Inorganic Chemistry

The Kinetics of Structural Transformation of Hydrated Cobalt(II) and Zinc(II) Ions in Aqueous Solution

BY T. J. SWIFT

Evidence was given for the presence of tetrahedral $Co(H_2O)_4^{+2}$ in aqueous solutions of Co^{+2} and of tetrahedral $Zn(H_2O)_4^{+2}$ in aqueous Zn^{+2} solutions through the use of the temperature-jump technique. The pseudo-first-order rate constant for the reaction, postulated to be $M(H_2O)_4^{+2} + 2H_2O \rightarrow M(H_2O)_6^{+2}$, was measured near room temperature for both Co^{+2} and Zn^{+2}. The rate constants were found to be primarily entropy controlled and were interpreted in terms of the postulated structural transformation. Values of ΔH^* and ΔS^* determined for the known tetrahedral cobalt thiocyanate complex were nearly the same as those obtained for the two aquo species. The results were used to yield information concerning the mechanism of ligand substitution involving complex metal ions in solution.

Introduction

There has been considerable interest in recent years concerning the mechanisms of ligand substitution reactions involving complex metal ions in solution.[1] Virtually all complex ions are now open to such study due to the recent advances in the use of relaxation techniques for the study of very rapid reactions.[2] One important application of such kinetic studies of complex ions is the possible determination of the partition of metal ion–ligand bonding energy of the complexes studied into various terms such as coulombic energy, crystal field stabilization, and covalent bond energy. If the structures of the various activated complexes can be sufficiently well determined, the variation of rate constant for ligand substitution with suitable parameters should yield the desired energies.

It is an extremely difficult problem to determine such structures of activated complexes, however. This problem is greatly simplified if there exists a group of ions for which the activated complexes for ligand substitution may be shown to possess the same basic structure. The variation of the experimental free energy of activation with the radius of the metal ion, metal d-electron ionization potential, relative crystal field stabilization energy, electric quadrupolar and magnetic dipolar coupling constants, etc., together with the information obtained experimentally concerning the structure of the activated complex should yield the desired result.

One such series of ions is the doubly-charged hexaaquo ions of the first transition series. It has been found[3,4] that the rate constant for substitution of coordinated water with Mn^{+2}, Fe^{+2}, Co^{+2}, Ni^{+2}, and Cu^{+2} encompasses four orders of magnitude. Sizable variations in the parameters mentioned above are also displayed in this series of ions. In addition the wide variety of substituting ligands permitted a good de-

termination of the effect of the substituting group on the rate constant and hence yielded valuable information concerning the activated complex.

Any substitution mechanism involving a hexacoordinated metal ion must involve a penta-or heptacoordinated activated complex. The former case is an S_N1 limiting mechanism and the latter S_N2 mechanism includes all the possible activated complexes in which the energy of the entering group makes an appreciable contribution to the activation energy of the process.

It has been indicated[3-6] that the rate constant for ligand substitution involving the series of ions mentioned above is virtually independent of the nature of the entering group. In addition, calculations of complex ion formation rate constants from stability constants and dissociation rate constants for a wide selection of ligands lead to the conclusion that the mechanism closely approximates the S_N1 limit.[7]

However, it may not be assumed from this information that the structures of the activated complexes are essentially the same. The designations S_N1 and S_N2 refer only to the contributions to the energy of activation from the entering and departing groups. Both types of mechanism may also include large contributions from rearrangement of the remaining ligands. In substitution reactions involving complex ions which possess crystal field stabilization this is an especially important consideration.

An additional difficulty arises from the possibility that the coordination sites are nonequivalent as is the case with the hexaaquo ion of Cu^{+2}. Thus a water molecule may be substituted more rapidly at site a than at site b and subsequently the sites may be transposed through a rapid inversion process. This process is an alternate substitution mechanism at site b and is undoubtedly the mechanism which accounts for the anomalously rapid substitutions involving $Cu(H_2O)_6^{+2}$ in solution. Such a process is independent of an S_N1 or S_N2 designation.

(1) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958.
(2) M. Eigen and J. S. Johnson, *Ann. Rev. Phys. Chem.*, **11**, 307 (1960).
(3) T. J. Swift and R. E. Connick, *J. Chem. Phys.*, **37**, 307 (1962).
(4) M. Eigen in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961.
(5) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).
(6) R. G. Pearson, J. Palmer, M. M. Anderson, and A. L. Allred, *ibid.*, **64**, 110 (1960).
(7) R. G. Wilkins and M. Eigen, Max-Planck-Institute for Physical Chemistry, Göttingen, Germany, private communication.

The n.m.r. studies of Swift and Connick[3] reveal the possibility of such a mechanism for a number of ions in addition to Cu(H$_2$O)$_6^{+2}$. This conclusion follows from the author's evidence for the existence of a species in Co(ClO$_4$)$_2$ solutions having a nonoctahedral structure and a coordination number less than six. In the event that the ligand substitution with the species which the authors term Co′ is more rapid than the corresponding reaction with Co(H$_2$O)$_6^{+2}$ and the rate of conversion of the substituted Co′ to the octahedral form also is very rapid, the observed mechanism of substitution would be essentially the same as that of Cu(H$_2$O)$_6^{+2}$.

Although such a species was detected only in the case of Co^{+2}, it is reasonable that the substitution mechanism mentioned above could also proceed through such possible species as square-planar Ni(H$_2$O)$_4^{+2}$, tetrahedral Zn(H$_2$O)$_4^{+2}$, etc. It is necessary to determine the extent to which these additional considerations affect the observed substitution rates in order to confirm or disprove the hypothesis that the series of ions in question pass through the same type of activated complex in the process of ligand substitution. The Co^{+2} system mentioned above would seem to be ideal for the resolution of the problem. The authors have postulated the existence of tetrahedral Co(H$_2$O)$_4^{+2}$. It would seem possible to verify the existence of this ion, to give additional evidence for its structure, and to determine the rate constant governing its conversion to the octahedral form. This rate constant is an upper limit to the over-all rate arising from the mechanism discussed above and it also applies to a process which likely involves a rearrangement of ligands.

Experimental

One of the pieces of evidence given by Swift and Connick for the existence of Co(H$_2$O)$_4^{+2}$ is the appearance of an absorption peak at 560 mμ when the temperature of a solution containing Co^{+2} is raised. The temperature-jump technique[8] is then ideally suited for the attempted verification of the existence of the new species and for the determination of the desired rate constant since the change in concentrations produced by the *ca.* 10° temperature rise is followed spectrophotometrically. Experiments were performed with two Co^{+2} solutions. The first contained 0.1 M Co(NO$_3$)$_2$, 0.1 M KNO$_3$, and 0.01 M HNO$_3$. The acid was added to prevent complications from hydrolyzed species and the KNO$_3$ was added to prevent some transient spectra effects, resembling those due to cavitation, which were observed under conditions in which only Co^{+2} and NO$_3^-$ were present to transmit the electrical current used to produce the temperature jump.

The second solution contained 0.01 M Co(NO$_3$)$_2$, 0.1 M KSCN, 0.1 M KNO$_3$, and 0.01 M HNO$_3$. In both solutions the concentration of Co^{+2} was chosen so as to yield an optical density as close as possible to 0.86, the value representing the maximum signal/noise. A limit was reached near 0.1 M Co^{+2}, above which the spurious spectral effects mentioned above appeared. The spectral changes of the former solution accompanying the temperature jump were observed at 500 mμ, while those with the latter solution were best observed at 580 mμ.

(8) M. Eigen and L. DeMaeyer, "Technique of Organic Chemistry," Vol. VII, 2nd Ed., A. Weissberger, Ed., Interscience Publishers Inc., New York. N. Y.

TABLE I
RELAXATION TIMES OBSERVED WITH Co^{+2} AND Zn^{+2} SOLUTIONS BY THE TEMPERATURE-JUMP METHOD

Cation	Anion	Temp., °C.	τ, sec.
Co^{+2}	NO$_3^-$	33.5	0.056 ± 0.002
Co^{+2}	NO$_3^-$	43	0.045 ± 0.004
Co^{+2}	SCN$^-$	32	0.220 ± 0.010
Co^{+2}	SCN$^-$	41.5	0.158 ± 0.016
Zn^{+2}	NO$_3^-$	12.5	0.175 ± 0.005
Zn^{+2}	NO$_3^-$	24	0.130 ± 0.005
Zn^{+2}	NO$_3^-$	34	0.101 ± 0.010

Experiments were performed at two equilibrium temperatures (temperature resulting from the temperature jump) with each solution. The solution containing no thiocyanate was studied at 33.5 and 43°, while the other solution was studied at 32 and 41.5°. Higher temperatures could not be attained due to the nature of the temperature-jump cell. Likewise studies at lower temperatures could not be performed since the observed relaxation times were very close to the limit of long times of the range of applicability of the temperature-jump method.

The results of the temperature-jump experiments with Co^{+2} solutions were such as to warrant further experiments with other metal ion solutions in which the presence of a tetrahedral tetra-aquo ion was suspected, and the ion chosen was Zn^{+2}. Since a Zn(NO$_3$)$_2$ solution displays no appreciable absorption in the visible range, some means had to be devised for the detection of Zn(H$_2$O)$_4^{+2}$. It was considered unlikely that two aquo ions of different structure would be characterized by the same hydrolysis constant. Therefore the shift in the equilibrium between the two aquo ions could be followed by the observation of the accompanying pH shift. The solution employed contained 5.0 × 10^{-4} M Zn(NO$_3$)$_2$ and 0.1 M KNO$_3$. The pH was adjusted to 8.0 by addition of NaOH, and the indicator employed was phenol red. Solubility problems prevented experiments at a pH nearer to the pK of Zn(H$_2$O)$_6^{+2}$. The problems with temperature encountered with Co^{+2} solutions were not encountered with the Zn^{+2} solution and therefore experiments were performed at equilibrium temperatures of 12.5, 24, and 34°. Additional experiments were performed with Co^{+2} and Zn^{+2} solutions of varying concentrations in order to determine the concentration dependence of the observed relaxation times. One experiment was performed with a Zn^{+2} solution at pH 8.5 in order to ascertain the hydrogen ion dependence of the observed relaxation process.

Finally the results of the experiments with Co^{+2} were verified through the use of the temperature-jump, pH indicator method mentioned above. The solution employed contained 1.0 × 10^{-3} M Co(NO$_3$)$_2$ and 0.1 M KNO$_3$. Phenol red was used as the indicator and the pH was 8.0. Since the resulting relaxation time was in agreement with that obtained from the direct spectral change, only one experiment was performed, that being at an equilibrium temperature of 32°. Blank experiments were performed with a 0.1 M Ni(NO$_3$)$_2$ solution and also with a 0.1 M Cu(NO$_3$)$_2$ solution. In neither case was a relaxation effect observed.

Results and Discussion

The relaxation times observed with the Co(NO$_3$)$_2$ solution at two temperatures are shown in Table I. The limits of error given in Table I represent the largest observed deviations from the averages of five relaxation times.

Some additional facts must be mentioned concerning the observed relaxation phenomena. The relaxation with the Co(NO$_3$)$_2$ solution was observed as an increase of ∼0.02 optical density unit. In addition this relaxational increase in optical density was preceded

by a very rapid ($<20\mu$ sec.) increase in optical density of approximately the same magnitude as the relaxational increase. This rapid increase was not observed with the Ni^{+2} and Cu^{+2} used as blanks.

Some detailed consideration must be given concerning the possible chemical processes to which these spectral phenomena might be related. The species originally thought to be present which could interact with $Co(H_2O)_6^{+2}$ are Co' and one or more nitrate complexes of $Co(H_2O)_6^{+2}$ and Co'. Therefore there are several sets of equilibria governing the concentrations of species present in this solution and all are of potential importance in the determination of the observed relaxation time. The complete relaxation spectrum of such a solution may be derived theoretically; however it would be extremely complicated and is not needed in this instance. It will be shown that only one set of reactions describing the behavior of species in this solution could possibly result in the long relaxation time observed. All other possible reactions involve much shorter times and are not involved in a preequilibrium with the observed reaction set and therefore could not be involved in any way with the observed relaxation.

The nitrate complex reactions are all of the form
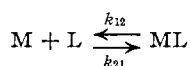
$$M + L \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} ML$$

Any such system taken independently results in a relaxation time of the form

$$1/\tau = k_{12}([M] + [L]) + k_{21} \qquad (1)$$

The observed relaxation time was found to be concentration independent over a range of $[Co^{+2}] + [NO_3^-]$ extending from 0.12 to 0.30 M. The conclusion is that the process observed is the transition between Co' or one of its nitrate complexes to $Co(H_2O)_6^{+2}$ or the corresponding octahedral nitrate complex. If the observed reaction involves transitions between nitrate complexes, the magnitude of the observed relaxation effect should be strongly dependent on the concentration of NO_3^-. No such dependence was observed when the concentration of NO_3^- was increased from 0.2 to 0.4 M, and therefore the observed relaxation time must be due to the equilibrium between Co' and $Co(H_2O)_6^{+2}$.

The equilibrium between Co' and $Co(H_2O)_6^{+2}$ will not fully account for the observed spectral effects since it cannot yield both the rapid and relaxational increases in optical density. Another species, Co'', must be present in sufficient concentration to affect the observed spectrum.[9] The observed relaxation time arises from the equilibrium between $Co(H_2O)_6^{+2}$, Co', and Co''. It was necessary, however, to perform further experiments in order to determine which rate constant or combination of rate constants was being observed.

From the temperature dependence of the relaxation time the enthalpy of activation was found to be $5.4^{+1.1}_{-4.0}$ kcal./mole and the entropy is -35^{+3}_{-12} e.u. The limits

of error of ΔH^* and ΔS^* were calculated from the maximum observed deviations in τ given in Table I. The fact that the observed relaxation time is primarily entropy determined suggests that the chemical transformation measured involves species which differ considerably in geometry. The large negative entropy would arise from the small probability of occurrence of the proper structural distortions in the course of the transformation.

Since the geometries of the species involved were thought to be of primary importance in the determination of the relaxation time, it was of interest to investigate the relaxation effects in a Co^{+2} solution known to contain species of differing geometries. Such a solution is the aqueous solution of Co^{+2} and thiocyanate known to contain the octahedral $Co-H_2O)_6^{+2}$ ion and one or more tetrahedral Co(II) thiocyanate complexes.

The relaxation times resulting from two experiments with this solution are given in Table I. The arguments given previously against nitrate complexing apply equally as well to thiocyanate complexing. In addition the relaxation time observed with the $Co(NO_3)_2$ solution is observed also with the thiocyanate solution and is unchanged by the addition of the thiocyanate. Apart from the rapid optical density increase mentioned previously no rapid increase was observed due to the presence of the thiocyanate. The new relaxation time was observed as an increase of ~ 0.05 optical density unit.

The enthalpy of activation of the observed process was found to be $6.0^{+3.0}_{-2.8}$ kcal./mole and the entropy is 36^{+10}_{-9} e.u.

The new relaxation time due to the presence of thiocyanate is undoubtedly due to the tetrahedral complex $\rightleftarrows Co(H_2O)_6^{+2}$ equilibrium since these are the only species present in detectable concentrations which could yield a relaxation of the type observed.

Since the rate constant, enthalpy, and entropy of activation of this transition are so similar to those observed with the $Co(NO_3)_2$ solution it would be quite fortuitous if the observed transition with that solution were essentially any other than $Co(H_2O)_4^{+2} \rightleftarrows Co(H_2O)_6^{+2}$.[10]

In addition it may be easily shown[8] that since the octahedral form is the predominant species in both solutions the observed rate constants are primarily those for the tetrahedral → octahedral conversion.

Since the postulated tetrahedral → octahedral conversion rate was found to display no large dependence on the nature of the ligands in the case of Co^{+2}, it was thought possible that it would display a similar insensitivity to the nature of the metal ion. For this reason further temperature-jump experiments were carried out with the $Zn(NO_3)_2$ solution described above. The resulting relaxation effect was much more pro-

(9) For a detailed mathematical treatment of the relaxational behavior of the three species system see ref. 8.

(10) Three aquo species have been detected, $Co(H_2O)_6^{+2}$, Co', and Co'''. It is quite possible that one of these is a five-coordinated cobalt(II). The data and conclusions given above are consistent with that possibility provided the (4) → (5) rate constant is much smaller than the (5) → (6) rate constant.

nounced than was the case with Co^{+2} and the relaxation times at three temperatures are given in Table I. The values of ΔH^* and ΔS^* were calculated to be $3.8^{+1.0}_{-0.6}$ kcal./mole and -42^{+4}_{-2} e.u. The observed relaxation time was found to be independent of the concentrations of Zn^{+2}, NO_3^-, and H^+. Just as with Co^{+2} the relaxation time can be interpreted only in terms of the presence of another aquo zinc ion in addition to $Zn(H_2O)_6^{+2}$. The similarity of τ, ΔH^*, and ΔS^* to those observed with Co^{+2} is strong evidence for this species being tetrahedral $Zn(H_2O)_4^{+2}$.

Since the temperature-jump, pH indicator method was successful with Zn^{+2}, it was thought advisable to check the Co^{+2} results by the same method. The resulting relaxation effect, although not as large as that observed with Zn^{+2}, was nevertheless in perfect agreement with the result obtained from the direct spectral change.

Due to the large decrease in optical density associated with the temperature dependence of the indicator pK, the rapid increase in optical density of Co^{+2} solutions mentioned previously could not be observed for either Co^{+2} or Zn^{+2} with the temperature-jump, pH indicator method.

In the light of this conclusion the results have a strong bearing on the problems proposed above concerning the mechanism of ligand substitution. The large entropy observed for the tetrahedral–octahedral transition undoubtedly arises from the distortion necessary to change the tetrahedral structure to a structure suit-ably near the octahedral. Such a distortion places severe restrictions on the positions of all the ligands with respect to the internal coordinate system of the complex and would be expected to have a relatively low probability of occurrence. The result is that the conversion to the much more thermodynamically stable octahedral form is relatively slow.

One of the problems proposed concerned the probability of a rearrangement of ligands in a complex in order to increase the crystal field stabilization during the process of ligand substitution. It would seem that this process also would encounter a sizable entropy barrier and therefore it is very unlikely that the ligand substitution rate constants are affected by it in the series of ions previously mentioned. Finally the upper limit of the rate of an alternate ligand substitution mechanism such as discussed in the Introduction was measured for Co^{+2} and Zn^{+2}, and it is much too slow to be a contributing factor in the observed substitution rates. Because of the presence of the entropy barrier to structural changes it is likely that such an alternate substitution mechanism would also be too slow to be observed with the other doubly charged ions of the first transition series.

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The Crystal Structure of Manganese Dichloride Tetrahydrate[1]

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The stable room temperature form of $MnCl_2 \cdot 4H_2O$ (α form) has a monoclinic cell, $a = 11.186$, $b = 9.513$, $c = 6.186$ Å., and $\beta = 99.74°$. The space group is $P2_1/n$ with four formula units per unit cell and $d_x = 2.03$ g./cc. An X-ray diffraction study of this material yielded the positions of all of the atoms including the hydrogens. The structure consists of discrete octahedra of four oxygen atoms and two chlorine atoms about the manganese, and with the chlorine atoms adjacent to each other. The four Mn–O distances are nearly equidistant, being 2.224, 2.209, 2.185, and 2.206 Å.; the two Mn–Cl distances are 2.475 and 2.500 Å. Only four of the eight hydrogen atoms make hydrogen bonds. Three of the hydrogen bonds are between oxygen and chlorine and one between two water molecules.

Introduction

Groth[2] reports two monoclinic crystal modifications of $MnCl_2 \cdot 4H_2O$. One form is metastable at room temperature (Dawson and Williams[3]) and is isomorphous with $FeCl_2 \cdot 4H_2O$, the structure of which has been described by Penfold and Grigor[4] with comments on the proton sites by El Saffar and Murtz.[5] Our paper deals with the form that is stable at room temperature, and in keeping with the nomenclature of Dawson and Williams[3] we refer to this modification as the α form and to the metastable modification as the β form. It should be noted here that Groth[2] in his publication has reversed the naming of these two forms from the above convention.

Delain[6] has reported the cell dimensions and space group of the α form, and Gardner[7] has reported some preliminary results on the proton sites. We became

(1) Work done under the auspices of the U. S. Atomic Energy Commission.
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