)_5OPO_3$ | 1.0 | 11–12.6 | Na(ClO₄,OH) | $5.0 \times 10^{-7}$ | 36.8 | 36.0 | R | 95 |
| $Co(en)_3^{3+}$ | >0.1 | >13 | NaOH | $(1.1 \times 10^{-9})$ | 38.6 | 30 | – | 221 |
| $cis$-$Co(en)_2NH_3NO_2^{2+}$ | 0.033–0.1 | 12.5–13.0 | NaOH | $5.1 \times 10^{-5}$ | 33.3 | 33.5 | S; 90% *cis* prod. | 236 |
| $cis$-$Co(en)_2NH_3NCS^{2+}$ | 0.033–0.1 | 12.5–13.0 | NaOH | $2.9 \times 10^{-3}$ | 30.6 | 32.5 | T; 100% *cis* prod. | 237 |
| $cis$-$Co(en)_2NH_3Cl^{2+}$ | 0.10 | 9.2–9.8 | KCl | 8.1 | — | — | – | 238 |
| $cis$-$Co(en)_2(NH_2OH)Cl^{2+}$ | 0.1 | 11.5–12 | NaClO₄ | 7.0 | 23.4 | 23.8 | T | 111 |
| $cis$-$Co(en)_2(NH_2OH)Br^{2+}$ | 0.1 | 11.5–12 | NaClO₄ | 48 | 23.7 | 28.7 | T | 111 |
| $cis$-$Co(en)_2(NH_2Me)Cl^{2+}$ | 0.10 | 11.5–12 | NaClO₄ | 7.3 | 23.4 | 23.9 | T | 111 |
| $cis$-$Co(en)_2(NH_2Me)Cl^{2+}$ | 0.10 | 9.2–10.0 | KCl | 13 | — | — | T; 100% *cis* prod. | 238 |

DATA TABLE IV. (Cont.)

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| $cis$-Co(en)$_2$(NH$_2$Me)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 50 | 23.7 | 28.8 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$Et)Cl$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 6.5 | 23.5 | 24.0 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$Et)Cl$^{2+}$ | 0.1 | 4.65–5.65 | Buffer (Na,H)OCOCH$_3$ (Na,H)OCOH | 12 | 25.4 | 32 | T | 112 |
| $cis$-Co(en)(NH$_2$Et)Cl$^{2+}$ | 0.1 | 9.2–10.2 | KCl | 13 | – | – | T; 100% $cis$ prod. | 238 |
| $cis$-Co(en)$_2$(NH$_2$Et)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 47 | 23.7 | 28.6 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-n-Pr)Cl$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 11 | 23.4 | 24.8 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-n-Pr)Cl$^{2+}$ | 0.1 | 9.2–10.0 | K(Cl,NO$_2$) | 13 | 23.7 | – | T; 100% $cis$ prod. | 238 |
| $cis$-Co(en)$_2$(NH$_2$-n-Pr)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | $2.7\times10^{2}$ | 23.7 | 32.1 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-i-Pr)Cl$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 17 | 23.4 | 25.6 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-i-Pr)Cl$^{2+}$ | 0.1 | 8.8–9.6 | KCl | 52 | – | – | T; 100% $cis$ prod. | 238 |
| $cis$-Co(en)$_2$(NH$_2$-i-Pr)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | $4.2\times10^{2}$ | 23.7 | 33 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-n-Bu)Cl$^{2+}$ | 0.1 | 9.2–10.0 | KCl | 13 | – | – | T; 100% $cis$ prod. | 238 |
| $cis$-Co(en)$_2$(NH$_2$-n-Bu)Cl$^{2+}$ | 0.5 | 12.4–13.7 | KCl-NaOH | 6.5 | – | – | S$_{SF}$ | 239 |
| $cis$-Co(en)$_2$(NH$_2$-Allyl)Cl$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 6.4 | 23.4 | 23.7 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-Allyl)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | $1.2\times10^{2}$ | 23.8 | 30.8 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$CH$_2$CH$_2$OH)Cl$^{2+}$ | 0.1 | 9.0–9.6 | KCl | 20 | – | – | T; 100% $cis$ prod. | 238 |
| $cis$-Co(en)$_2$(NH$_2$(CH$_2$)$_3$CH$_2$OH)Cl$^{2+}$ | – | – | – | $2.7\times10^{-1}$ | – | – | S,T | 347 |
| $cis$-Co(en)$_2$(NH$_2$(CH$_2$)$_4$CH$_2$OH)Cl$^{2+}$ | – | – | – | $2.7\times10^{-1}$ | – | – | S,T | 347 |
| $cis$-Co(en)$_2$(NH$_2$(CH$_2$)$_5$CH$_2$OH)Cl$^{2+}$ | – | – | – | $2.5\times10^{-1}$ | – | – | S,T | 347 |
| $cis$-Co(en)$_2$(NH$_2$-Prop-2-ynyl)Cl$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 3.3 | 23.4 | 22.3 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$-Prop-2-ynyl)Br$^{2+}$ | 0.1 | 11.5–12 | NaClO$_4$ | 57 | 23.7 | 29.0 | T | 111 |
| $cis$-Co(en)$_2$(NH$_2$(CH$_2$)$_5$COOMe)Cl$^{2+}$ | 0.1 | 12.4–13 | borax buffers | 14 | – | – | S$_{SF}$, pH stat | 361 |
| $cis$-Co(en)$_2$(NH$_2$(CH$_2$)$_5$COO$^-$)Cl$^{2+}$ | 0.1 | 11–11.5 | borax buffers | $1.5\times10^{-1}$ | – | – | S$_{SF}$, pH stat | 361 |
| $cis$-Co(en)$_2$pyCl$^{2+}$ | – | – | – | $1.6\times10^{-3}$ | – | – | T | 159 |
| $cis$-Co(en)$_2$($\beta$-pic)Cl$^{2+}$ | – | – | – | $1.3\times10^{-3}$ | – | – | T | 159 |
| $cis$-Co(en)$_2$($\gamma$-pic)Cl$^{2+}$ | – | – | – | $1.3\times10^{-3}$ | – | – | T | 159 |
| $cis$-Co(en)$_2$($\gamma$-CH$_3$O-py)Cl$^{2+}$ | – | – | – | $1.2\times10^{-3}$ | – | – | T | 159 |
| $cis$-Co(en)$_2$Cl$_2^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | $7.1\times10^{2}$ | 24.0 | 35.0 | T; 37% $cis$ prod. | 240 |
| $cis$-Co(en)$_2$ClBr$^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | $2.6\times10^{3}$ | 22.5 | 32.6 | T; 30% $cis$ prod. | 240 |
| $cis$-Co(en)$_2$BrCl$^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | $8.4\times10^{2}$ | 22.1 | 29.0 | T; 40% $cis$ prod. | 240 |
| $cis$-Co(en)$_2$(OH)F$^+$ | 0.10 | 11.5–12.0 | Na(NO$_3$,OH) | $1.2\times10^{-1}$ | 22.7 | 13.4 | T | 129 |
| $cis$-Co(en)$_2$(OH)Cl$^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | 12 | 21.8 | 19.5 | T; 97% $cis$ prod. | 240 |
| $cis$-Co(en)$_2$(OH)Br$^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | 86 | 21.9 | 23.8 | T; 96% $cis$ prod. | 240 |
| $cis$-Co(en)$_2$(OH)(NO$_2$)$^+$ | 0.10 | 13.0 | NaOH | – | 30.3 | – | S | 236 |
| $cis$-Co(en)$_2$(OH)(NO$_2$)$^+$ | 0.050–0.10 · | 12.7–13.0 | NaOH | $2.5\times10^{-4}$ | – | – | T | 241 |
| $cis$-Co(en)$_2$(OH)N$_3^+$ | 0.05 | 12.7 | NaOH | $2.8\times10^{-3}$ | – | – | S,T | 138 |
| $cis$-Co(en)$_2$(OH)(NCS)$^+$ | – | – | – | $2.3\times10^{-3}$ | – | – | T | 242 |
| $cis$-Co(en)$_2$(OH)(NCS)$^+$ | 0.050–0.1 | 12–12.3 | NaOH | $1.6\times10^{-2}$ (35°C) | – | – | T | 241 |

| Complex | | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| cis-Co(en)$_2$(OH)(OCOCH$_3$)$^+$ | 0.014 | 12.0 | NaOH | $8.2 \times 10^{-3}$ | 25.8 | 15.8(18.5) | T; 95% *cis* prod. | 243 |
| cis-Co(en)$_2$(OH)mal | – | 12–14 | NaOH | $4.3 \times 10^{-4}$ | 26.5 | 14.9 | S | 245 |
| cis-Co(en)$_2$(N$_3$)N$_3^+$ | 0.05 | 12.7 | NaOH | $6.6 \times 10^{-3}$ | – | – | S,T; 55% *cis* prod. | 138 |
| cis-Co(en)$_2$(N$_3$)NCS$^+$ | – | – | – | $2.7 \times 10^{-3}$ | – | – | T; 100% *cis* prod. | 242 |
| cis-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.001–0.01 | 11.0–12.0 | NaOH | 1.2 | 22.5 | 17.3 | T; 67% *cis* prod. | 240 |
| cis-Co(en)$_2$(NO$_2$)NO$_2^+$ | 0.033–0.10 | 12.5–13.0 | NaOH | $3.7 \times 10^{-5}$ | 31.9 | 28.2 | T | 236 |
| cis-Co(en)$_2$(NO$_2$)NCS$^+$ | 0.050–0.10 | 12.7–13.0 | NaOH | $4.3 \times 10^{-4}$ | 29.6 | 25.4 | T; 45–55% *cis* prod. | 241 |
| cis-Co(en)$_2$(NCS)N$_3^+$ | – | – | – | $6.0 \times 10^{-3}$ | – | – | T; 65–70% *cis* prod. | 242 |
| cis-Co(en)$_2$(NCS)NO$_2^+$ | 0.05–0.10 | 12.7–13.0 | NaOH | $1.5 \times 10^{-3}$ | 29.3 | 33.6 | T | 241 |
| cis-Co(en)$_2$(NCS)NCS$^+$ | 0.01–0.05 | 12.0–12.7 | NaOH | $4.6 \times 10^{-2}$ | 25.6 | 18.4 | T | 237 |
| cis-Co(en)$_2$(OCOCH$_3$)$_2^+$ | 0.014 | 12.0 | NaOH | $2.4 \times 10^{-2}$ | 22.0 | 3.6 | T; *cis* prod. | 243 |
| Co(en)$_2$O$_2$CO$^+$ | 1.0 | 11.1–14 | Na(ClO$_4$,OH) | $2.7 \times 10^{-3}$ | 33.4 | 31.2 | S; CoO | 145 |
| Co(en)$_2$ox$^+$ | 0.01–0.03 | 12.0–12.5 | NaOH | $1.3 \times 10^{-5}$ | | | S, P$_m$ | 244 |
| Co(en)$_2$ox$^+$ | 3.4 | 14 | NaOH | $5.3 \times 10^{-3}$ | | | S; The rate const. refers to the formation of cis-Co(en)$_2$(OH)ox | 362 |
| Co(en)$_2$mal$^+$ | – | 12–14 | NaOH | $2.8 \times 10^{-4}$ | 29.1 | 22.8 | S | 363 |
| trans-Co(NH$_3$)$_4$(NO$_2$)Cl$^+$ | 0.3 | 13.0–13.5 | Na(NO$_3$,OH) | $1.4 \times 10^{-1}$ | 24.3 | 19.2 | S; 100% *trans* prod. | 333 |
| trans-Co(NH$_3$)$_4$(NO$_2$)Br$^+$ | 0.3 | 13.0–13.5 | Na(NO$_3$,OH) | $3.7 \times 10^{-1}$ | 20.4 | 8.2 | S; 100% *trans* prod. | 333 |
| trans-Co(NH$_3$)$_4$(NCS)Cl$^+$ | 0.21 | – | {Piperidine,2,6-dimethylpyridine–HNO$_3$ buffers} | 4.8 | 29.6 | 44 | S | 346 |
| trans-Co(en)$_2$(NH$_3$)NO$_2^{2+}$ | 0.033–0.10 | 12.5–13.0 | NaOH | $7.6 \times 10^{-5}$ | 33.3 | 34.3 | T | 236 |
| trans-Co(en)$_2$(NH$_3$)NCS$^{2+}$ | 0.050–0.10 | 12.7–13.0 | NaOH | $5.9 \times 10^{-3}$ | 31.8 | 38.0 | S; 30% *trans* prod. | 237 |
| trans-Co(en)$_2$F$_2^+$ | – | – | – | 64 | – | – | S | 128 |
| trans-Co(en)$_2$Cl$_2^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | $3.2 \times 10^3$ | 22.6 | 33.3 | T; 95% *trans* prod. | 240 |
| trans-Co(en)$_2$ClBr$^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | $1.2 \times 10^4$ | 23.6 | 39.3 | T; 95% *trans* prod. | 240 |
| trans-Co(en)$_2$Br$_2^+$ | – | – | – | $1.2 \times 10^4$ | – | – | S | 128 |
| trans-Co(en)$_2$BrCl$^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | $5.3 \times 10^3$ | 24.3 | 40.0 | T; 100% *trans* prod. | 240 |
| trans-Co(en)$_2$(OH)F$^+$ | 0.10 | 13 | Na(NO$_3$,OH) | $9.0 \times 10^{-3}$ | 23.3 | 10.3 | T; 11% *trans* prod. | 129 |
| trans-Co(en)$_2$(OH)Cl$^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | $5.6 \times 10^{-1}$ | 22.2 | 14.8 | T; 6% *trans* prod. | 240 |
| trans-Co(en)$_2$(OH)Br$^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | 7.0 | 23.1 | 22.8 | T; 10% *trans* prod. | 240 |
| trans-Co(en)$_2$(NH$_3$)NCS$^{2+}$ | 0.050–0.10 | 12.7–13.0 | NaOH | $5.9 \times 10^{-3}$ | 31.8 | 38.0 | S; 30% *trans* prod. | 237 |
| trans-Co(en)$_2$F$_2^+$ | – | – | – | 64 | – | – | S | 128 |
| trans-Co(en)$_2$(OH)NO$_2^+$ | 0.001–0.01 | 11–12 | NaOH | $3.2 \times 10^3$ | 22.6 | 33.3 | T; 95% *trans* prod. | 240 |
| trans-Co(en)$_2$(OH)NO$_2^+$ | 0.033–0.10 | 12.5–13.0 | NaOH | $7.2 \times 10^{-6}$ | 28.0 | 11.9 | T | 236 |
| trans-Co(en)$_2$(OH)N$_3^+$ | 0.05–0.10 | 12.7–13.0 | NaOH | $3.5 \times 10^{-5}$ | | | T | 241 |
| trans-Co(en)$_2$(OH)N$_3^+$ | 0.05 | 12.7 | NaOH | $1.2 \times 10^{-3}$ | | | S,T | 138 |
| trans-Co(en)$_2$(OH)NCS$^+$ | – | – | – | $1.2 \times 10^{-3}$ | | | T | 242 |
| trans-Co(en)$_2$(OH)NCS$^+$ | 0.05–0.10 | 12.7–13.0 | NaOH | $4.3 \times 10^{-4}$ | | | T | 241 |
| trans-Co(en)$_2$(OH)NQS$^+$ | – | – | – | $7.0 \times 10^{-5}$ | | | T | 242 |
| trans-Co(en)$_2$(OH)OCOCH$_3^+$ | 0.014 | 12.0 | NaOH | $1.3 \times 10^{-3}$ | 27.8 | 21.4 | T; 5% *trans* prod. | 243 |
| trans-Co(en)$_2$(CN)Cl$^+$ | 0.010 | 12.0 | NaOH | 4.9 | 22.6 | 20.6 | T; 100% *trans* prod. | 164 |
| trans-Co(en)$_2$(CN)Br$^+$ | 0.005 | 11.7 | NaOH | 67 | 22.8 | 26.3 | T; 100% *trans* prod. | 166 |
| trans-Co(en)$_2$(NO$_2$)Cl$^+$ | 0.0010–0.010 | 11.0–12.0 | NaOH | 3.7 | 23.8 | 23.9 | T; 94% *trans* prod. | 240 |
| trans-Co(en)$_2$(NO$_2$)$_2^+$ | 0.033–0.10 | 12.5–13.0 | NaOH | $1.6 \times 10^{-4}$ | 30.0 | 24.7 | T; 85–90% *trans* prod. | 236 |
| trans-Co(en)$_2$(NO$_2$)NCS$^+$ | 0.10–0.050 | 12.7–13.0 | NaOH | $4.6 \times 10^{-4}$ | 31.3 | 31.2 | T; 85–90% *trans* prod. | 241 |

DATA TABLE IV. (Cont.)

| Complex | $\mu(M)$ | pH | Medium | $k$ | $\Delta H^{\#}$ | $\Delta S^{\#}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| trans-Co(en)₂N₃Cl⁺ | 0.0050 | 11.7 | NaOH | $4.1 \times 10^{-1}$ (0°C) | – | – | S,T; 87% *trans* prod. | 138 |
| trans-Co(en)₂(N₃)₂⁺ | 0.025 | 12.4 | NaOH | $1.1 \times 10^{-2}$ | – | – | S,T; 70% *trans* prod. | 138 |
| trans-Co(en)₂(N₃)NCS⁺ | – | – | – | $2.2 \times 10^{-3}$ | – | – | T; 60–90% *cis* prod. | 242 |
| trans-Co(en)₂(NCS)Cl⁺ | 0.0018–0.0021 | 11.3 | NaOH | 13 | 22.6 | 22.3 | S; 26% *trans* prod. | 165 |
| trans-Co(en)₂(NCS)NO₂⁺ | 0.050–0.10 | 12.7–13.0 | NaOH | $2.0 \times 10^{-4}$ | – | – | T | 241 |
| trans-Co(en)₂(NCS)N₃⁺ | – | – | – | $3.3 \times 10^{-3}$ | – | – | T | 242 |
| trans-Co(en)₂(NCS)₂⁺ | 0.033–0.10 | 12.5–13.0 | NaOH | $6.6 \times 10^{-3}$ | 33.6 | 44.2 | T; 70% *cis* prod. | 237 |
| trans-Co(en)₂(OCOCH₃)Cl⁺ | 0.1 | 1.3–2.3 | Na(ClO₄,OH) | 11 | 22.6 | 22 | T; 40% *trans* prod. | 323 |
| trans-Co(en)₂(OCOCH₃)₂⁺ | 0.014 | 12.0 | NaOH | $5.1 \times 10^{-2}$ | 26.3 | 23 | S$_{SF}$; 80% *trans* prod. | 243 |
| trans-Co(en)₂(OCOPh)Cl⁺ | 0.1 | 2.0–2.3 | Na(ClO₄,OH) | 7.8 | 24.8 | 28 | S$_{SF}$; 100% *trans* prod. | 323 |
| trans-Co(en)₂(OCOPh)₂⁺ | 0.0027 | 11.3 | NaOH | $3.2 \times 10^{-2}$ | – | – | S$_{SF}$ | 245 |
| trans-Co(Me-en)₂Cl₂⁺ | – | – | – | $1.2 \times 10^{4}$ | 23.3 | 38.3 | T$_F$ | 246 |
| trans-Co(Et-en)₂Cl₂⁺ | – | – | – | $1.6 \times 10^{4}$ | 22.6 | 36.5 | T$_F$ | 246 |
| trans-Co(d,l-pn)₂Cl₂⁺ | – | – | – | $2.5 \times 10^{3}$ | 23.6 | 36.2 | T$_F$ | 243 |
| trans-Co(d,l-bn)₂Cl₂⁺ | – | – | – | $2.3 \times 10^{3}$ | 24.2 | 38.0 | T$_F$ | 246 |
| trans-Co(meso-bn)₂Cl₂⁺ | – | – | – | $1.0 \times 10^{4}$ | 24.0 | 40.4 | T$_F$ | 246 |
| trans-Co(teta)Cl₂⁺ | 0.20 | 5.7–6.8 | 2,6-lutidine buffer | $5.7 \times 10^{5}$ (19.8°C) | – | – | S | 247 |
| trans-Co (trans-14-diene)Cl₂⁺ | 0.20 | 6.0–6.8 | HNO₃/2,6-lutidine buffer | $2.2 \times 10^{5}$ (19.8°C) | – | – | S | 247 |
| trans-Co(cyclam)Cl₂⁺ | 0.1 | – | LiNO₃ | $6.7 \times 10^{4}$ | – | – | S | 168 |
| trans-Co(cyclam)(NO₂)Cl⁺ | 0.3 | 8.4–9.4 | Borax buffer | $7.6 \times 10^{2}$ (26.9°C) | – | – | S$_{SF}$; 100% *trans* prod. | 348 |
| trans-Co(cyclam)(NO₂)Br⁺ | 0.05 | 7.2–8.0 | γ-collidine/HNO₃ buffer | $1.0 \times 10^{4}$ (22.3°C) | – | – | S$_{SF}$; 100% *trans* prod. | 348 |
| trans-Co(cyclam)(NCS)Cl⁺ | 0.25 | – | γ-collidine/HNO₃ buffer | $8.9 \times 10^{2}$ | 21.1 | 25 | S | 346 |
| Ru(NH₃)₅Cl²⁺ | 0.002 | 11.3–11.7 | NaOH + CH₃–⟨◯⟩–SO₃Na | 5.2 | 26.7 | 34.2 | S,T | 248 |
| Ru(NH₃)₅Cl²⁺ | – | 11–12.1 | NaOH | 5.0 (24.6°C) | – | – | S | 180 |
| Ru(NH₃)₅Br²⁺ | – | 11–12.1 | NaOH | 18 | – | – | S; Preliminary value | 180 |
| Ru(NH₃)₅Br²⁺ | 0.001 | 11.0–11.4 | NaOH + CH₃–⟨◯⟩–SO₃Na | 11.7 | 22.5 | 21.8 | S, T | 248 |
| Ru(NH₃)₅I²⁺ | 0.002 | 11.0–11.3 | NaOH + CH₃–⟨◯⟩–SO₃Na | 5.3 | 23.7 | 24.2 | S, T | 248 |
| cis-Ru(en)₂Cl₂⁺ | – | 11.3–12.0 | – | Fast (0°C) | – | – | S, T | 248 |
| cis-Ru(en)₂Br₂⁺ | – | 10.0 | – | Fast (0°C) | – | – | S, T | 248 |

| Complex | μ | pH range | Medium | k | | | Notes | Ref. |
|---|---|---|---|---|---|---|---|---|
| cis-Ru(en)₂(OH)Cl⁺ | 0.004 | 11.7–12.0 | NaOH + CH₃-○-SO₃Na | 0.5 | — | — | S, T; 100% *cis* prod. | 248 |
| cis-Ru(en)₂(OH)Br⁺ | 0.040 | 11.4–12.0 | NaOH + CH₃-○-SO₃Na | 1.42 | 20.3 | 10.3 | S, T; 100% *cis* prod. | 248 |
| Rh(NH₃)₅Cl²⁺ | 0.1 | — | Na(ClO₄,OH) | 1.09 × 10⁻⁴ | 27.5 | 15.6 | T | 186 |
| Rh(NH₃)₅Cl²⁺ | 0(ext.) | — | NaOH | 4.1 × 10⁻⁴ | 27.9 | 19.5 | S | 249 |
| Rh(ND₃)₅Cl²⁺ | 0.1 | — | Na(ClO₄,OD) | 1.8 × 10⁻⁴ | 25.6 | 9.8 | S; D₂O as solvent, 10° range | 339 |
| Rh(NH₃)₅Br²⁺ | 0.1 | — | Na(ClO₄,OH) | 9.6 × 10⁻⁵ | 29.5 | 22.1 | T | 186 |
| Rh(NH₃)₅Br²⁺ | 0(ext.) | — | NaOH | 3.5 × 10⁻⁴ | 30.0 | 26.1 | S | 249 |
| Rh(ND₃)₅Br²⁺ | 0.1 | — | Na(ClO₄,OD) | 1.6 × 10⁻⁴ | 26.3 | 12.9 | S; D₂O as solvent, 10° range | 339 |
| Rh(NH₃)₅I²⁺ | 0.1 | — | Na(ClO₄,OH) | 2.3 × 10⁻⁵ | 31.8 | 27.0 | T | 186 |
| Rh(NH₃)₅I²⁺ | 0(ext.) | — | NaOH | 7.3 × 10⁻⁵ | 32.2 | 30.8 | S | 249 |
| Rh(ND₃)₅I²⁺ | 0.1 | — | Na(ClO₄,OD) | 3.1 × 10⁻⁵ | 29.0 | 18.2 | S; D₂O as solvent, 10° range | 339 |
| Rh(NH₃)₅N₃²⁺ | 0 | — | — | 3.1 × 10⁻⁷ | 34.0 | 25.8 | S | 250 |
| Rh(NH₃)₅ONO²⁺ | 1.0 | 12.0–13.3 | Na(ClO₄,OH) | 1.8 × 10⁻² | 27.5 | 26 | S | 160 |
| Rh(NH₃)₅OSO₃⁺ | 1.0 | 12.8–13.0 | Na(ClO₄,OH) | 1.3 × 10⁻³ | 24.5 | 10 | S | 102 |
| Rh(NH₃)₅OCOH²⁺ | 1.0 | 12.0–12.4 | Na(Cl,OH) | 3.6 × 10⁻⁶ | 33.2 | 28 | S | 251 |
| Rh(NH₃)₅OCOCH₃²⁺ | 1.0 | 13.4–13.7 | Na(Cl,OH) | 2.1 × 10⁻⁶ | 31.9 | 22 | S | 251 |
| Rh(NH₃)₅(OCOCH₂F)²⁺ | 1.0 | 13.4–14.0 | Na(Cl,OH) | 1.3 × 10⁻⁵ | 31.9 | 26 | S | 251 |
| Rh(NH₃)₅(OCOCHF₂)²⁺ | 1.0 | 12.7–13.4 | Na(Cl,OH) | 5 × 10⁻⁵ | 30.1 | 22 | S | 251 |
| Rh(NH₃)₅(OCOCF₃)²⁺ | 1.0 | 12.0–12.7 | Na(Cl,OH) | 1.0 × 10⁻³ | 18.0 | −12 | S; OC suggested | 251 |
| Rh(NH₃)₅(OCOCCl₃)²⁺ | 1.0 | 12.5–13.3 | Na(Cl,OH) | 3 × 10⁻⁴ | 26.4 | 14 | S; OC suggested | 251 |
| Ir(NH₃)₅Cl²⁺ | 0(ext.) | 12.5–12.7 | NaOH | 4.8 × 10⁻⁸ | 33.2 | 19 | T | 340 |
| Ir(NH₃)₅Br²⁺ | — | — | none | 1.1 × 10⁻⁹ | 22.5 | −24.1 | R | 192 |
| Ir(NH₃)₅Br²⁺ | 0(ext.) | 12.5–12.7 | NaOH | 2.2 × 10⁻⁸ | 34.6 | 22 | S | 9 340 |
| Ir(NH₃)₅I²⁺ | 0(ext.) | — | NaOH | 8.3 × 10⁻⁹ | 35.7 | 24.2 | S | 253, 340 |
| Ir(NH₃)₅ONO₂²⁺ | 1.0 | 13.0–13.9 | Na(ClO₄,OH) | 1.9 × 10⁻⁶ | 31.0 | 19 | S | 160 |
| Ir(NH₃)₅OCOCF₃²⁺ | 1.0 | 12.0–12.7 | Na(Cl,OH) | 5 × 10⁻⁴ | — | — | S | 251 |

no clear variation with central metal ion. It is indeed obvious that the values from experiments agree not at all with the estimates for the first mechanism and are in very good agreement with the estimates available for the second mechanism.

Rate constants and activation parameters for the base-catalyzed process for aquocomplexes (M = Cr, Fe) are more frequently expressed in the literature in terms of the rate law

$$R = k_{-1}[H^+]^{-1}[\text{complex}]$$

In such cases the data reported in Data Table IV have been changed to conform to the rate equation

$$R = k_2[OH^-][\text{complex}]$$

by use of the values $K_w = 1.0 \times 10^{-14} M^2$, $\Delta H° = 13.5$ kcal mol$^{-1}$ and $\Delta S° = -19.3$ cal mol$^{-1}$ deg$^{-1}$ for the process

$$H_2O \rightleftharpoons OH^- + H^+$$
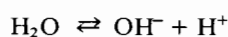
For these aquocomplexes the formation of a conjugate base through the dissociation of an acidic coordinated water is quite obvious and it can be readily seen that when interpreted according to the rate law $R = k_2[OH^-][\text{complex}]$ the experimental data lead to $\Delta S^+$ values which fall into the range expected for a conjugate base mechanism. This result lay unrecognized among the data available during the long and heated discussion of the base hydrolysis mechanism.

## 9. Leaving Group Effects

If the solvation entropy of complexes $ML_5X^{2+}$ is less dependent on the nature of the leaving ligand $X^-$ than is the solvation entropy of the free ligand, then one might expect to see a part of this difference in the $\Delta S^+$ values when a substitution mechanism is predominantly dissociative. Taking as examples of $X^-$ the halide ions, we would expect to see the lowest value (*e.g.*, the most negative or the least positive) of $\Delta S^+$ for $F^-$ and the highest value for $I^-$. Some data which show this trend are presented in Table IX. These are .base hydrolysis reactions involving the pentaamminehalo complexes of four different cations.

TABLE IX. Activation Entropies for Base Hydrolysis of some Halocomplexes.[a]

| Complex | $F^-$ | $Cl^-$ | $Br^-$ | $I^-$ |
|---|---|---|---|---|
| $Cr(NH_3)_5X^{2+}$ | − 6.2 | +16.5 | +22.5 | +26.8 |
| $Co(NH_3)_5X^{2+}$ | +20.4 | +34.8 | +37.7 | +42.6 |
| $Rh(NH_3)_5X^{2+}$ | − | +19.5 | +26.1 | +30.8 |
| $Ir(NH_3)_5X^{2+}$ | − | +19 | +22 | +24.2 |

[a] These data are taken from Data Table IX.

A similar variation of $\Delta S^+$ values should appear in the aquation reactions of Data Table I. Although it is not always as clear (as a consequence of the already mentioned scatter of experimental activation data), the expected trend is seen for aquations of $Cr(H_2O)_5 X^{2+}$ (except for $F^-$ which very likely has a different hydrolysis mechanism), $Ru(NH_3)_5X^{2+}$, *cis*-$Ru(en)_2 (H_2O)X^{2+}$, and $Rh(NH_3)_5X^{2+}$.

We deem it important to reiterate here that ideas presented in this review are not necessarily original with us. The correlation of entropies of activation with ground state entropies of free ions in solution has been discussed often,[27] and the relation of this to solvation is expected. Nevertheless, the generality of this entropy correlation is made clear by the data summarized here.

## 10. Isomerization

The change in configuration of an octahedral complex can be related to the lability of the complex towards ligand substitution. Complexes which are labile to substitution tend to be labile to isomerization as well. Also isomerization rates decrease as crystal field stabilization energy in the ground state increases; for example, isomerization rates for cobalt and chromium complexes are measurable but there is little or no evidence for isomerization in the more inert rhodium and iridium complexes.

Isomerization may be a direct consequence of a ligand substitution mechanism; a clear example of this is seen in the mechanistic postulations of Nordmeyer[24b] for chloropentaaminecobalt(III) base hydrolysis. In other cases, isomerization may proceed by a mechanism unrelated to a replacement; the "Bailar twist" mechanism[29] is an example.

In Table X, a set of data for hydrolyses of cobalt and rhodium complexes with chloride ion as leaving group is reported. The striking thing about these numbers, mostly collected by Tobe,[30] is that a positive entropy is accompanied by a considerable steric change (*trans*-reactant goes to *cis*-product). When the value of $\Delta S^+$ is negative, only *trans*-product (*i.e.*, retention of configuration) is obtained.

It is reassuring therefore to see that the numbers in Data Table V on isomerizations (leaving out oxalate complexes, of course) show predominance of positive entropy values. One can conclude that, in order for an isomerization to occur, considerable loosening of the metal–ligand bonding must take place. Such a loosening is expected to decrease bond force constants for both stretching and bending modes and thus to increase the entropy of the reacting system.

It is interesting to observe that for the *trans–cis* isomerization of the complexes $Co(en)_2(OH_2)X^{2+}$, the values of $\Delta S^+$ are always positive and fall generally in the range from +10 to +20 cal mol$^{-1}$ deg$^{-1}$ (see

DATA TABLE V. Isomerization.

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| cis-Cr(OH₂)₄Cl₂⁺ | 0.20 | 0.7 | HClO₄ | $6.2 \times 10^{-5}$ (34.8°C) | – | – | S | 263 |
| trans-Cr(OH₂)₄Cl₂⁺ | 0.20 | 0.7 | HClO₄ | $7.8 \times 10^{-5}$ (34.8°C) | – | – | S | 263 |
| cis-Cr(en)₂(OH)₂⁺ | 0.10 | 10.9–11.4 | en–LiClO₄ | $1.0 \times 10^{-6}$ | 31.4 | 19.4 | S | 262 |
| cis-Cr(en)₂(OH₂)₂³⁺ | 0.01 | 2.0 | HCl | $2.9 \times 10^{-5}$ | – | – | S | 54 |
| trans-Cr(en)₂(OH)₂⁺ | 0.10 | 10.9–11.4 | en–LiClO₄ | $5.1 \times 10^{-6}$ | 26.4 | 5.8 | S | 262 |
| trans-Cr(en)₂(OH₂)₂³⁺ | 0.01 | 2.0 | HCl | $2.2 \times 10^{-5}$ | – | – | S | 54 |
| trans Cr(en)₂(DMSO)Cl²⁺ | – | – | DMSO | $(2.6 \times 10^{-4})$ | 23.2 | 2.9 | S | 367 |
| trans-Cr(en)₂(DMSO)Br²⁺ | – | – | DMSO | $(2.5 \times 10^{-5})$ | 23 | –7 | S | 366 |
| trans-Cr(en)₂(DMSO)₂³⁺ | – | – | DMSO | $(3.0 \times 10^{-6})$ | 22 | –10 | S | 366 |
| trans-Cr(en)₂(DMSO)₂³⁺ | – | – | DMSO | $(9.0 \times 10^{-4})$ | 21.9 | 1.0 | S | 367 |
| trans-Cr(ox)₂(OH)₂³⁻ | 0.10 | ~12 | Na(ClO₄,OH) | $1.9 \times 10^{-2}$ | 13.8 | –20.3 | S | 70 |
| trans-Cr(ox)₂(OH₂)OH²⁻ | 0.10 | ~8 | Na(ClO₄,OH) | $2.0 \times 10^{-3}$ | 14.0 | –23.9 | S | 70 |
| trans-Cr(ox)₂(OH₂)₂⁻ | 1.0 | 3.0 | (H,Na)ClO₄ | $5.9 \times 10^{-4}$ | 17.9 | –13 | S | 265 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | 1.8–4.4 | – | $4.2 \times 10^{-4}$ | 17.5 | –15.3 | S; ox one end dissociation | 264 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | | 50%(w)H₂O–Acetone | $6.5 \times 10^{-5}$ | – | – | S | 368 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | | 50%(w)H₂O–Dioxane | $6.2 \times 10^{-5}$ | – | – | S | 368 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | | 50%(w)H₂O–Methanol | $1.0 \times 10^{-4}$ | – | – | S | 368 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | | 50%(w)H₂O–Ethanol | $7.8 \times 10^{-5}$ | – | – | S | 368 |
| trans-Cr(ox)₂(OH₂)₂⁻ | – | | 50%(w)H₂O–Isopropanol | $9.7 \times 10^{-5}$ | – | – | S | 368 |
| trans-Cr(mal)₂(OH)₂³⁻ | 0.10 | ~12 | Na(OH,ClO₄) | $2.5 \times 10^{-4}$ | 17.9 | –15.1 | S | 70 |
| trans-Cr(mal)₂(OH₂)OH²⁻ | 0.10 | 7–9 | Na(OH,ClO₄) | $1.4 \times 10^{-3}$ | 24.3 | 9.9 | S | 70 |
| trans-Cr(mal)₂(OH₂)₂⁻ | 0.10 | 1.0–3.0 | (Na,H)ClO₄ | $1.8 \times 10^{-6}$ | 31.8 | 21.5 | S | 70 |
| trans-Cr(mal)₂(OH₂)₂⁻ | 1.0 | 2.8 | LiClO₄ | $1.8 \times 10^{-6}$ | 28.7 | 11.3 | S; NO₃⁻ increases k | 330 |
| αβR-Co(tetren)NCS²⁺ | 1.4 | 2.15–2.4 | Na(ClO₄,NCS) CH₃COOH | $3 \times 10^{-8}$ | 30.3 | 6 | S; fast exchange of H on NH group; NCS is N-bonded; isomerization to the αβS form | 283 |
| cis-Co(NH₃)₄(OH₂)₂³⁺ | | | H₂O | $2.7 \times 10^{-4}$ | 24.4 | (7.0) | S | 256 |
| cis-Co(NH₃)₄(OH₂)NO₂²⁺ | | | H₂O | $8.3 \times 10^{-6}$ (30°) | – | – | S | 256 |
| cis-Co(en)₂Cl₂⁺ | – | – | H₂O | $1.9 \times 10^{-5}$ | (41.1) | 57.8 | S | 261 |
| cis-Co(en)₂Cl₂⁺ | – | – | TMS | $(1.2 \times 10^{-7})$ | 25.0 | –6.4 | S | 267 |
| cis-Co(en)₂Cl₂⁺ | – | – | MeOH | $5.3 \times 10^{-5}$ | – | – | S; 35° | 133 |

DATA TABLE V. (Cont.)

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\#}$ | $\Delta S^{\#}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| cis-Co(en)₂Cl₂⁺ | — | — | MeOH | $2.2 \times 10^{-5}$ | 22.8 | 3.5 (−3.3) | S | 268 |
| cis-Co(en)₂Cl₂⁺ | — | — | MeOH | $2.2 \times 10^{-5}$ | — | — | S; Very accurate rate constant | 132 |
| cis-Co(en)₂Cl₂⁺ | — | — | EtOH | $1.7 \times 10^{-5}$ | 22.9 | 3.4 | S | 268 |
| cis-Co(en)₂Cl₂⁺ | — | — | — | $9.2 \times 10^{-6}$ | 20.7 | −12 | S; 2.9<[LiCl]<7.8 | 269 |
| cis-Co(en)₂Br₂⁺ | — | — | DMA | — | 22.5 | — | S | 270 |
| cis-Co(en)₂(OH₂)Cl²⁺ | 0.012 | 1.92 | HClO₄ | $(7.4 \times 10^{-7})$ | 26.4 | 2 | S | 257 |
| cis-Co(en)₂(OH₂)Cl²⁺ | 0.01 | 2.0 | HNO₃ | $2.6 \times 10^{-5}$ | — | — | S | 133 |
| cis-Co(en)₂(OH)₂⁺ | 2.5 | 14 | Na(NO₃,OH) | $3.6 \times 10^{-6}$ | — | — | nmr | 324 |
| cis-Co(en)₂(OH)₂⁺ | (uncontr) | >7 | Na(ClO₄,OH) | $3.6 \times 10^{-6}$ | 28.9 | 13.5 | S | 260 |
| cis-Co(en)₂(NH₃)OH²⁺ | (uncontr) | ~11 | Na(NO₃,OH) | $1.8 \times 10^{-6}$ | — | — | nmr | 324 |
| cis-Co(pn)₂Cl₂⁺ | — | — | MeOH | $2.38 \times 10^{-5}$ | 23.3 | 5.4 (−1.5) | S | 268 |
| cis-Co(pn)₂Cl₂⁺ | — | — | EtOH | $1.0 \times 10^{-5}$ | 23.9 | 5.9 (−1.2) | S | 268 |
| cis-Co(pn)₂Cl₂⁺ | — | — | n-PrOH | $7.26 \times 10^{-6}$ | 24.6 | 6.8 (0.5) | S | 268 |
| trans-Co(en)₂Cl₂⁺ | — | — | TMS | $(1.7 \times 10^{-9})$ | 27.5 | −6.4 | S | 267 |
| trans-Co(en)₂Br₂⁺ | — | — | DMA | — | 24.5 | — | S | 270 |
| trans-Co(en)₂(OH)₂⁺ | 1.0 | 13.7 | Na(NO₃,OH) | $7.6 \times 10^{-6}$ | — | — | S; rate constant is dependent on purity of complex | 254 |
| trans-Co(en)₂(OH)₂⁺ | (uncontr) | >7 | Na(ClO₄,OH) | $2.9 \times 10^{-6}$ | 27.9 | 9.7 | S | 260 |
| trans-Co(en)₂(OH)₂⁺ | 2.5 | 14 | Na(NO₃,OH) | $1.8 \times 10^{-6}$ | — | — | nmr | 324 |
| trans-Co(en)₂(OH)NO₂⁺ | — | ~7 | self-buffering mixtures | $1.7 \times 10^{-7}$ | — | — | S; intramol, rearrang. | 258 |
| trans-Co(en)₂(OH)NH₃²⁺ | 0.10 | 10.2 | — | $2.1 \times 10^{-6}$ | 40.3 | 50.7 | S | 106 |
| trans-Co(en)₂(OH)NH₃²⁺ | (uncontr) | ~11 | Na(NO₃,OH) | $4.3 \times 10^{-6}$ | — | — | nmr | 324 |
| trans-Co(en)₂(OH₂)Cl²⁺ | 0.01 | 2.0 | HNO₃ | $7.1 \times 10^{-5}$ | 26.6 | 11.7 | S | 131 |
| trans-Co(en)₂(OH₂)Cl²⁺ | 0.012 | 1.92 | HClO₄ | $(1.2 \times 10^{-6})$ | 26.4 | 3 | S | 257 |
| trans-Co(en)₂(CH₃OH)Cl²⁺ | 0.01 | — | MeOH | $1.2 \times 10^{-2}$ | 25.4 | (17.8) | S | 266 |
| trans-Co(en)₂Cl(DMF)²⁺ | ~0 | — | DMF | $1.5 \times 10^{-4}$ | 23.6 | 3.0 | S | 205 |
| trans-Co(en)₂Cl(DMSO)²⁺ | ~0 | — | DMSO | $8.5 \times 10^{-5}$ (37.6°) | — | — | S | 205 |
| trans-Co(en)₂(OH₂)Br²⁺ | 0.01 | 2.0 | HNO₃ | $1.63 \times 10^{-4}$ | 26.4 | 12.7 | S | 136 |
| trans-Co(en)₂(OH₂)OH²⁺ | — | — | H₂O | $3.0 \times 10^{-3}$ | 27.5 | 22.2 | S | 131 |
| trans-Co(en)₂(OH₂)₂³⁺ | 0.050–0.10 | 1.3–1.0 | HNO₃ | $1.18 \times 10^{-5}$ | — | — | S; Rate constant is dependent on purity of complex | 254 |
| trans-Co(en)₂(OH₂)₂³⁺ | 1.07 | 0 | (Na,H)(ClO₄,NO₃) | $6.92 \times 10^{-6}$ | — | — | S | 255 |
| trans-Co(en)₂(OH₂)₂³⁺ | 0.8 | — | — | $6.84 \times 10^{-6}$ | 25.6 | 4 | S | 125 |

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| *trans*-Co(en)₂(OH₂)N₃²⁺ | 0.01 | 2.0 | HClO₄ | $7.3 \times 10^{-5}$ | – | – | S | 138 |
| *trans*-Co(en)₂(OH₂)NO₂²⁺ | – | 1–3.6 | – | $1.7 \times 10^{-7}$ | 32.8 | 6.2 (20.5) | S; Intramolecular rearrangement since the OH form has identical rate | 258 |
| *trans*-Co(en)₂(OH₂)NCS²⁺ | – | 0.28–2.16 | – | $6.5 \times 10^{-7}$ | 26.8 | 3.1 | S | 165 |
| *trans*-Co(en)₂(OH₂)NH₃³⁺ | 0.1 | 1.22 | (Na,H)ClO₄ | $1.8 \times 10^{-8}$ | 33.3 | (17.8) | S | 106 |
| *trans*-Co(en)₂(OH₂)(OCOCH₃)²⁺ | 0.1 | 1.0–4.5 | (Na,H)ClO₄ | $2.4 \times 10^{-5}$ | 26.9 | 11.1 | S | 259 |
| *trans*-Co(dipy)₂(OH₂)NO₂²⁺ | 2.5 | 0.2–2.5 | (Na,H)NO₃ | $3.4 \times 10^{-8}$ | 32.9 | 17.7 | S | 169 |
| *cis,cis*-Co(en)(NH₃)₂(OH)₂⁺ | – | 10.3 | Na(Cl,OH) | $4.3 \times 10^{-5}$ | – | – | nmr; *trans, trans* prod. | 324 |
| *trans,cis*-Co(en)(NH₃)₂(OH)₂⁺ | – | 10.3 | Na(Cl,OH) | $1.0 \times 10^{-5}$ | – | – | nmr; *cis, cis* prod. | 324 |
| *trans*-Co(en)(NH₃)₂(OH)₂⁺ | – | 10.3 | Na(Cl,OH) | $3.5 \times 10^{-5}$ | – | – | nmr; *cis, cis* prod. | 324 |
| *trans-RR,SS*-Co(2,3,2-tet)(OH₂)Cl²⁺ | 0.014 | 2.0 | HClO₄ | $3.8 \times 10^{-3}$ | – | – | S | 152 |

DATA TABLE VI. Ligand Isomerization.

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| Cr(OH₂)₅SCN²⁺ | 1.0 | 1.92 | (Na,H)ClO₄ | $4.2 \times 10^{-5}$ | 23.5 | 1.0 | S; $\Delta S^{\neq} = 0.3$ if aquation and isom. proceed through different transition states | 18 |
| *cis + trans*-Cr(H₂O)₄(NCS)(SCN)⁺ | 1.0 | 0–1 | (Na,H)ClO₄ | $8.3 \times 10^{-5}$ | 19.6 | – 9.8 | S; SCN⁻ from S- to N-bonded | 331 |
| Co(NH₃)₅ONO²⁺ | – | – | H₂O | $3.2 \times 10^{-5}$ | 21.9 | – 5.6 | S | 284 |
| Co(NH₃)₅ONO²⁺ | – | – | H₂O | $3.3 \times 10^{-5}$ | 22 | – 5 | S; Intramol. rearrang. | 285 |
| *cis*-Co(NH₃)₄(OH₂)ONO²⁺ | – | – | H₂O | $3.8 \times 10^{-6}$ | – | – | S | 256 |
| *cis*-Co(NH₃)₄(ONO)ONO²⁺ | – | – | H₂O | $2.5 \times 10^{-4}$ (30°) | 7.7 | –49 | S; the final product is *cis*-Co(NH₃)₄(NO₂)₂⁺ | 256 |
| *trans*-Co(en)₂(NCS)ONO⁺ | – | – | H₂O | $1.5 \times 10^{-6}$ | 22.7 | – 8.9 | S | 184 |
| Rh(NH₃)₅ONO²⁺ | – | – | H₂O | $9.6 \times 10^{-4}$ | 18 | –12 | S; Intramol. mech. | 285 |
| Ir(NH₃)₅ONO²⁺ | – | – | H₂O | $4.4 \times 10^{-5}$ | 19 | –14 | S; Intramol. mech. | 285 |

TABLE X. Activation Parameters and Steric Courses of the Reactions[a] *trans*-$(MLACl)^{n+}$ + $H_2O \rightarrow (MLAH_2O)^{n+1}$ + $Cl^-$.

| M | L | A | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | % steric change |
|---|---|---|---|---|---|
| Co | (en)₂ | OH | 25.6 | +14.6 | 75 |
| Co | (en)₂ | Cl | 27.5 | +13.1 | 35 |
| Co | (en)₂ | Br | 24.6 | + 4.1 | 50 ± 5 |
| Co | (en)₂ | NCS | 29.8 | + 7.8 | 60 ± 10 |
| Co | SS-trien | Cl | 25.4 | +15.3 | 100 |
| Co | RR,SS-2,3,2-tet | Cl | 25.9 | +12 | 50 ± 20 |
| Co | (en)₂ | N₃ | 20.7 | − 6 | 0 |
| Co | (en)₂ | NH₃ | 23.0 | −11 | 0 |
| Co | (en)₂ | CN | 22.0 | − 3.4 | 0 |
| Co | (en)₂ | NO₂ | 20.9 | − 2.2 | 0 |
| Co | cyclam | OH | 18.8 | − 4.2 | 0 |
| Co | cyclam | Cl | 24.3 | − 4.3 | 0 |
| Co | RS-2,2,2-tet | Cl | 24.3 | + 1 | 0 |
| Rh | en₂ | Cl | 24.7 | − 9 | 0 |
| Rh | en₂ | Br | 23.2 | −11.7 | 0 |
| Rh | en₂ | I | 21.1 | − 7.5 | 0 |

[a] The values of $\Delta H^{\ddagger}$ quoted in this table are generally reliable to better than ±0.5 kcal mol⁻¹ and the $\Delta S^{\ddagger}$ to better than ±1.5 cal mol⁻¹ deg⁻¹. The numbers in this table have been taken from Data Table I wherein original sources are given.

Data Table XIV). We estimate that the contribution to $\Delta S^{\ddagger}$ from the dissociation of a water molecule should be near to +7 cal mol⁻¹ deg⁻¹. This seems to suggest that the isomerization proceeds through a dissociative mechanism involving cleavage of the metal–water bond and subsequent rearrangement of the pentacoordinate complex. Owing to the fact that some degrees of freedom not present in the octahedral reactant are acquired by the pentacoordinate intermediate, the observed $\Delta S^{\ddagger}$ values are in agreement with the dissociation of a bound water.

A dissociative mechanism is also consistent with the postulation that, in the hydroxo complexes $Co(en)_2$ $(OH)_2^+$ and $Co(en)_2(OH)(NH_3)^{2+}$, the isomerization involves dissociation of one end of the ethylenediamine chelate link.

There are some interesting observations on the isomerizations of anionic chromium complexes with oxalato and malonato ligands. The relevant numbers are given in Table XI. The differences in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are large enough to signal a change in mechanism.

One possible explanation is that the oxalate complexes isomerize through a cleavage of the chelate ring assisted by solvent water molecules. The negative values of $\Delta S^{\ddagger}$ led to the suggestion of water participation and this recently has been supported by the activation volume of the reaction (see Data Table XX).

For malonato complexes, the high values of $\Delta H^{\ddagger}$ and the positive values of $\Delta S^{\ddagger}$ (when one ligand is water) suggest that the isomerization proceeds through dissociation of a coordinated water molecule or spontaneous opening of the chelate ring without any participation of the solvent. However, the observation that *trans*- $Cr(mal)_2(OH)_2^-$ shows activation parameters analogous to the oxalato complexes and the consideration that the malonato six-membered ring should be more inert than the five-membered ring indicates that the mechanism involving dissociation of the water molecule is to be preferred.

## 11. Ligand Isomerization

The change in point of attachment of a ligand at the ligand–metal bond is a matter of considerable interest because the factors which govern the position of bonding, as in the case

$$M{-}O{-}N\diagdown_O \;\;\rightleftharpoons\;\; M{-}N\diagup^O_{\diagdown O}$$
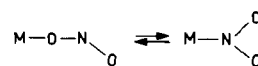
are not at all clear. For thiocyanate ion, isomerization in both directions is accompanied by a positive entropy, suggesting metal to ligand loosening in the transition state. By way of comparison, isomerization of nitrito complexes to the nitro form (as in the equation above) occurs with a negative value of $\Delta S^{\ddagger}$. This suggests that the transition state is more restricted in conformation than is the reactant. A configuration such as

TABLE XI. Isomerization Reactions of *trans*-$Cr(AA)_2XY$.[a,b,c]

| Complex | ox | | mal | | mal–ox | |
|---|---|---|---|---|---|---|
| | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\delta\Delta H^{\ddagger}$ | $\delta\Delta S^{\ddagger}$ |
| $Cr(AA)_2(H_2O)_2^-$ | 17.9 | −13 | 31.8 | +21.5 | 13.9 | +34.5 |
| $Cr(AA)_2(OH)(H_2O)^{2-}$ | 14.0 | −23.9 | 24.3 | + 9.9 | 10.3 | +33.8 |
| $Cr(AA)_2(OH)_2^{3-}$ | 13.8 | −20.3 | 17.9 | −15.1 | 6 | + 5.2 |

[a] The symbols are defined as follows: ox = oxalate, mal = malonate, AA represents both of the bidentate ligands, and X and Y represent $H_2O$ and/or $OH^-$. [b] The reaction is *trans* to *cis* isomerization. [c] Data taken from Data Table Ref. 70.

M⎯⎯⎯⎯N⎯O (diagram)
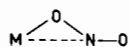
for the transition state is possible. The available data are presented in Data Table VI.

## 12. Racemization

Coordination compounds with three bidentate ligands (or with related configurations) can exist in optically-active forms. Thus, for example, it is possible to have a D-$Cr(ox)_3^{3-}$ and L-$Cr(ox)_3^{3-}$. The racemization process (which is a type of isomerization) leads to the d,l-mixture. This process can occur more rapidly, at the same rate, or more slowly than exchange of ligands with those in the surrounding medium. Some data on the racemization process for a variety of complexes are given in Data Table VII.

With one significant exception, the data are too limited to allow worthwhile discussion. The exception is the group of chromium(III) oxalate complexes. The activation entropies are very close to those for *cis-trans* isomerization of chromium(III) oxalate complexes. This suggests a common mechanism for racemization and isomerization. A possibility might be as follows:

$$Cr(ox)_3^{3-} + H_2O \rightleftharpoons (ox)_2\,Cr\underset{OH}{\overset{\displaystyle |}{-}}O\overset{O}{\overset{\|}{-}}C\overset{O}{\overset{\|}{-}}C-OH$$

with the intermediate species able (a) to add water to the carbonyl group of the monodentate oxalate and accomplish hydrolysis, (b) to reform into the opposite optical form, (c) to add another oxalate and accomplish exchange, *etc.* These mechanisms have been discussed in some detail in the references given in the Data Table and also in reference 25a.

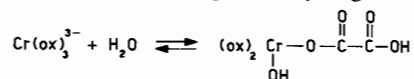Some cobalt(III) racemizations, including Co$(ox)_3^{3-}$, show positive values of $\Delta S^{\ne}$, whereas for the chromium complexes negative values have been found. This sharp difference in the entropy of activation values can be explained on the basis of some recent studies of the exchange between water and the bound oxalato ligand.[31] Although a definite mechanism for reaction of the cobalt(III) complexes could not be offered, any mechanism such as that suggested for the chromium complexes (equation above) can be ruled out on the basis of the difference in $\Delta S^{\ne}$ values alone.

Also the negative entropy values for racemizations of $Cr(ox)_2(NN)^-$ and $Co(ox)(NN)_2^+$ complexes may involve attack of water at the carbonyl carbon (see next section and Data Table XVII).

## 13. Ambiguity in Site of Attack

When a nucleophile reacts with a coordination compound, it is generally assumed (often implicitly) that the prime interaction is between metal atom and nucleophile. This is usually the case (albeit the interaction may be weak), but there are unquestioned exceptions. For example, the reaction

$$Co(NH_3)_5OCOR^{2+} + OH^- \rightleftharpoons$$
$$Co(NH_3)_5OH^{2+} + RCO_2^-$$
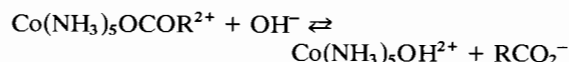
can proceed by direct nucleophilic attack on carbonyl carbon as well as by attack at metal or as by $S_N1CB$ mechanisms. The distinction between the possibilities can be made by an isotope tracer experiment, for the bimolecular reaction of the equation above with labeled hydroxide ion would yield labeled acetate and unlabeled $Co(NH_3)_5OH^{2+}$. The alternative mechanisms ($S_N1CB$ and direct displacement on cobalt) would yield unlabeled acetate and labeled complex. Electronic effects and activation entropies also are helpful in making these mechanistic assignments.

The alkaline hydrolysis of cobalt(III) carboxylato complexes has a complicated rate law with one rate term of form

$$v = k[Co(NH_3)_5OCOR^{2+}][OH^-]$$

For this term, the rate constants are similar to those for loss of other ligands from the cobalt coordination sphere and rather small electronic and steric effects are found.[32,33] Study of the alkaline hydrolysis of the first displaced benzoato ligand in some *trans*-Co(en)$_2$ (OCOC$_6$H$_4$X)$_2^+$ ions indicated that the Hammett equation is followed with a reaction constant $\varrho$ of 0.745.[33c] This is significantly less than the value of about +2 expected for OH$^-$ attack at carbonyl carbon. Mass spectrometric investigations of the benzoate product from base hydrolysis of Co(en)$_2$(OCOAr)$_2^+$ in $^{18}$O enriched water showed no enrichment therein,[33e] thus the cobalt–oxygen bond is cleaved in the reaction. The values of $\Delta S^{\ne}$ observed for base hydrolysis of *cis*- and *trans*-Co(en)$_2$(OCOCH$_3$)$_2^+$ are the +18.4 and +22.4 cal mol$^{-1}$ deg$^{-1}$;[33g] the sign and magnitudes are fully consistent with the $S_N1CB$ mechanism.

When the carboxylato ligand has a strong electron-attracting group attached to the carbonyl center, a second rate law term is observed and a new mechanism intrudes. The complex Co(NH$_3$)$_5$OCOCF$_3^{2+}$ hydrolyzes with the law

$$v = \{k_1[OH^-] + k_2[OH^-]^2\}[Co(NH_3)_5OCOCF_3^{2+}]$$

with the new term being second-order in base concentration.[34] For the first term, values of 22.7 kcal mol$^{-1}$ and +10 cal mol$^{-1}$ deg$^{-1}$ were obtained for $\Delta H^{\ne}$ and $\Delta S^{\ne}$, respectively; again these are consistent with the $S_N1CB$ path. For the second term, the respective values are 6.8 kcal mol$^{-1}$ and −37 cal mol$^{-1}$ deg$^{-1}$ which suggest considerable bond formation. Tracer studies showed that the $k_1$ path takes place with cobalt–oxygen bond breaking and the $k_2$ path

DATA TABLE VII. Racemization.

| Complex | $\mu(M)$ | pH | Medium | k | $\Delta H^{\neq}$ | $\Delta S^{\neq}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|
| Cr(ox)$_3^{3-}$ | – | – | H$_2$O | $3.1 \times 10^{-4}$ | 15.2 | −23.7 | P$_M$ | 272 |
| Cr(ox)$_3^{3-}$ | 1.0 | 0 | HClO$_4$ | $1.4 \times 10^{-2}$ | – | – | P$_M$ | 297 |
| cis-Cr(ox)$_2$(OH$_2$)$_2^-$ | – | 2.5–7 | HClO$_4$ | $3.3 \times 10^{-4}$ | 13.4 | −28 | P$_M$ | 275 |
| cis-Cr(ox)$_2$(OH$_2$)$_2^-$ | 1.0 | 2.6–7 | (H,Na)ClO$_4$ | $4.3 \times 10^{-4}$ | 13.4 | −29 | P$_M$ | 276 |
| Cr(ox)$_2$(en)$^-$ | – | – | H$_2$O | $2.1 \times 10^{-3}$ | 15.2 | −19.8 | P$_M$ | 272 |
| Cr(ox)$_2$(dipy)$^-$ | 1.0 | 0 | HCl | $5.3 \times 10^{-4}$ | 17.8 | −13.8 | P$_M$ | 273 |
| Cr(ox)$_2$(dipy)$^-$ | – | – | H$_2$O | $2.1 \times 10^{-4}$ | 15.5 | −24 | P$_M$ | 274 |
| Cr(ox)$_2$(dipy)$^-$ | 0.1 | 1.0 | HCl | $2.3 \times 10^{-4}$ | 17.1 | −21(−18) | P$_M$ | 274 |
| Cr(ox)$_2$(dipy)$^-$ | 0.9 | 14 | KOH | $1.3 \times 10^{-3}$ | 15.3 | −19 | P$_M$ | 274 |
| Cr(ox)$_2$(phen)$^-$ | – | – | H$_2$O | $2.3 \times 10^{-4}$ | 17.4 | −17 | P$_M$ | 274 |
| Cr(ox)$_2$(phen)$^-$ | 0.1 | 1.0 | HCl | $3.0 \times 10^{-4}$ | 17.3 | −17 | P$_M$ | 274 |
| Cr(ox)$_2$(phen)$^-$ | 0.9 | 14 | KOH | $1.6 \times 10^{-3}$ | 15.2 | −21 | P$_M$ | 274 |
| Cr(ox)$_2$(phen)$^-$ | 1.0 | 0 | HCl | $6.4 \times 10^{-4}$ | 17.7 | −13.7 | P$_M$ | 273 |
| Cr(ox)(en)$_2^+$ | 1.0 | 0 | HCl | $1.7 \times 10^{-5}$ | 20.5 | −12.0 | P$_M$; k includes aquation | 281 |
| Cr(ox)(bipy)$_2^+$ | 1.0 | 0 | HCl | $3.2 \times 10^{-5}$ | 19.0 | −14.5 | P$_M$ | 281 |
| Cr(ox)(phen)$_2^+$ | 1.0 | 0 | HCl | $2.1 \times 10^{-5}$ | 19.8 | −13.6 | P$_M$ | 281 |
| (+)-trans-Co(dien)$_2$ (?) | 2.0 | 7.1–8.27 | NaNO$_3$ + HNO$_3$, collidine buffer | 62 | 23.5 | 29 | P$_M$; OH$^-$ induces racemiz.; k is 2nd order (k$_{obs}$/[OH$^-$]) rate constant. | 341 |
| l-cis-Co(en)$_2$Cl$_2^+$ | 0.002–0.09 | – | MeOH, LiCl | $3.6 \times 10^{-5}$ | 22.0 | − 5.1 | P$_M$ | 282 |
| (+)-cis-Co(en)$_2$(NH$_3$)OH$_2^{3+}$ | – | 1.0 | HClO$_4$ | $2.1 \times 10^{-8}$ | 27.7 | (−0.7) | P$_M$ | 106 |
| (+)-cis-Co(en)$_2$Cl(OH$_2$)$^{2+}$ | 0.012 | 1.92 | HClO$_4$ | $1.4 \times 10^{-6}$ | 26.1 | 2.3 | P$_M$ | 257 |
| (+)-CoEDTA$^-$ | – | 2–4 | HNO$_3$ + nitrates | $4.0 \times 10^{-12}$ | 40.0 | 20.6 (23.5) | P$_M$; Intramol. rearrang. | 271 |
| Co(ox)$_3^{3-}$ | – | – | H$_2$O | $2.9 \times 10^{-5}$ | 25.4 | 6.0 | P$_M$ | 272 |
| Co(ox)$_3^{3-}$ | 1 | 0 | HCl | $1.8 \times 10^{-5}$ | 28.1 | 14.1 | P$_M$; the one-ended dissociation is excluded. The exchange | 344 |
| Co(ox)$_3^{3-}$ | – | – | H$_2$O | $1.9 \times 10^{-5}$ | 26.5 | 8.8 | P$_M$ of the more labile (carbonyl) oxygens has $\Delta H^{\neq}$ = 16.3, $\Delta S^{\neq}$ = −19.9 | 344 |
| Rh(ox)$_3^{3-}$ | 0.54 | 0.4–7.0 | (Na,H)ClO$_4$ | $8.7 \times 10^{-7}$ | <u>23.3</u> | <u>− 8.2</u> | P$_M$ | 342 |
| Rh(ox)$_3^{3-}$ | 0.54 | 0.4–7.0 | (Na,H)ClO$_4$ | $2.8 \times 10^{-6}$ | <u>26.8</u> | + 5.8 | P$_M$; H$^+$ induced racemization, k is 2nd order (k$_{obs}$/[OH$^-$]) rate constant. | 342 |

with carbon–oxygen bond breaking. The postulated mechanism is

$$(NH_3)_5Co^{2+}\!-\!O\!-\!\underset{\underset{O}{|}}{\overset{\overset{CF_3}{|}}{C}}\!-\!OH^-\!-\!-OH^- \longrightarrow (NH_3)_5CoO^+ + \underset{O\diagdown\!\diagup O^-}{\overset{CF_3}{\underset{|}{C}}} + H_2O$$
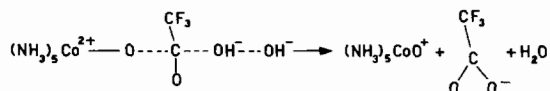
The base hydrolysis of a series of carboxylatopenta-amminerhodium(III) complexes shows the same general behavior.[35] If the R group of RCOO⁻ ligand is H, CH₃, CH₂F, or CHF₂, both the enthalpy and the entropy of activation related to the $k_1$ path are virtually insensitive to the nature of R and are in agreement with the $S_N1CB$ mechanism. When R is a powerful electron-attracting group like CCl₃ or CF₃, both the enthalpy and the entropy of activation values are lower, as can be seen in Table XII.

This fact together with an observed deviation in an otherwise linear $\log k_1$ *versus* $pK_a$ plot (where $K_a$ is the dissociation constant for the acid RCOOH) suggest a change in mechanism from the $S_N1CB$ to a bimolecular attack on the carbonyl carbon of the carboxylato ligand. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values of the $k_2$ path are consistent with the proposed termolecular mechanism with C–O bond breaking.

Also consistent with the above mechanistic hypotheses are the facts that the $k_1$ term depends on the nature of the metal whereas the $k_2$ term does not so depend; in some instances comparison is not possible. Data relevant to the postulated mechanisms for reactions of the type

$$M(NH_3)_5OCOCF_3{}^{2+} + OH^- \longrightarrow$$
$$M(NH_3)_5OH^{2+} + CF_3CO_2{}^-$$
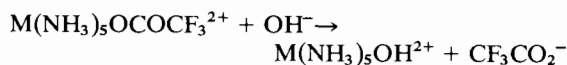
are as follows:

a) The rate constants at $25°C$ for the first term $(k_1)$ are $1.6 \times 10^{-2}$, $1.0 \times 10^{-3}$, and $5 \times 10^{-4} M^{-1}$ sec⁻¹ for Co, Rh, and Ir, respectively;

b) The rate constants for the second term $(k_2)$ are $5.0 \times 10^{-1}$, $2.9 \times 10^{-1}$ and $2.7 \times 10^{-1} M^{-2}$ sec⁻¹ for the three metals, respectively. The expectations are

fulfilled,[35] for the values of $k_1$ change by a factor of 16 on going from Co to Rh and by a factor of 2 on going from Rh to Ir. On the other hand, the overall change in $k_2$ values is less than a factor of two.

Some other possible examples of attack at carbonyl carbon include:

a) Cr(NH₃)₅OCOCF₃, aquation, $\Delta S^{\neq} = -25$;

b) *trans*-Cr(ox)₂(H₂O)OCOCH₃²⁻, aquation, $\Delta S^{\neq} = -18.8$;

c) *trans*-Cr(ox)₂(OH)OCOCH₃³⁻, aquation, $\Delta S^{\neq} = -38.8$;

d) *trans*-Cr(ox)₂(H₂O)₂⁻, isomerization, $\Delta S^{\neq} = -14$; and

e) Cr(ox)₂(NN)⁻, where NN is en, dipy, phen, or ox, racemization, average $\Delta S^{\neq} \simeq -20$.

A carboxylato ligand when bound as a monodentate ligand has two distinct oxygen environments. Thus exchange between the carbonyl carbon and water without concomitant hydrolysis is possible. Unless properly accounted for, the isotope data obtained in the hydrolysis reactions can be misleading. This danger is not so severe, generally, as to vitiate the conclusions given above on the position of bond cleavage.

Although this ambiguity is most often seen with complexes having carboxylato ligands, it is not limited to them. Some other ligands that can show similar electrophilic behavior are acetylacetonate, nitrito, nitro, carbonato, nitrato, phosphato, arsenato, perrhenato, iodato, etc.

## 14. Second-Order Anations

The anation process which is the interchange reaction involving a solvent molecule as leaving group in the coordination shell and an entering ligand (often an anion, thus anation)

$$ML_5H_2O^{3+} + X^- \rightleftarrows ML_5X^{2+} + H_2O$$
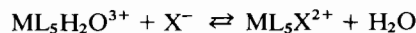
is the reverse of aquation. Since there is no reason to believe that water in the coordination sphere is essentially different from other ligands, it seems reasonable to assume that microscopic reversibility holds and that a dissociative interchange mechanism is probable for anation of aquocobalt(III) complexes. Whatever the cause may be, the data given in Data Table VIII are not very convincing as to this point. There is considerable variability in the numbers for the same reaction from different research groups. In part, this may be due to the nature of the anation process which is postulated to be a two-step sequence

$$ML_5H_2O^{3+} + X^- \rightleftarrows \{ML_5H_2O^{3+} \cdot X^-\} \qquad \text{(fast)}$$
$$\{ML_5H_2O^{3+} \cdot X^-\} \rightarrow ML_5X^{2+} + H_2O \qquad \text{(rate)}$$
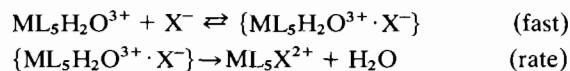
with the first step being a rapid ion-pair formation and the second step being the slow interchange. If there

TABLE XII. Activation Parameters[a] for Base Hydrolysis of Pentaamminerhodium(III) Carboxylato Complexes.[b]

| R | Path I | | Path II | |
|---|---|---|---|---|
| | $\Delta H_1^{\neq}$ | $\Delta S_1^{\neq}$ | $\Delta H_2^{\neq}$ | $\Delta S_2^{\neq}$ |
| CF₃ | 18.0 | −13 | 7.5 | −36 |
| CCl₃ | 26.4 | 14 | 8.4 | −39 |
| CHF₂ | 30.1 | 22 | 10.5 | −32 |
| CH₂F | 31.9 | 26 | 19.1 | −17 |
| H | 33.2 | 28 | 25.6 | 2 |
| CH₃ | 31.9 | 22 | | |

[a] The average precision of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are ±0.5 kcal/mole and ±2 cal mol⁻¹ deg⁻¹ respectively. [b] Data of reference 35.

DATA TABLE VIII. Anation (Interchange); 2nd-Order Rate Constants.

| Compound | Replacing Ligand | $\mu(M)$ | pH | Ionic Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|---|
| $V(H_2O)_6^{3+}$ | $SCN^-$ | 1.0 | - | $(Na,H)ClO_4$ | $1.0\times10^{+2}$ (23°C) | - | - | $S_{TI}$ | 286 |
| $V(H_2O)_6^{3+}$ | $SCN^-$ | 1.0 | - | $(Na,H)ClO_4$ | $1.1\times10^{+2}$ | 7.6 | $-23.8$ | $S_{SF}$ | 1 |
| $V(DMSO)_6^{3+}$ | $NCS^-$ | 0.15 | - | DMSO | $2.1\times10^{+2}$ | - | $-25$ | $S_{SF}$ | 202 |
| $V(DMSO)_6^{3+}$ | dipy | - | - | DMSO | $1.1\times10^{-1}$ | 11.7 | - | $S_{SF}$ | 202 |
| $V(DMSO)_6^{3+}$ | SSA | - | - | DMSO | $2.1\times10^{-1}$ | - | - | $S_{SF}$ | 202 |
| $Cr(H_2O)_6^{3+}$ | $NCS^-$ | 0(ext) | - | - | $1.1\times10^{-5}$ | 25.4 | 4.0 | S | 17 |
| $Cr(H_2O)_6^{3+}$ | $H_3PO_2$ | 1.0 | 0.7–0 | $(Na,H)ClO_4$ | $3.0\times10^{-5}$ | 20.3 | $-11.2$ | S | 211 |
| $Cr(H_2O)_6^{3+}$ | $NH_2$ | - | - | none | $6.2\times10^{-7}$ | (21.4) | (−15.0) | S | 289 |
| | $CONH_2$ | | | | | | | | |
| $Cr(H_2O)_6^{3+}$ | $^-OCOCH_3$ | 0.1 | 4.85 | $KNO_3$ | - | 21.0 | - | P | 290 |
| $Cr(H_2O)_6^{3+}$ | $ox^{2-}$ | 0.1 | 4.85 | $KNO_3$ | - | 23.2 | - | P | 290 |
| $Cr(H_2O)_6^{3+}$ | $oxH_2$ | 2.0 | <0.7 | $(Na,H)ClO_4$ | $4.7\times10^{-6}$ | 29.0 | 14.1 | S | 291 |
| $Cr(H_2O)_6^{3+}$ | $mal^{2-}$ | 0.1 | 4.85 | $KNO_3$ | - | 22.4 | - | P | 290 |
| $Cr(H_2O)_6^{3+}$ | $malH^-$ | 1.0 | - | - | $1.0\times10^{-5}$ | 24.4 | $-0.1$ | P | 292 |
| $Cr(H_2O)_6^{3+}$ | citrate | 0.1 | 4.85 | $KNO_3$ | - | 22.2 | - | P | 290 |
| $Cr(H_2O)_6^{3+}$ | $o$-phthalate | 0.1 | 4.85 | $KNO_3$ | - | 22.4 | - | P | 290 |
| $cis$-$Cr(H_2O)_4Cl(OH_2)^{2+}$ | $Cl^-$ | 1(7) | - | - | $9.8\times10^{-7}$ | - | - | S; k obtained by using rate consts. at $\mu = 1$ and eq. ratio at $\mu = 7$ | 27 |
| $trans$-$Cr(H_2O)_4Cl(OH_2)^{2+}$ | $Cl^-$ | 1(7) | - | - | $9.8\times10^{-7}$ | - | - | S; k obtained by using rate consts. at $\mu = 1$ and eq. ratio at $\mu = 7$ | 27 |
| $Cr(NH_3)_5OH_2^{3+}$ | $Cl^-$ | 0.52 | <3 | $NaClO_4$ | $1.6\times10^{-6}$ | 24.0 | $-4.5$ | S | 43 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $Cl^-$ | 0.106 | 1.3 | $Na(ClO_4,Cl)$ | $3.5\times10^{-6}$ | _26.6_ | _7_ | S | 34 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $Cl^-$ | 1.71 | 1.3 | $Na(ClO_4,Cl)$ | $1.4\times10^{-6}$ | 25.6 | _2_ | S | 34 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $NCS^-$ | 0.106 | 1.3 | $Na(ClO_4,Cl)$ | $2.4\times10^{-5}$ | _24.2_ | _3_ | S | 34 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $NCS^-$ | 1.71 | 1.2 | $Na(NCS,Br)$ | $1.2\times10^{-5}$ | _27.2_ | _9_ | S | 34 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $NCS^-$ | - | 2 | $(Na,H)(ClO_4,NCS)$ | $(8\times10^{-7})$ | 23.4 | $-5.9$ | S | 287 |
| $cis$-$Cr(en)_2Cl(OH_2)^{2+}$ | $Cl^-$ | 10.9 | - | HCl | $1.3\times10^{-4}$ (35°C) | - | - | S | 288 |
| $trans$-$Cr(en)_2Cl(OH_2)^{2+}$ | $Cl^-$ | 10.2 | - | HCl | $1.7\times10^{-5}$ (35°C) | - | - | S | 288 |
| $cis$-$Cr(en)_2(DMSO)_2^{3+}$ | $Cl^-$ | 0–0.031 | - | DMSO | $(9.6\times10^{-2})$ | 19.4 | 1.9 | S | 367 |
| $cis$-$Cr(en)_2(DMSO)_2^{3+}$ | $Br^-$ | 0–0.45 | - | DMSO | $(5.3\times10^{-6})$ | 30 | 18 | S | 366 |
| $cis$-$Crox_2(H_2O)_2^-$ | $oxH^-$ | 0.5 | 2.7 | $(n\text{-}Bu)_4NBr$ $(Na,H)$ $(ClO, \frac{ox}{2})$ | - | 21.7 | - | S; $\Delta H^{\ddagger}$ refers to the variation with temp of the observ. k measured when $[oxH^-] \equiv 0.1M$ | 293 |

| Complex | ox²⁻ | I / [Cl⁻] | pH | Medium | k | ΔH‡ | ΔS‡ | S; ΔH‡ refers to the variation with temp. of the obs. k measured when [ox²⁻] = 0.1M | Ref |
|---|---|---|---|---|---|---|---|---|---|
| cis-Crox₂(H₂O)₂⁻ | ox²⁻ | 0.5 | 6.0 | (Na,H)(ClO₄, $\frac{ox}{2}$) | — | 21.7 | — | | 293 |
| Fe(H₂O)₆³⁺ | Cl⁻ | 1.0 | →7 | NaClO₄ | 9.4 | 16.6 | 2 | S$_{FM}$ | 299 |
| Fe(H₂O)₆³⁺ | NCS⁻ | 0.40 | 0.7–1.5 | (Na,H)ClO₄ | $1.3 \times 10^{+2}$ | 13.0 | −5 | S$_{FM}$ | 76 |
| Fe(H₂O)₆³⁺ | oxH⁻ | 0.03–0.45 | 0.50 | NaClO₄ | $1.4 \times 10^{+3}$ | 18 | 16 | S | 298 |
| Fe(H₂O)₆³⁺ | SO₄²⁻ | 0.5 | 0.7–1.3 | { (Na,H)ClO₄ Na₂SO₄ } | $6.4 \times 10^{+3}$ | 18.0 | 19.4 | S$_{SF}$ | 296 |
| Fe(H₂O)₆³⁺ | HN₃ | 1.0 | 0 | HClO₄ | $4.0 \times 10^{3}$ | — | — | S$_{SF}$ | 300 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | Cl⁻ | 1.0 | 0–1.2 | (Na,H)ClO₄ | $1.1 \times 10^{4}$ | 13.1 | 3.9 | S$_{FM}$ | 299 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | NCS⁻ | 0.40 | 0–1.5 | (Na,H)ClO₄ | $1.0 \times 10^{4}$ | 10.0 | −6.7 | S$_{FM}$ | 299 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | CH₃COOH | 0.50 | 0.5–1.5 | (Na,H)ClO₄ | $2.8 \times 10^{3}$ | 11.1 | 5.4 | S$_{SF}$ | 351 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | HN₃ | 1.0 | 0 | HClO₄ | $6.8 \times 10^{+3}$ | — | — | S$_{SF}$ | 300 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | H₂Sal | 1.0 | 0.2–2 | KNO₃ | $5.5 \times 10^{+3}$ | 12 | −2 | S$_{SF}$ | 301 |
| Fe(H₂O)₄(OH)(OH₂)²⁺ | HSal⁻ | 1.0 | 0.2–2 | KNO₃ | $1.4 \times 10^{+4}$ | 11 | −3 | S$_{SF}$ | 301 |
| Fe(CN)₅OH₂²⁻ | NCS⁻ | 1.0 | 1.0–1.7 | (Na,H)(ClO₄,NCS) | $2.0 \times 10^{-2}$ | — | — | S | 322 |
| Co(NH₃)₅OH₂³⁺ | Cl⁻ | 1.0 | 3.0 | Na(ClO₄,Cl) | $6.5 \times 10^{-5}$ (45°C) | — | — | S | 303 |
| Co(NH₃)₅OH₂³⁺ | Cl⁻ | 0.1 | 2.0 | K(ClO₄,Cl) | $2.8 \times 10^{-6}$ | _24.1_ | _−3.2_ | S; (2T, 10° range) | 88 |
| Co(NH₃)₅OH₂³⁺ | N₃⁻ | 0.5 | 4.0–4.9 | Na(ClO₄,N₃) | $1.7 \times 10^{-6}$ | 26.9 | 5.2 | S | 304 |
| Co(NH₃)₅OH₂³⁺ | NCS⁻ | 1.0 | 5.0 | Na(ClO₄,NCS) | $6.9 \times 10^{-6}$ (45°C) | — | — | S | 303 |
| Co(NH₃)₅OH₂³⁺ | H₂PO₄⁻ | — | — | H₂O | $2.2 \times 10^{-6}$ (45°C) | — | — | S | 81 |
| Co(NH₃)₅OS₂O₂⁺ | Cl⁻ | 1.0 | — | (K, $\frac{Ba}{2}$, $\frac{La}{3}$)Cl | $7.3 \times 10^{-7}$ | 14.7 | −37.7 | T | 103 |
| Co(NH₃)₅OS₂O₂⁺ | NH₃ | 1.0 | — | NH₄NO₃ | $1.4 \times 10^{-7}$ | 12 | −49.3 | T | 103 |
| cis-Co(en)₂(NH₂Et)(OH₂)³⁺ | Cl⁻ | 0.001 | — | HNO₃ | $8.5 \times 10^{-10}$ | 34.2 | 28.4 (14.6) | T | 113 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $4.1 \times 10^{-3} M$ | — | DMA | — | 25.9 | — | S | 306 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $3.8 \times 10^{-2} M$ | — | DMA | — | 26.9 | — | S | 306 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $4.0 \times 10^{-3} M$ | — | TMS | — | 25.9 | — | S | 306 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $9.15 \times 10^{-2} M$ | — | TMS | — | 28.4 | — | S | 306 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $7.1 \times 10^{-3} M$ | — | DMF | — | 26.9 | — | S | 306 |
| cis-Co(en)₂Cl(DMSO)²⁺ | Cl⁻ | [Cl⁻]= $5.3 \times 10^{-2} M$ | — | DMF | — | 26.9 | — | S | 306 |
| cis-Co(en)₂Br(DMF)²⁺ | Br⁻ | — | — | DMF | — | 33.4 | — | S | 270 |
| cis-Co(en)₂Br(DMA)²⁺ | Br⁻ | — | — | DMA | — | 33.4 | — | S; Products are cis and trans | 270 |

DATA TABLE VIII. (Cont.)

| Compound | Replacing Ligand | $\mu(M)$ | pH | Ionic Medium | k | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | Comments | Table Ref. No. |
|---|---|---|---|---|---|---|---|---|---|
| cis-Co(en)₂Br(DMA)²⁺ | Br⁻ | — | — | DMA | — | 18.4 | — | S; 100% trans prod. | 270 |
| trans-Co(DH)₂I(OH₂) | Br⁻ | 1.0 | 2.5–2.9 | KNO₃ | $3.0 \times 10^{-4}$ | 17.8 | −14 | S | 307 |
| trans-Co(DH)₂I(OH₂) | HSO₃⁻ | 1.0 | 2.7–3.1 | KNO₃ | $3.4 \times 10^{-3}$ | 14.4 | −21 | S | 307 |
| trans-Co(DH)₂NO₂(OH₂) | Br⁻ | 1.0 | 3.0–4.7 | KNO₃ | $1.6 \times 10^{-4}$ | 22.5 | 0 | S | 307 |
| trans-Co(DH)₂NO₂(OH₂) | NCS⁻ | 1.0 | 3.7–6.0 | KNO₃ | $5.8 \times 10^{-4}$ | 19.1 | −9 | S | 307 |
| trans-Co(DH)₂NO₂(OH₂) | N₃⁻ | 1.0 | 5.1–5.9 | KNO₃ | $5.7 \times 10^{-3}$ | 16.2 | −19 | S | 307 |
| trans-Co(DH)₂NO₂(OH₂) | HSO₃⁻ | 1.0 | 4.1–4.5 | KNO₃ | $8.5 \times 10^{-3}$ | 15.0 | −17 | S | 307 |
| Co(DH)₂(CH₃)(OH₂) | Py | — | — | Py | $6.8 \times 10^{-1}$ | 20.5 | 19(9.5) | S_SF | 294 |
| Co(DH)₂(CH₃)(OH₂) | NCS⁻ | — | — | NaNCS | 1.5 | 17.5 | 10 (1.0) | S_SF | 294 |
| Ru(NH₃)₅OH₂³⁺ | Cl⁻ | 0.26 | 1.0 | (Na,H)Cl | $2.1 \times 10^{-3}$ (54.7°C) | — | — | S | 310 |
| Ru(NH₃)₅OH₂³⁺ | Br⁻ | 0.26 | 1.0 | (Na,H)Br | $1.3 \times 10^{-3}$ (54.7°C) | — | — | S | 310 |
| Ru(NH₃)₅OH₂³⁺ | I⁻ | 0.26 | 1.0 | NaI | $7.4 \times 10^{-4}$ (54.7°C) | — | — | S | 310 |
| cis-Ru(en)₂(OH₂)₂³⁺ | Cl⁻ | 0.26 | 0.6 | (Na,H)Cl | $2.5 \times 10^{-3}$ | 18.8 | − 7.3 | S | 310 |
| cis-Ru(en)₂(OH₂)₂³⁺ | Br⁻ | 0.26 | 0.6 | (Na,H)Br | $1.8 \times 10^{-3}$ | 19.6 | − 5.3 | S | 310 |
| cis-Ru(en)₂ClOH₂²⁺ | Cl⁻ | 0.10 | 1.0 | HCl | $4.3 \times 10^{-4}$ | 23.4 | 4.6 | S; k↓μ↑ and ΔH⁺↓μ↑ | 310 |
| cis-Ru(en)₂BrOH₂²⁺ | Br⁻ | 0.50 | 0.3 | HBr | $1.9 \times 10^{-4}$ | 21.4 | − 3.7 | S | 310 |
| Rh(NH₃)₅OH₂³⁺ | Cl⁻ | 0.0125 | 2.6 | (Na,H)(Cl,ClO₄) | $1.5 \times 10^{-5}$ | 27.6 | 12.0 | S | 185 |
| Rh(NH₃)₅OH₂³⁺ | Cl⁻ | 0.20 | large excess | Na(Cl,ClO₄) | $6.8 \times 10^{-6}$ | 25.5 | 3.2 | S | 187 |
| Rh(NH₃)₅OH₂³⁺ | Br⁻ | 0.20 | large excess | Na(Br,ClO₄) | $4.6 \times 10^{-6}$ | 25.3 | 1.9 | S | 187 |
| Rh(NH₃)₅OH₂³⁺ | I⁻ | 0.20 | large excess | Na(I,ClO₄) | $4.3 \times 10^{-6}$ | 24.4 | − 1.4 | S | 187 |
| Rh(NH₃)₅OH₂³⁺ | NCS⁻ | 0.20 | large excess | Na(NCS,ClO₄) | $5.0 \times 10^{-6}$ | 23.8 | − 3.0 | S | 187 |
| trans-Rh(en)₂NH₃(OH₂)³⁺ | Cl⁻ | — | — | — | — | 25.2 | — | — | 312 |
| trans-Rh(en)₂Cl(OH₂)²⁺ | Cl⁻ | 0.20 | 4 | Na(Cl,ClO₄) | $2.4 \times 10^{-5}$ | 25.3 | 5.2 | S | 313 |
| trans-Rh(en)₂Cl(OH₂)²⁺ | Br⁻ | 0.20 | 4 | Na(Br,ClO₄) | $2.3 \times 10^{-5}$ | 24.4 | 2.0 | S | 313 |
| trans-Rh(en)₂Br(OH₂)²⁺ | Cl⁻ | 0.20 | 4 | Na(Cl,ClO₄) | $3.5 \times 10^{-4}$ | 22.0 | 0.5 | S | 313 |
| trans-Rh(en)₂Br(OH₂)²⁺ | Br⁻ | 0.20 | 4 | Na(Br,ClO₄) | $2.6 \times 10^{-4}$ | 22.3 | 0.4 | S | 313 |
| trans-Rh(en)₂I(OH₂)²⁺ | Cl⁻ | 0.50 | 4 | Na(Cl,ClO₄) | $6.1 \times 10^{-2}$ | 19.5 | 0.6 | S | 313 |
| trans-Rh(en)₂I(OH₂)²⁺ | Br⁻ | 0.20 | 4 | Na(Br,ClO₄) | $6.0 \times 10^{-2}$ | 18.6 | − 1.4 | S | 313 |
| trans-Rh(en)₂I(OH₂)²⁺ | I⁻ | 0.50 | 4 | Na(I,ClO₄) | $5.1 \times 10^{-2}$ | 18.0 | 0.3 (−4.1) | S | 313 |
| trans-RhCl₄(OH₂)₂⁻ | Cl⁻ | 4.0 | <0 | H(Cl,ClO₄) | $3.5 \times 10^{-4}$ | 21.3 | −2.9 | S | 193 |
| RhCl₅(OH₂)²⁻ | Cl⁻ | 4.0 | <0 | H(Cl,ClO₄) | $2.2 \times 10^{-4}$ | 16.5 | −19.9 | S | 194 |
| IrCl₃(OH₂)₃ | Cl⁻ | 3.7 | <0 | (Na,H)ClO₄ | $5 \times 10^{-7}$ | 28.2 | 7.3 | S | 198 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $IrCl_4(OH_2)_2^-$ | $Cl^-$ | 3.7 | <0 | $(Na,H)ClO_4$ | $1.8 \times 10^{-6}$ | 27.2 | 6.5 | S,T | 199 |
| $IrCl_5(OH_2)^{2-}$ | $Cl^-$ | 2.2 | 0 | $(Na,H)(Cl,ClO_4)$ | $4.7 \times 10^{-5}$ (50°) | — | — | S | 316 |

is so little ion-pairing that the reaction is truly second-order under the conditions chosen, the values obtained by different groups should agree. If, however, the changeover from second-order to first-order has started, agreement on "second-order rate constants" could be poor.

In spite of this variability in results, there are some interesting mechanistic clues in Data Table VIII that may be useful in the general context of this review:

a) The two values of $\Delta S^{\ddagger}$ for anation of V(III) complexes are very negative as is the value for aquation of $V(H_2O)_5NCS^{2+}$ in Data Table I. This is felt to be good evidence for a fair amount of associative behavior in the mechanism of replacement in V(III) complexes.

b) The two $\Delta S^{\ddagger}$ values for anation of $Co(NH_3)_5$ $OS_2O_2^+$ are so far from other Co(III) data that some doubt as to the nature of the process investigated is justified.

c) The values of $\Delta S^{\ddagger}$ for anation of *trans*-$Co(DH)_2$ $X(H_2O)$ from reference 307 are more negative than for most cobalt complexes. Since a significant *trans*-effect may obtain in these complexes, one must consider the possibility that the *trans*-effect in these complexes is a consequence of a mechanistic shift towards a greater degree of associative character.

## 15. First-Order Anations

First-order anations can arise from two different types of reaction. If the complex is cationic and the entering ligand is an anion, the two-step sequence

$$ML_5(H_2O)^{3+} + X^- \rightleftharpoons \{ML_5(H_2O) \cdot X\}^{2+}$$

$$\{ML_5(H_2O) \cdot X\}^{2+} \rightarrow ML_5X^{2+} + H_2O$$
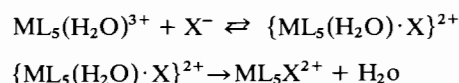
wherein the wavy brackets denote an ion-pair, is often postulated.

When the amount of entering anion ligand is sufficiently high so that all of the reactant complex is in the form of the ion-pair $\{ML_5H_2O \cdot X\}^{2+}$, the kinetics are changed over to first-order in ion-pair and the rate becomes independent of anion concentration (but not necessarily of anion nature). For example, the ion pair $\{Co(NH_3)_5(H_2O) \cdot Cl\}^{2+}$ has been postulated[36] in the reaction for formation of the chloropentaammine complex. This mechanism is much favored by inorganic chemists at the present time.

Another path leading to first-order rate constants can obtain in the absence of ion-pairing. This mechanism also has two steps, as follows:

$$ML_5(H_2O)^n \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5^n + H_2O$$

$$ML_5^n + X^- \overset{k_2}{\rightarrow} ML_5X^{n-1}$$
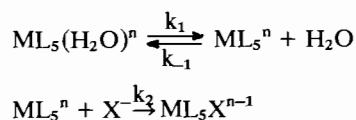
Here a five coordinate intermediate is formed Using the steady-state approximation it can be shown that when $k_2[X^-] \gg k_{-1}[H_2O]$ the rate law is

$$v = k_1[ML_5(H_2O)^n]$$

This first-order anation will obtain when $X^-$ is a much stronger nucleophile, in this case, the observed rate is independent of both nature and concentration of nucleophile (provided of course that it is strong) [23d] This type of mechanism seems appropriate for anation of $Co(CN)_5(H_2O)^{2-}$

The results for first-order anations are given in Data Table IX In view of the importance of this type of kinetics to our understanding of the ligand replacement processes in octahedral systems the amount of data is disappointing some high quality data are needed

## 16 Activation Volumes

The eleven pieces of data in Data Table X are useful for they give confirmation to some of the conclusions discussed above The activation volume for water exchange of $Rh(NH_3)_5(H_2O)^{3+}$ is more negative than for $Co(NH_3)_5(H_2O)^{3+}$ this is reasonable on the basis that replacements in rhodium(III) complexes have a greater degree of associative character than do those of cobalt(III) For $Cr(NH_3)_5(H_2O)^{3+}$ a similar behavior is expected Also the value of $\Delta V^+$ for exchange between $Cr(H_2O)_6^{3+}$ and $H_2O$ is sufficiently negative to indicate associative character

It is interesting to note and it is not unexpected to see that as $\Delta V^+$ decreases (becomes more negative) the corresponding value of $\Delta S^+$ also decreases

The other insight in these data is to be found in the values of $\Delta V^+$ for aquations of complexes of the type $Co(NH_3)_5X^{n+}$ As the charge on the leaving ligand becomes more negative charge separation in the transition state becomes a more important factor Ions tend to shrink the solvent around themselves and this process is known as electrostriction In going from ground state to a transition state with charge separation the contribution of electrostriction to the value of $\Delta V^+$ would be negative (smaller net volume) No charge separation obtains when X is $H_2O$ There is some charge separation when X is a mononegative ion ($Cl^-$ $Br^-$ and $NO_3^-$) Charge separation is very important when X is sulfate ion The values of $\Delta V^+$ for the three cases are $+1\ 2$ $-8\ 1$ (average of the three values) and $-16\ 9$ cm$^3$ mol$^{-1}$ The order is as predicted on the basis of electrostriction Further evidence that electrostriction is a correct (although incomplete) explanation comes from the observation[37] that $\Delta V^+$ is virtually identical of $\Delta V$ for the overall reaction This also is consistent with bond breaking being very

DATA TABLE IX Anation (Interchange) 1st Order Rate Constants

| Compound | Replacing Ligand | $\mu(M)$ | pH | Medium | $k$ | $\Delta H^+$ | $\Delta S^+$ | Comments | Table Ref No |
|---|---|---|---|---|---|---|---|---|---|
| $Cr(OH_2)_6^{3+}$ | $ClO_4^-$ | 5 11 | — | $HClO_4$ | $3\ 0 \times 10^{-4}$ | 22 1 | $-0\ 5$ | S 2T 10 range | 21 |
| $Cr(OH_2)_6^{3+}$ | $oxH_2$ | 2 0 | $\leq 0\ 7$ | $(Na\ H)ClO_4$ | $4\ 7 \times 10^{-6}$ | 29 0 | 14 1 | S | 291 |
| cis $Cr(ox)_2(OH_2)_2^-$ | oxH | 0 5 | 2 7-6 0 | $(Na\ H)(ox/2\ ClO_4)$ | $1\ 3 \times 10^{-4}$ | 22 | $-2$ | S | 293 |
| cis $Cr(ox)_2(OH_2)_2^-$ | ox | 0 5 | 2 7-6 0 | $(Na\ H)(ox/2\ ClO_4)$ | $1\ 3 \times 10^{-4}$ | 22 | $-2$ | S | 293 |
| $Co(NH_3)_5OH_2^{3+}$ | $Cl^-$ | 1 0 | 3 0 | $Na(ClO_4\ Cl)$ | $2\ 1 \times 10^{-5}$ | — | — | S 45 | 303 |
| $Co(NH_3)_5OH_2^{3+}$ | $NCS^-$ | 1 0 | 5 0 | $Na(ClO_4\ NCS)$ | $1\ 6 \times 10^{-5}$ | — | — | S 45 | 303 |
| $Co(NH_3)_5OH_2^{3+}$ | $H_2PO_4^-$ | — | — | $H_2O$ | $7\ 6 \times 10^{-7}$ | — | — | S | 81 |
| cis $Co(en)_2Cl(DMF)^{2+}$ | $Br^-$ | — | — | DMF | $2\ 2 \times 10^{-5}$ | 17 1 | $-27\ 1$ | S | 207 |
| cis $Co(en)_2(ox)(OH_2)^+$ | ox ring closure | 0 37 | 7 8-8 1 | $Na(NO_3\ ox/2)$ | $\sim 10^{-4}$ | 23 0 | $-6\ 5$ | S 10 range | 308 |
| trans $Co(en)_2Cl(OHMe)^{2+}$ | $Cl^-$ | — | — | MeOH | $1\ 0 \times 10^{-2}$ | — | — | S | 266 |
| $Rh(OH_2)_6^{3+}$ | $Cl^-$ | 2 5 | — | $(Na\ H)(Cl\ ClO_4)$ | $6\ 7 \times 10^{-10}$ | 36 5 | 21 9 | S | 314 |
| $Rh(OH_2)_6^{3+}$ | $Cl^-$ | 1 2 | 0 3-1 0 | $(Na\ H)(ClO_4\ Cl)$ | $8\ 6 \times 10^{-9}$ | 32 1 | 16 | T | 315 |
| $Rh(OH_2)_5OH^{2+}$ | $Cl^-$ | 2 5 | 0 88-<0 | $(Na\ H)(Cl\ ClO_4)$ | $2\ 4 \times 10^{-6}$ | 38 5 | 44 9 | S | 314 |

DATA TABLE X. Activation Volumes.

| Complex | $\Delta V^{\neq}$ (cm$^3$/mol) | Reaction | Table Ref. No |
|---|---|---|---|
| $Cr(H_2O)_6^{3+}$ | $-9.3$ | Exchange | 317 |
| $Cr(H_2O)_5(ONO_2)^{2+}$ | $-12.7$ | Aquation | 311 |
| $Cr(NH_3)_5(OH_2)^{3+}$ | $-5.8$ | Exchange | 318 |
| $Co(NH_3)_5(OH_2)^{3+}$ | $1.2$ | Exchange | 80 |
| $Co(NH_3)_5Cl^{2+}$ | $-9.7$ | Aquation[a] | 319 |
| $Co(NH_3)_5Br^{2+}$ | $-8.6$ | Aquation[a] | 319 |
| $Co(NH_3)_5(ONO_2)^{2+}$ | $-5.9$ | Aquation[a] | 319 |
| $Co(NH_3)_5(OSO_3)^+$ | $-16.9$ | Aquation[a] | 319 |
| $CoNH_3)_5Br^{2+}$ | $8.5$ | Base hydrolysis | 226 |
| $Rh(NH_3)_5(OH_2)^{3+}$ | $-4.1$ | Exchange | 318 |
| *trans*-$Cr(ox)_2(H_2O)_2^-$ | $-16$ | Trans→cis isomerization[b] | 365 |

[a] $\Delta V^{\neq}$ is virtually coincident with the change of volume of the overall reaction.

[b] $\Delta V^{\neq}$ becomes $-9.8$ cm$^3$/mol in the presence of $Ca(NO_3)_2$ and $-5.4$ in the presence of $HClO_4$.

important, since the closeness in size of $\Delta V^{\neq}$ and $\Delta V$ suggests that the leaving group is nearly as free in the transition state as in the final state. The positive (albeit small) value of the activation volume for water exchange is in agreement with such an interpretation.

## 17. Summary Conclusions

The present compilation is, to the best of our knowledge, the most complete set of data dealing with rates and mechanisms of octahedral complexes having the central metal in oxidation state three. We hope that the numbers collected and calculated will be useful to inorganic chemists. Also it is our opinion that good activation parameter data (specifically, $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta V^{\neq}$) can be helpful in elucidating the mechanisms of ligand replacement in complexes and that such data should be obtained carefully (whenever possible) in reaction mechanisms studies.

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