THE AQUATION OF ACIDOPENTAAQUOCHROMIUM(III) COMPLEXES: 
A CONSIDERATION OF TRANSITION ENTHALPIES

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The aquation reaction
\[
\text{Cr(H}_2\text{O)}_5\text{X}^{2+} + \text{H}_2\text{O} \rightarrow \text{Cr(H}_2\text{O)}_6^{3+} + \text{X}^-
\]
(1)
is known to proceed by both acid-dependent and acid-independent paths. When
HX is a strong acid (X\(^-\) = NO\(_3\)^-, Cl\(^-\), Br\(^-\), I\(^-\), NCS\(^-\)) the rate expression is
\[
\text{rate} = [\text{complex}](k_0 + k_{-1}[H^+]^{-1} + ...)
\]
with the two specific rate constants corresponding to the reactants Cr(H\(_2\)O\(_5\))\(_{5}\)X\(^{2+}\)
and Cr(H\(_2\)O\(_4\))\(_{4}\)(OH)\(_{2}\)X\(^{+}\) respectively.\(^1\)\(^-\)\(^4\) In this paper we consider the "transition
enthalpies" for the acid-independent aquation reaction and discuss the nature of
the transition state species.

For reaction (1) the transition enthalpy \(\Delta H_T\) is defined as \(\Delta H_a - \Delta H_R\) where
\(\Delta H_a\) is the activation enthalpy and \(\Delta H_R\) is the enthalpy change for the reaction.\(^5\)\(^-\)\(^6\)
\(\Delta H_T\) measures the heat content of the transition state species relative to the enthalpy
of formation of the reaction products. For an associative mechanism \(\Delta H_T\) will vary
with the leaving group X whereas for a dissociative mechanism\(^\dagger\) \(\Delta H_T\) will be indepen-
dent of X.\(^6\) For the base hydrolysis\(^6\) and the aquation\(^7\) reaction of complexes
Co(NH\(_3\))\(_5\)X\(^{2+}\) an observed constant value of \(\Delta H_T\) suggests a dissociative mechanism
with the leaving group substantially dissociated and solvated in the transition state.

Table 1 presents values of \(\Delta H_a\), \(\Delta H_R\), and \(\Delta H_T\) for reaction (1). The observed
spread of values for \(\Delta H_T\) (6 ± 1·3 kcal mol\(^{-1}\)) is larger than for the base hydrolysis\(^6\)
(2·0 kcal mol\(^{-1}\), six compounds) or the aquation\(^7\) (2·9 ± 1·3 kcal mol\(^{-1}\), four com-
ounds) of Co(NH\(_3\))\(_5\)X\(^{2+}\). The enthalpy of hydration of the leaving group X is
increasingly exothermic in the sequence H\(_2\)O, NO\(_3\)^-, Br\(^-\), Cl\(^-\), and the data in

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\(\dagger\) The terms "associative" and "dissociative" are defined in ref. 6.


Table I show that the instability of the transition state species relative to the reaction products (i.e. $\Delta H_T$) increases in this order. These results suggest that in the transition state the leaving group $X$ is less strongly dissociated and solvated in the reaction of the chromium compounds than in the reaction of the analogous cobalt compounds.

<table>
<thead>
<tr>
<th>$X$</th>
<th>$\Delta H_R$</th>
<th>$\Delta H_a$</th>
<th>$\Delta H_T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>0.0</td>
<td>26.1±1.0</td>
<td>26.1±1.0</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>-6.6±0.5</td>
<td>24.3±0.2</td>
<td>30.9±0.7</td>
</tr>
<tr>
<td>$Br^-$</td>
<td>-5.1±0.2</td>
<td>23.8±0.3</td>
<td>28.9±0.5</td>
</tr>
<tr>
<td>$SCN^-$</td>
<td>1.4±0.2</td>
<td>27.5</td>
<td>26.1±0.3</td>
</tr>
<tr>
<td>$NO_3^-$</td>
<td>-4.5±0.2</td>
<td>21.6±0.1</td>
<td>26.1±0.3</td>
</tr>
</tbody>
</table>

*f* Ref. 2.  
*g* Ref. 3.  
*h* Ref. 4; $\Delta H_a = E_a - RT$.  
*i* Ref. 1.

This deduction is consistent with the observed correlation between $S_X^0$ (corrected for rotation of $X^-$) and $\Delta S^2$ for reaction (1): 

$$\Delta S^2 = p S_X^0 + C \quad (X = Cl^-, Br^-, I^-, NO_3^-, SCN^-)$$

where $p = 0.53$. In contrast $p \approx 1.0$ for Co(NH$_3$)$_5$X$^{2+}$ aquation, and for this reaction linear free energy and transition enthalpy correlations indicate that the leaving group $X$ is substantially dissociated and solvated in the transition state.

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