

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

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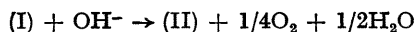
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**Summary** Oxidation of hydroxide ion to  $O^{\cdot-}$  by "ruthenium brown" is kinetically first order in each reagent ( $E_a = 18.7$  kcal/mole) and a rate-limiting attack by  $OH^-$  appears likely.

HYDROXIDE ion has been reported<sup>1</sup> 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).<sup>2</sup> 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)  $\rightarrow$  (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 stoichiometry



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  $O^{\cdot-}$  species<sup>4</sup> 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  $1.6 \times 10^4 M^{-1} s^{-1}$  at 25.0° in 0.25M-LiClO<sub>4</sub> containing 0.05M-tris-hydroxymethylaminomethane ("tris-ma base") buffer.

Spectra of trimeric cations (I) and (II)

| (I)                                      |                   | (II)                                     |                   | Assignment <sup>a</sup> |
|--|-------------------|--|-------------------|-------------------------|
| $\nu \times 10^3$<br>(cm <sup>-1</sup> ) | $\epsilon$        | $\nu \times 10^3$<br>(cm <sup>-1</sup> ) | $\epsilon$        |                         |
| 7.4                                      | $1.5 \times 10^3$ |  |                   | $n \rightarrow n'$      |
| 11.3                                     | $1.7 \times 10^3$ | 13.2                                     | $9.9 \times 10^3$ | $n' \rightarrow \pi^*$  |
| 21.5                                     | $4.4 \times 10^4$ | 18.8                                     | $6.9 \times 10^4$ | $n \rightarrow \pi^*$   |
| 28.5                                     | $1.4 \times 10^4$ | 26.6                                     | $6.3 \times 10^3$ | $\pi \rightarrow \pi^*$ |

<sup>a</sup> In  $D_{3h}$  combination<sup>3</sup> 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 ( $\pi$ ) and  $E_g'$  antibonding ( $\pi^*$ ). 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  $\mu$ -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.<sup>5</sup> The attack of  $OH^-$  on oxygen could be facilitated by the interaction of the empty  $\pi^*$  set to reduce electronic crowding around the bridging oxygen during the activation process.

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