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THEORY OF THE KINETICS OF THE LIGAND SUBSTITUTION PROCESSES IN THE COORDINATION SPHERE OF THE METAL COMPLEXES

By

E. D. GERMAN* and R. R. DOGONADZE*

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Abstract

The ligand substitution processes in the coordination sphere of the octahedral metal complexes of Cr(III), Co(III) and Rh(III) is analyzed on the basis of previously developed quantum mechanicl theory of chemical reactions. The expression obtained for the energy of activation contains three parameters. One of this is estimated theoretically, two the others from a comparison of the theory with experimental data for the aquation reactions of [Cr(H₂O)₆]³⁺ complexes. The values obtained for the kinetic parameters have been applied in the calculation of energies of activation for some other ligand substitution reactions.

Introduction

The ligand substitution reactions in the coordination sphere of the metal complexes are often intermediate stages in the catalysis by metal complexes so that the investigation of such processes is of considerable interest.

The modern concepts about the mechanism of the substitution reactions in the complexes are based primarily on the experimental studies.

In the present paper the theoretical investigation of these reactions is presented. As a model processes the aquation reactions of octahedral metal complexes of Cr(III) and Co(III)

\[ [\text{ML}_6X]^+ + \text{H}_2\text{O} \rightleftharpoons [\text{ML}_6\text{H}_2\text{O}]^+ + X^- \]

where \( L = \text{H}_2\text{O}, \text{NH}_3; \) \( X^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NCS}^-, \text{NO}_3^-, \text{N}_3^- \) are considered.

Such processes also involve a charge transfer from the complex \([\text{ML}_6X]^+\) to the ligand \( X^- \), resoluting in the formation of a new ion \([\text{ML}_6\text{H}_2\text{O}]^+\), of charge \( 3|e| \), and a free ion \( X^- \).

A quantum-mechanical theory of the kinetics of reactions involving

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charge transfer or redistribution in polar media was developed in a series of papers\textsuperscript{2,3}, the basic conclusions of which can be summarized as follows.

All degrees of freedom, which characterize the reacting particles and solvent, can be divided into classical and quantum degrees of freedom. The general basis of the division is given in reference\textsuperscript{4}, but qualitatively the criteria for a quantum (classical) degree of freedom can be formulated in the following way: if the energy of the characteristic frequency ($\hbar \omega_{cl}$) of a given degree of freedom is smaller than $4kT$, then the motion along this degree of freedom is classical, \textit{i.e.} it goes over the potential barrier. Motion along a degree of freedom, the characteristic vibration energy ($\hbar \omega_{qu}$) of which is higher than $4kT$ is a quantum motion, \textit{i.e.} of subbarrier nature.

A dynamical model\textsuperscript{*} for the solvent is applied in the quantum theory. The physical idea of this model can be illustrated by redox reactions in which an electron is transferred from an ion $A^{z1}$ to an ion $B^{z1}$. When a redox reaction takes place in the gas phase, then according to the energy conservation law, the electron energy change must be compensated by a change of the kinetic energy of the particles $A^{z1+1}$ and $B^{z1-1}$, \textit{i.e.} by a change of their velocities. The velocities of the heavy particles must change practically instantaneously, as the characteristic time of the electron jump from one ion to another is of the order of $10^{-15}$ sec. This leads to a very small electron transfer probability for large values of $(E_A - E_B)$. Experiments show that the transition probability is in fact different from zero only if $E_A$ is approximately equal to $E_B$. This experimental fact is known as the Frank-Condon principle. Considering the same reaction in a polar liquid one must take into account, that the electron energy levels of the ions $A^{z1}$ and $B^{z1}$ depend not only on the interaction of the electron with the ion cores, as in the gas phase, but also on the interaction of the electron with the polarized medium, \textit{i.e.} with the dipoles of the solvent. This change of electron energy in going from the gaseous phase to a polar liquid is comparable with the electrostatic part of the solvation energy of the ions and can amount to several dozens of kcal/mole. It is important for

\textsuperscript{*} Within this theory the solvent is considered in a way which differs essentially from the approach of the theory of absolute rates. In the latter theory the influence of the solvent is accounted for by including in the activation energy, the difference of the solvation energies of transition and initial states. The energies of these states are calculated by means of the Born formula or some improved formula of this kind. When calculating the solvation energy of the initial and final states, it is usually assumed that the medium polarization is in equilibrium with the electrostatic field. Therefore, according to the theory of absolute rates, the whole influence of the solvent upon the kinetics can be described by means of one single parameter — the static dielectric permeability of the medium.
the electron transfer kinetics that the thermal motion of the solvent dipoles, \textit{i.e.} the polarization fluctuations, changes the interaction energy of the electron with the polarization of the medium. Thus, the electron energy levels essentially depend on the dipole configuration in every moment, as opposed to the gas phase reactions. This dependence is shown schematically in Fig. 1. Here \( q \) is some set of normal coordinates, describing the time-dependent configuration of the dipoles, \textit{i.e.} the fluctuating polarization of the medium. It can be seen easily, that according to the Frank-Condon principle, the electron transfer can take place only if \( \epsilon_A \), as a consequence of the polarization fluctuation of the medium, becomes approximately equal to \( \epsilon_B \). In the situation where the coordinate \( q \) is equal to \( q^* \), the electron energy change during the transition is practically equal to zero, and the velocities of the heavy particles, \textit{i.e.} of the ions and dipoles of the medium, do not necessarily change instantaneously, \textit{i.e.} during \( 10^{-15} \) sec, here, in the transition state, \textit{i.e.} activated complex, the solvent dipoles have a definite configuration \( q^* \).

Thus the dynamical properties of the medium, \textit{i.e.} the characteristic frequencies \( \omega \) and the intensity of the polarization fluctuations—which can be found from the dependence of the dielectric permeability on the frequencies—are important in the theory. For water the most intensive absorption takes place in the frequency range \( 1-10 \text{ cm}^{-1} \), which is considerably smaller than \( 4kT \). This classifies, according to the criteria given above, the vibration frequencies along the coordinates \( q \) as classical.

Thus, in electron transfer reactions the electron, as the only quantum subsystem, undertakes a subbarrier motion while the movement along the solvent coordinate is classical and passes over the barrier.

The principles mentioned may be summarized to explain the mechanism of the elementary act of arbitrary chemical reactions involving a charge transfer or a charge redistribution. In the transition state of an arbitrary chemical reaction, levelling of the energy levels must take place for each degree of freedom along which quantum motions occur. This may be effec-
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tuated by means of fluctuation of the solvent polarization and fluctuational
deformation of the intra-molecular degrees of freedom, along which the
classical overbarrier motions occur. Consequently, the activation energy will
be determined exclusively by the classical subsystem.

Analysis of Experimental Data

We now consider substitution processes within the quantum-mechanical
tory of chemical reaction\textsuperscript{1-3}. At present the question of the mechanism
of aquation reactions of octahedral complexes is not settled definitely. Thus,
in general distinction between \textit{S}_\text{N}1 and \textit{S}_\text{N}2 mechanisms can not be given unambiguously. Below we shall analyze reaction (1) assuming a bimolecular
substitution mechanism. We shall consider a model, in which no formation
of a kinetically independent seven-coordinate intermediate occurs. Obviously,
other mechanism must be taken into account. For example the H\textsubscript{2}O molecule
may move to a position between X\textsuperscript{−} and a neighboring water molecule in
the complex. This mechanism as well as the \textit{S}_\text{N}1 mechanism will be con­
sidered in later communication.

In general the stretching frequencies of the M-X bond in complexes
[ML\textsubscript{6}X]\textsuperscript{2+} do not exceed 700 cm\textsuperscript{−1}.\textsuperscript{3} The vibration frequencies of the free
ions X\textsuperscript{−} in the solvent are much smaller the order of magnitude being
roughly the same as the reverse Debye relaxation time. On the other hand,
the vibration frequency along the degree of freedom, describing the motion
of the H\textsubscript{2}O molecule, undergoes an abrupt increase during the reaction, as

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{U}
\end{figure}
the water passes from the solvent into the complex, where the characteristic M–OH$_2$ bond stretching frequencies lay in the range 400–650 cm$^{-1}$. This is illustrated in Fig. 2a and b, where the terms of the initial and final states are shown. The chemical bond M–X in the activated state is practically not stretched ($R^* \approx R^0$) and the coordinate of H$_2$O almost coincides with the equilibrium coordinate in the final state ($R_{eq} \approx R_{eq}^o$). The activated state along the coordinate of the solvent is shown in Fig. 3. These figures also define the parameters, which are important in the theory, i.e. the reorganization energies corresponding to the various degrees of freedom in the initial and the final equilibrium state ($E_r^x$, $E_r^{eq}$ and $E_a$) (A more detailed description of $E_a$ can be found in ref. 2). The expression for the activation energy, of the assumed reaction mechanism (1) has the form

$$E_a = E_r^{eq} + \frac{[E_a + \Delta I + E_r^x - E_r^{eq}]}{4E_a} \quad (2)$$

where $\Delta I$ is the distance between the minima of the potential energy surfaces of the initial and final state. For the reactions considered it practically coincides with heat of reaction ($\Delta H_a$).

According to equation (2) the Brønsted coefficient $\alpha$ determined by $\alpha = dE_a/d(\Delta I)$, has the form

$$\alpha = 1/2 + \frac{\Delta I + E_r^x - E_r^{eq}}{2E_a} \quad (2a)$$

and depends not only on the relative positions of the terms of the initial and final states (that is from $\Delta I$), but also on the values of the three reorganization energies.

The kinetic parameter $E_a$ contained in the formula (1), can be calculated theoretically$^6$, when the configuration of the reacting particles in the initial and final states, as well as their charge distributions are known. To estimate theoretically the parameters $E_r^x$ and $E_r^{eq}$ one has to know the particular kind of potentials which determine the movement of the particles $X^-$ and H$_2$O in the proximity of the complex. It should be noted that the form of the
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potential curves depends on the direction in which the H₂O molecule attacks the position occupied by the ion X⁻ in the complex, and also on the direction along which X⁻ leaves the complex. This form can only be found by means of quantum-mechanical calculations. In the present work we estimated \( E_x \) and \( E_{eq} \) from two experimental points of known \( E_a \) and \( \Delta I \) assuming that (2) contains values of the quantities \( E_x \) and \( E_{eq} \) corresponding to the most probable directions of the motion and orientation of the reagents and products, and assuming that they only undergo an insignificant change throughout the series of reactions considered.

To calculate the parameter \( E_a \) we shall represent the original complex [ML₅X]⁺ and the final complex [ML₅H₂O]³⁺ as spheres of radius \( a \). According to X-ray data, the value of \( a \) is about 3 Å. The radii of the ions X⁻ in the solutions will be assumed to be equal to their crystallographic radii. Also, in estimating \( E_a \) we shall neglect any asymmetry of the charge distribution in [ML₅X]⁺, assuming that the magnitude of the effective charge on X is small. Thus, the initial state is represented by a sphere of radius \( a \) on which the charge \((+2|e|)\) is uniformly distributed. The final state is represented by one sphere of charge \((3|e|)\) and one sphere of charge \((-|e|)\) at a distance \( r \) from the first sphere (fig. 4). Using this model the expression for \( E_a \) takes a form analogous to the one obtained by Marcus for electron transfer reactions

\[
E_a = C \cdot (1/2a + 1/2b - 1/r)
\]

where \( C \) is a constant, which for reactions in water, equals 186 (kcal/mol)Å, when \( a, \ b, \) and \( r \) are expressed in Å. The distance \( r \) was chosen in such a way \((r\approx5 \text{ Å})\) that the average value of \( E_a \) for three different \( X^- \) (e.g. \( X^- = \text{Cl}^-, \text{Br}^- \) and \( \Gamma^- \)) corresponded to the average value of \( E_a \) determined by equation (2) from three experimental points of the same \( X^- \), neglecting any variation of the parameters \( E_a, E_x \) and \( E_{eq} \). The values of \( E_a \) and \( \Delta I (\equiv \Delta H_0) \) used in estimating the average value of \( E_a \) are given in Table 1. The values of \( E_a \) calculated from equation (3) for \( X^- = \text{Cl}^-, \text{Br}^- \) and \( \Gamma^- \) varied from 47 to 40 kcal/mol, while the value for the fluoride ion was found to be higher (65 kcal/mol).

Estimates of \( E_x \) and \( E_{eq} \) were also made...
TABLE 1. Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction \([\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow \text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{X}^-\):

<table>
<thead>
<tr>
<th>(\text{X} )</th>
<th>(\log k_1^a)</th>
<th>(-\log K_x^b)</th>
<th>(\Delta H^{*e}) kcal/mole</th>
<th>(\Delta S^{*e}) e.u.</th>
<th>(\Delta H_o) kcal/mole</th>
<th>(\Delta S_o) e.u.</th>
<th>Ref.</th>
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<td>-5.1</td>
<td>-3.1</td>
<td>10,13</td>
<td></td>
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<td>-0.2±0.9</td>
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<td></td>
<td>9</td>
<td></td>
</tr>
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<td></td>
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</tr>
<tr>
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<td>2.1±0.6</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>N(_3)</td>
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<td>27.5</td>
<td>1.9</td>
<td>2.1</td>
<td>1.1</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

*) at 25°C in aqueous solution.

a) \(k_1\) sec\(^{-1}\); b) \(K_x = \left[\text{[Cr}(\text{H}_2\text{O})_5\text{X}]^{2+} \right] / \left[\left[\text{X}^-\right] \cdot \left[\text{[Cr}(\text{H}_2\text{O})_6^{3+} \right] \right];\) c) \(E_a = \Delta H^* + RT\); d) evaluated using the frequency factor \(v = 10^{13\text{ sec}^{-1}}\); e) \(\Delta S_0 = \Delta S_{ox} + 8, \Delta S_{ox}\) being the experimental entropy \(\Delta S_{ox} = 2.3RT(\log K_x + \Delta H_0/kT)\)

using data for substitution reactions in complexes of Cr(III) (Table 1). For \(E_r^x\) and \(E_r^{\#}\) the values \(\sim 5\text{ kcal/mole}\) and \(\sim 21\text{ kcal/mole}\) respectively, were obtained. It should be noted that the reorganization energy of the water molecule \(E_r^{\#}\) for reactions in aqueous solution is independent of \(\text{X}^-\) and \(\text{M}\). As follows from equation (2) \(E_r^{\#}\) is the minimum activation energy for such reactions. In fact, when comparing with the experimental data given in Tables 2-4, one can see that activation energies smaller than 21 kcal/mole are practically not observed. Therefore, we can conclude that \(E_r^{\#}\) contributes to a large extent to the total activation energy of a aquation reactions of octahedral complexes, and this accounts for the rather small variation of experimental values of activation energies.
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TABLE 2. Experimental values of the kinetic and thermodynamic parameters of the aquation reaction $\text{[Cr(NH}_3\text{)_5X]}^{2+} + \text{H}_2\text{O} \xrightarrow{k_1} \text{[Cr(NH}_3\text{)_5(H}_2\text{O)I}^{3+} + \text{X}^-$

<table>
<thead>
<tr>
<th>$\text{X}$</th>
<th>$\log k_1$</th>
<th>$-\log K_T$</th>
<th>$\delta H^*$ kcal/mole</th>
<th>$\delta S^*$ e.u.</th>
<th>$\delta H_0$ kcal/mole</th>
<th>$\delta S_0$ e.u.</th>
<th>Ref.</th>
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<td>25</td>
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</table>

*) at 25°C in aqueous solution; see footnotes. a)-e) of Table 1.

In order to calculate the activation energy series of analogous processes, use will be made of kinetic parameters of $\text{[Cr(H}_2\text{O)_5X]}^{2+}$ complexes for all the series considered. Estimates of the energies of activation can be made in cases where the heats of the actual reactions are known. Results of the calculations, together with the average experimental values are gived in Table 5. Taking into account the approximations made, the agreement can be considered satisfactory. This gives some support to the assumption that the reactions considered above really take place by an $\text{SN}_2$ mechanism. A definite answer to this question can only be given after a theoretical analysis of other mechanisms.

It should be noted that for constant values of the kinetic parameters $E_n$, $E_{r_{\text{av}}}$ and $E_r$, equation (2) expresses a correlations between activation energies and reaction heats $\Delta I(=\Delta H_0)$. Thus, if the change in entropy of reaction and the entropy of activation throughout a series of reactions is not too drastic, equation (2) gives the relation (strictly speaking, non-linear) between the logarithm of the rate constant (log $k$) and the logarithm of the
**Table 3.** Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction $[\text{Co}(\text{NH}_3)_5X]^2^+ + \text{H}_2\text{O}$

\[
\begin{array}{cccccccc}
X & \log k_i & -\log K_x & \Delta H^\circ & \Delta S^\circ & \Delta H_0 & \Delta S_0 & \text{Ref.} \\
\hline
\text{F} & -7.1 & 20.7 & -23.3 & 21, 30 \\
& -5.2 & & & & 31 \\
& -5.8 & -4.0 & 23.3 & -6.9 & -2.4 & -18.2 & 30, 32, 33 \\
& -5.8 & 23.7 & -6.0 & 34 \\
\text{Cl} & -0.15 & -3.4 & 4.0 & 35 \\
& -0.18 & -0.4 & 1.6 & 22 \\
& -0.10 & & & 36, 37 \\
\text{Br} & -5.2 & 23.2 & 2.7 & 30, 32 \\
& 0.43 & 24.0 & -4.0 & 36, 37 \\
\text{I} & -5.0 & 19 & -27.6 & 21 \\
\text{NO}_3 & -4.6 & 1.1 & 25.4 & 6.4 & 30, 36, 37 \\
& 24.3 & 1.9 & & 38 \\
\text{NCS} & -9.5 & -2.67 & 30.1 & \sim 0 & 27, 36, 37 \\
& -8.6 & 26.8 & -8.4 & 28 \\
\text{N}_3 & -8.7 & 33.1 \pm 1.0 & 14 & 32 \\
& -2.9 & 13.5 & \sim 0 & 39 \\
\end{array}
\]

*) at 25°C in aqueous solution; see footnotes. a)-e), Table 1.

...corresponding equilibrim constant ($\log K$). Here it must be emphasized that the existence of a correlation between the $\log k$ and $\log K$ (Fig. 5), or between the activation energy and the reaction heat (Fig. 6) is not a criterion of a given mechanism, and therefore it can not be used to distinguish, e.g. between an $S_{N1}$ and $S_{N2}$ mechanism, as it was done for example in a book by Langford and Gray\textsuperscript{40}.

If a relation between the rate constants and the corresponding equilibrium constants is established, then significant changes in $\Delta S^*$ and $\Delta S_0$ may lead to an erroneous inclusion in the series, of reactions having other values of the kinetic parameters $E_a$, $E_a^x$ or $E_a^{xx}$, i.e. to a violation of the assumption that $\Delta H_0$ is the only parameter changing throughout the series. Thus, from the plots of $E_a$ against $\Delta H_0$ for the aquation reactions of Cr(III) complexes (Fig. 6)
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**Table 4.** Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction \([\text{Rh} (\text{NH}_3)_5X]^{2+} + \text{H}_2\text{O} \xrightarrow[k_1]{\text{}} [\text{Rh} (\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-\)

<table>
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<tr>
<th>X</th>
<th>log (k_1)</th>
<th>-log (K_X)</th>
<th>(\Delta H^*) kcal/mole</th>
<th>(\Delta S^*) e.u.</th>
<th>(\Delta H_0) kcal/mole</th>
<th>(\Delta S_0) e.u.</th>
<th>Ref.</th>
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<td>Cl</td>
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<td>1.9±0.3</td>
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</table>

*) at 25°C in aqueous solution; see footnotes. a)-e), Table 1.

**Fig. 5.**

\(\text{log } k_1\) vs. \(-\text{log } K_X\) for various ligands.
### Table 5. Comparison of Experimental\(^*\) and Calculated Energies of Activation

<table>
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<th>Reaction</th>
<th>(E_{\text{calc}}) kcal/mole</th>
<th>(\Delta H_0) kcal/mole</th>
<th>(E_{\text{exp}}) kcal/mole</th>
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</thead>
<tbody>
<tr>
<td>([\text{Co}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{1+} + \text{X}^-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X = \text{Cl})</td>
<td>24.8</td>
<td>-2.9</td>
<td>24.1</td>
</tr>
<tr>
<td>(N_3)</td>
<td>28</td>
<td>6.5</td>
<td>33.1</td>
</tr>
<tr>
<td>([\text{Rh}(\text{NH}_3)_5\text{X}]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{1+} + \text{X}^-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X = \text{Cl})</td>
<td>25.0</td>
<td>-2.6</td>
<td>24.6</td>
</tr>
<tr>
<td>(\text{Br})</td>
<td>25.5</td>
<td>-0.7</td>
<td>25.1</td>
</tr>
<tr>
<td>(I)</td>
<td>26.3</td>
<td>1.9</td>
<td>27.1</td>
</tr>
<tr>
<td>([\text{Cr}(\text{NH}_3(S\text{X})_5]^{3+} + \text{H}_2\text{O} \rightleftharpoons [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{1+} + \text{X}^-)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(X = \text{Cl})</td>
<td>24.5</td>
<td>-3.9</td>
<td>22.6</td>
</tr>
<tr>
<td>(\text{NCS})</td>
<td>27.8</td>
<td>6.9</td>
<td>26.7</td>
</tr>
</tbody>
</table>

\(^*\) at 25°C in aqueous solution

---

**Fig. 6.**
it can be seen that the fluoride complex does not belong to the general series. It was found from estimates based on equation (3) that $E_a$ in this case ($\sim 65$ kcal/mol) greatly exceeds the average value for the series ($\sim 45$ kcal/mol). If $E_a$ for the fluoride complex is calculated using the latter value of $E_a$, the corresponding point falls on the graph of Fig. 6.

The considerable change of $\Delta S^*$ and $\Delta S_0$ along the series means that the value of the Brönsted coefficient $\alpha$, determined from the dependence of log $k$ on log $K$, may differ noticeably from the value determined from the dependence of $E_a$ on $\Delta H_0$. Probably, this situation is found in the aquation reactions of $[\text{Co(NH}_3)_6\text{X}]^{2+}$ complexes. Thus the coefficient $\alpha$ characterizing the relation between the logarithms of the rates and the equilibrium constants in the aquation reactions is found to be close to 1 (Fig. 7.). We can assume however that if the Brönsted coefficient is obtained from the dependence of $E_a$ on $\Delta H_0$, it will have approximately the same value as for the aquation reactions of $[\text{Cr(H}_2\text{O}_6]\text{X}]^{3+}$ complexes (for the latter series, the value of $\alpha$ determined from the dependence of $E_a$ on $\Delta H_0$ is very close to the value determined from the relations between log $k$ and log $K$). The
assumption is justified by the fact that the estimated energies of activation of the Co(III) reactions, using, the kinetic parameters of the Cr(III) reactions, give good agreement with experiment, thus implying that the values of the two sets of parameters are very close to each other.

The difference in experimental values of $\alpha$ for aquation of the [Cr-(H$_2$O)$_6$X]$^{2+}$ and [Co(NH$_3$)$_6$X]$^{3+}$ complexes was used, in our opinion wrongly, to deduce different types of activated complex for the two series$^{42}$. According to the theory presented above, the transition states must be the same for both the chromium and cobalt series. Therefore, we found that it is more correct to investigate (where possible) the correlation between $E_a$ and $\Delta H_0$ and to consider separately the changes in entropy of activation and reaction.

Equations (2) also predict a relation between the rate constants of aquation reactions of [Co(NH$_3$)$_6$X]$^{3+}$ complexes and the energies ($h\nu$) of the first band of the absorption spectrum in UV-range (provided that the values of other kinetic parameters can be considered approximately constant). Such a relationship has been observed experimentally$^{42}$ and an analysis of the data shows that the assumption of constant $E_a$, $E^a$ and $E_\alpha^a$ is well obeyed, except for X$^-$=F$^-$ of N$_3^-$. Assuming that the energy of hydration of the [Co(NH$_3$)$_6$X]$^{3+}$ complexes does not depend on X (i.e. the sizes and charge distribution of the complexes are approximately constant), the change in the heat of the aquation reactions $\delta(\Delta H_0)$ with X$^-$ is given by

$$
\delta(\Delta H_0) = \delta(\Delta H_0^\alpha) + \delta(\Delta H_0^x)
$$

where $\delta(\Delta H_0^\alpha)$ is the change of the heat of hydration of ion X$^-$ and $\delta(\Delta H_0^x)$ the corresponding change of the bond energy Co–X. As this relation is linear, it follows that the values of change monotonously, this indicated that in the given series of reactions, as well the Co–X bond energy as the heat of hydration of X$^-$ decrease in absolute value. In general this correlation is not obvious, as the variation in the heats of bond formation depends on both X and the metal properties. If the value of one of the parameters $\delta(\Delta H_0^\alpha)$ or $\delta(\Delta H_0^x)$ increases and the other one decreases, a minimum should be observed in the plot of log $k$ against $h\nu$, provided that the range of reaction heats is wide enough.

We now consider, in terms of the theory given above, some experimental data concerning the kinetics of aquation of [Cr(NH$_3$R)Cl]$^{2+}$ complexes, where R=H, CH$_3$, C$_2$H$_5$, n-C$_3$H$_7$, n=C$_4$H$_9$.$^{23}$ (Table 6). If the difference in the bond energies of M–OH$_2$ and M–X in the complexes is denoted by $\delta(\Delta H_{M-OH_2,M-X})$, and the difference in hydration energy of [ML$_2$H$_2$O]$^{2+}$ and [ML$_2$X]$^{3+}$ (where M=Cr(III), L=NH$_3$R) by $\delta(\Delta H_{\text{compl}})$, then the change in
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Table 6. The kinetic and thermodynamic parameters of aquation reactions*) $[\text{Cr}(\text{NH}_2\text{R})_s\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{Cr}(\text{NH}_2\text{R})_s\text{H}_2\text{O}]^{3+} + \text{X}^-$

<table>
<thead>
<tr>
<th>R</th>
<th>$E_a$ kcal/mole</th>
<th>$a$ Å</th>
<th>$E_a$ kcal/mole</th>
<th>$\Delta H_{5}^{0}$ kcal/mole</th>
<th>$\Delta H_{5}^{0}$ kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>23.3</td>
<td>2.5</td>
<td>45.5</td>
<td>-6.0</td>
<td></td>
</tr>
<tr>
<td>CH$_3$</td>
<td>27.0</td>
<td>5.4</td>
<td>43.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_5$</td>
<td>27.0</td>
<td>6.5</td>
<td>43.5</td>
<td></td>
<td>$\sim$8</td>
</tr>
<tr>
<td>C$_3$H$_7$</td>
<td>27.0</td>
<td>7.7</td>
<td>44.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C$_4$H$_9$</td>
<td>27.0</td>
<td>8.9</td>
<td>44.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) at 25°C in aqueous solution.

reaction heat $\delta(\Delta H_0)$ corresponding to change in R equals:

$$\delta(\Delta H_0) = \delta(\Delta H_{\text{M-O,M-X}}) + \delta(\Delta H_{\text{compl}})$$

From equation (2), putting $r = a + b$, it is found that $E_a$ is practically constant (Table 6). As obviously also the values of the parameters $E_a^s$ and $E_a^{aa}$ are constant for a given $X$, it follows that practically all the change in the energy of activation throughout a series of reaction arises from a change in the heat of reaction $\delta(\Delta H_0)$. Considering a given series R, we can conclude that an abrupt change in activation energy takes place when H in L is replaced by CH$_3$, while the energy of activation remains nearly constant when the methyl group is replaced by higher aliphatic radicals. It was estimated that a substitution of H by CH$_3$ leads to a change in $\Delta H_0$ of about $\sim$14 kcal/mol, which apparently is the maximum value of $\delta(\Delta H_0)$. (Calculation of the heat of reaction from the energy of activation is considerably less accurate than the reverse calculation). The constancy of the reaction heat when replacing CH$_3$ by higher radicals implies, that the relative increase in the difference of the hydration energies of the $[\text{ML}_4\text{H}_2\text{O}]^{3+}$ and $[\text{ML}_2\text{X}]^{2+}$ complexes (decrease in the absolute value) is compensated by a decrease in the bond energies of M–OH$_2$ and M–X, i.e. $\delta(\Delta H_{\text{compl}}) = -\delta(\Delta H_{\text{M-O,M-X}})$. Apparently a more realistic situation is that one when the main change in the bond energy difference M–OH$_2$ and M–X occurs when replacing H by CH$_3$ while this difference remain nearly constant, when CH$_3$ is replaced by higher radicals. This assumption implies that the heat of reaction along a series of radicals from CH$_3$ to C$_4$H$_9$ does not stay constant, but increases somewhat, although not as sharply as when going from H to CH$_3$. Thus the energy of activation does not change and therefore, when going from CH$_3$ to C$_4$H$_9$ $E_a$ must change somewhat. The latter change is difficult to estimate theoretically within the framework of a tractable model.
E. D. German and R. R. Dogonadze

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References

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