Substitution as the Rate-determining Step in the Reduction of the Perchlorate Ion by Ruthenium(II)

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Summary Correlation of the activation parameters for the reduction of ClO_4^- by aquoruthenium(II) with those for substitution of Cl^-, Br^-, and I^- on the same cation indicates that substitution of ClO_4^- on to $Ru(H_2O)_6^{2+}$ is the rate-determining step in the reduction.

WE have studied the kinetics of the aquoruthenium(II)-catalysed formation of $Ru(H_2O)_5X^{2+}$ where $X = Cl^-, Br^-$, and I^- (reaction 1), as a means of determining substitution

$$\text{(1)}\ Ru(H_2O)_6^{3+} + X^- \xrightarrow{Ru^{2+}} Ru(H_2O)_5X^{2+} + H_2O$$

parameters for aquoruthenium(II). (Co-ordinated waters hereafter omitted).

Individual spectrophotometric kinetic runs followed zero-order kinetics for 20% ($[X^-] = 0{\cdot}02$ M) to 60% ($[X^-] = 0{\cdot}10$ M) of the reaction and conformed to the rate law:

$$\text{(2)}\ d[RuX^{2+}]/dt = k_x[Ru^{2+}][X^-][Ru^{3+}]^0[H^+]^0.$$

These results are consistent with the mechanism:

$$\text{(3)}\ Ru^{2+} + X^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} RuX^+$$

$$\text{(4)}\ RuX^+ + Ru^{3+} \xrightarrow{k} RuX^{2+} + Ru^{2+}$$

$$k >> k_1, k_2$$

During the period in which $k[Ru^{3+}] >> k_2$ the observed rate constant is identified as k_1. The assumption that $k > k_1, k_2$ is supported by the magnitude of the activation parameters for the observed process, since electron-transfer reactions like process 4 have small values for $\Delta H^\ddagger$ and large, negative values for $\Delta S^\ddagger$.[1] The similarity of the activation parameters for reactions involving the several halides implies a dissociative mechanism for the ruthenium(II) substitution reaction. Small differences in $-\Delta S^\ddagger$ correlate with the differences in S^0 of the aquated halides.[2]

We have studied polarographically the perchlorate oxidation of $Ru(H_2O)_6^{2+}$.

$$\text{(5)}\ 2Ru^{2+} + ClO_4^- + 2H^+ \rightarrow 2Ru^{3+} + ClO_3^- + H_2O.$$

The rate law is:

$$\text{(6)}\ d[Ru^{III}]/dt = 2k_3[Ru^{2+}][ClO_4^-][H^+]^0$$

and k_3 corresponds closely to the rate constant for ruthenium(II)-catalysed reduction of ClO_4^- by chromium(II).[3]

Comparison of the activation parameters for k_3 with those for the substitution reactions strongly suggests that the rate-determining process for the redox reaction is substitution on $Ru(H_2O)_6^{2+}$. The slower rate obtained for the reduction is predicted by the correlation of $-\Delta S^\ddagger$ with S^0 [2] for the substitution reactions.

The relative rate of reduction of the perchlorate ion by various aquo-ions is $Ru^{II} > Ti^{III}$ [4] $> Mo^{III}$ [5] $> V^{II} \approx V^{III}$ [6] $> Cr^{II}, Fe^{II} \approx 0$. The aquoruthenium (II) reduction rate is limited by the rate of substitution, and the reduction step must be more rapid than the observed rate. All other species are sufficiently labile that the observed rate must be that of the reduction step. Therefore, this order is a measure of the interaction of the metal ion with the perchlorate ion. The relative value of 10 *Dq* for members of this group is given by $Ru^{II} > Ti^{III} > Mo^{III} > V^{III} > Cr^{II} > V^{II} > Fe^{II}$.[7,8] Since 10 *Dq* is a measure of the polarizability of the *d*-orbitals of the metal ion, the excellent correlation between 10 *Dq* and the rate of reduction indicates intimate involvement of the metal ion *d*-orbitals in the mechanism of deformation and reduction of the perchlorate ion.

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Specific rate constants and activation parameters for aquoruthenium(II) *reactions*[a]

X	10^3k, M^{-1} sec^{-1} [b]	$\Delta H^\ddagger$, kcal mole^{-1} [c]	$\Delta S^\ddagger$, eu[c]	S_x^0, eu[d]
Cl^- [e]	$8{\cdot}5 \pm 0{\cdot}2$	$20{\cdot}2 \pm 0{\cdot}3$	$-0{\cdot}4 \pm 0{\cdot}4$	13·5
Br^- [e]	$9{\cdot}7 \pm 0{\cdot}9$	$19{\cdot}8 \pm 0{\cdot}4$	$-1{\cdot}2 \pm 1{\cdot}5$	19·7
I^- [e]	$9{\cdot}0 \pm 0{\cdot}4$	$19{\cdot}5 \pm 0{\cdot}7$	$-2{\cdot}4 \pm 1{\cdot}0$	25·3
ClO_4^- [f]	$3{\cdot}2 \pm 0{\cdot}1$	$19{\cdot}4 \pm 0{\cdot}3$	$-5{\cdot}0 \pm 1{\cdot}0$	43·6

[a] $\mu = 0{\cdot}3$ M (HBF_4), $0{\cdot}08$ M $< [H^+] < 0{\cdot}3$ M.

[b] $T = 25{\cdot}0°$.

[c] $T = 20$—$35°$.

[d] The absolute entropy of the aquated anion taken from ref. 2.

[e] Reaction 1, rate law 2.

[f] Reaction 5, rate law 6.

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