Hydroxide Ion as a Reducing Agent for Mixed-valence Ruthenium Trimers

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Summary Oxidation of hydroxide ion to O^I by "ruthenium brown" is kinetically first order in each reagent ($E_a = 18{\cdot}7$ kcal/mole) and a rate-limiting attack by OH^- appears likely.

HYDROXIDE ion has been reported[1] to function as a reducing agent in the transformation of the cation of "ruthenium brown" (I) $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{7+}$ to that of "ruthenium red" (II) $[(NH_3)_5RuORu(NH_3)_4ORu(NH_3)_5]^{6+}$. Elsewhere, we have reported confirmation of the linear oxygen-bridged trimeric structure of the chromophore of (II).[2] The close resemblance of the spectra of the two ions (Table) indicates structure similarity of (I) and (II).

Potentiometric titrations of (I) with OH^- and with Cr^{II} and of (II) in acid with Ce^{IV} confirm that the (I) → (II) change is a one-electron reduction that can be effected by OH^- but not reversed by H^+. Only quite minor decomposition (< 5%) accompanies these changes.

Polarographic analysis of solutions produced by reaction of (I) with OH^- demonstrates the presence of O_2 in amounts approaching (*ca.* 60%) that to be expected from the stoicheiometry

$$\text{(I)} + OH^- \rightarrow \text{(II)} + 1/4O_2 + 1/2H_2O$$

If a solution of (I) is made basic and then re-acidified at once, some (*ca.* 20%) of (I) is rapidly re-formed. O_2 oxidizes (II) to (I) only slowly under these conditions, but H_2O_2 reacts faster. On the basis of these results, we conclude that an initial product of reduction of OH^- is an O^I species[4] which then forms O_2. The reaction shows a single isosbestic point and between pH 6·6 and 9·8 follows the rate law

$$\frac{d[(II)]}{dt} = k[(I)][OH^-]$$

where k is $1{\cdot}6 \times 10^4\,\text{M}^{-1}\,\text{s}^{-1}$ at 25·0° in 0·25M-$LiClO_4$ containing 0·05M-trishydroxymethylaminomethane ("trisma base") buffer.

Spectra of trimeric cations (I) *and* (II)

(I)		(II)		
$\nu \times 10^3$ (cm^{-1})	ϵ	$\nu \times 10^3$ (cm^{-1})	ϵ	Assignment[a]
7·4	$1{\cdot}5 \times 10^3$			$n \rightarrow n'$
11·3	$1{\cdot}7 \times 10^3$	13·2	$9{\cdot}9 \times 10^2$	$n' \rightarrow \pi^*$
21·5	$4{\cdot}4 \times 10^4$	18·8	$6{\cdot}9 \times 10^4$	$n \rightarrow \pi^*$
28·5	$1{\cdot}4 \times 10^4$	26·6	$6{\cdot}3 \times 10^3$	$\pi \rightarrow \pi^*$

[a] In D_{4h}, combination[3] of the nine $d\epsilon$ orbitals of the set of three ruthenium atoms yield E_g, E_u, E_g', $2B_{1g}$ and B_{1u} molecular orbitals. E_g is bonding (π) and E_g' antibonding (π^*). It seems likely that the E_u set is slightly bonding (n) and lies lower than the B set (n').

E_a between 7° and 32° is 18·7 kcal/mole. Variation of buffer identity (borate, imidazole), buffer concentration, presence of nucleophiles (Br^-) and radical scavengers (aniline hydrochloride) do not alter the rate but monomeric Ru^{3+} has some catalytic effect. Some deviation from simple kinetics is noted at very low [(I)] (*ca.* 10^{-7}M).

These results are consistent with rate-determining attack of OH^- on (I) to form a μ-peroxo-intermediate such as $[(NH_3)_5RuORu(NH_3)_4(OOH)Ru(NH_3)_5]^{6+}$ which then rapidly decomposes, probably at least partly by a bimolecular mechanism.[5] The attack of OH^- on oxygen could be facilitated by the interaction of the empty π^* set to reduce electronic crowding around the bridging oxygen during the activation process.

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