

Kinetics of the Reductions of Oxyhalogens with Dimeric Tungsten(V) in Aqueous Acidic Medium

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Summary: The dinuclear tungsten(V)- $W_2O_4^{2+}$ (aq) dimer (structure 1) is readily oxidized to W(VI) by a number of oxyhalogen species in aqueous acidic media. Oxidizing agents, BrO_3^- , $HBrO_2$, $HOCl_2$ and $HOCl$ with excess reductant yield the corresponding halide ions, and reduction of ClO_3^- yield Cl^- , even when the oxidant is in large excess. The reaction of IO_3^- is complicated by relatively rapid reaction between I and IO_3^- at low pH, which undergoes further slow reduction yielding I_2 .

Reduction of ClO_3^- and BrO_3^- are independent of hydrogen ion concentration in the range 0.1 - 1.0 M $[H^+]$, but reduction of the acids $HBrO_2$, $HClO_2$ and H_5IO_6 are found to be inverse-first order in $[H^+]$. Hypochlorous acid appears to react via a $[(W^V)_2-ClOH]$ adduct, which undergoes deprotonation ($PK=1.5$), prior to electron transfer.

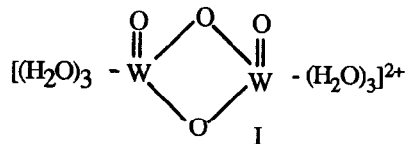
Introduction

Increased interest in the redox reactions of tungsten has been sparked by an enhanced awareness of the richness solution chemistry of that element [1], and by its recognized occurrence in an array of redox enzymes, most notably the nitrogenases, nitrate reductases, and xanthine dehydrogenases [2-3]. The aqua (or aqua-oxo) ions of different oxidation states of tungsten are more difficult to prepare than those of molybdenum [1]. Aqua form of tungsten ion via oxalato, cysteinato, and ethylenediamine-tetraacetate (edta) complexes have been recently reported [4]. The method for the preparation of W^V aqua ion of $[W_2O_4(H_2O)_6]^{2+}$ has been described [4]. The substitution and redox properties of W^V aqua ion are of interest.

Our initial interest in this area deals with the reduction of very low concentrations of $W(VI)$ with vitamin B_{12} (cob(I) albinin [5], but difficulties were encountered in the autocatalytic behaviour and uncertainty as to the identity of the reduced tungsten species. In the present study, which treats the oxidation of dimeric tungsten(V) with anionic oxyhalogen species, there is ambiguity concerning oxidation states. However, some unexpected variations in kinetic patterns, with the reduction of iodate appearing to be unusually complex.

Results and Discussion

The W^V species with which we are dealing have been shown to be dinuclear having a +2 charge [4]. Its structure is represented as I, in accord with structurally characterized $[W_2O_4(edta)]^{2-}$ complex [11], and by analogy with complexes of $[Mo_2O_4]^{2+}$, elongation of the bond to the axial H_2O is likely. ^{17}O NMR spectrum of the $[W_2O_4]^{2+}$ structure has been reported by Richens [12]. Within the acidity range examined, both ClO_3^- and BrO_3^- exist preponderantly in their non-protonated forms [13], whereas $Cl(III)$, $Br(III)$, $Cl(I)$ and $I(VII)$ are converted very largely to the weak acid $HClO_2$ ($pK_{a1}=1.64$) [14], $HBrO_2$ ($pK_a=4.9$) [15], $HOCl$ ($pK_a=7.5$) [16] and H_5IO_6 ($pK_a=1.64$) [17].



Reactions of $(W^V)_2$ with BrO_3^- and ClO_3^- are seen (Table-1) to consume very nearly 3 mol of dimer/mol of oxidant. Reductions of $HClO_2$ and $HBrO_2$ utilize nearly 2 mol of dimer, and $HOCl$ oxidizes just 1 mol (2 equiv) of $(W^V)_2$. Each of these oxyhalogen species is thus reduced to the -1 state. A similar conclusion probably applies to

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Table-1: Stoichiometries of the reaction of dimeric Tungsten(V) with Oxyhalogens species^a

Oxidant	[H ⁺] M	10 ⁴ M[(W ^V) ₂]	10 ⁴ M[OX]	10 ⁴ M[(W ^V) ₂] Δ[OX]	10 ⁴ M Δ[OX]	Δ[(W ^V) ₂] Δ[OX]
BrO ₃ ⁻	0.11	5.20	1.28	4.10	-	3.20
	0.11	5.20	0.85	2.67		3.15
	0.11	5.20	0.46	1.41		3.08
HBrO ₂	0.11	5.65	3.05	6.26		2.05
	0.11	5.65	1.55	3.37		2.18
	0.11	5.65	0.88	1.89		2.15
ClO ₃ ⁻	0.14	18.50	1000.00		6.55	2.82
	0.14	18.50	1000.00		6.17	2.99
HClO ₂	0.14	5.65	2.46	4.79		1.95
	0.14	5.65	1.26	2.36		1.88
	0.14	5.65	0.75	1.35		1.81
HOCl	0.10	5.05	3.58	3.51		0.98
	0.10	5.05	1.48	1.40		0.95
H ₃ IO ₆	0.10	2.20	0.60	0.57		0.96
	0.10	2.20	0.22	0.21		0.96
IO ₃ ^{-b}	0.10	4.21	60.00		1.50	2.81
	0.10	4.21	60.00		1.50	2.71

^aReaction with (W^V)₂ in excess followed at 430 nm (see text).

^bReaction mixture with IO₃⁻ in excess were analysed for I₂ spectrophotometrically. - Δ[IO₃⁻] was taken as 2 Δ[I₂].

the reaction with excess IO₃⁻, but this reaction is complicated by the relatively rapid reaction between I⁻ and IO₃⁻ at low pH [18]. Formation of halide is not unexpected when the reductant is in excess, but determination with ClO₃⁻ in very large excess are more informative, for they indicate that reduction of intervening states, Cl(II), and Cl(I), are much more rapid than reduction of Cl(V). Such a conclusion is in accord with our kinetic measurements.

Kinetic data pertaining to two representative oxidants, BrO₃⁻ and H₃IO₆ are given in Table-2. Note that the rate of reduction of bromate is essentially independent of acidity in the range 0.05-1.0M[H⁺], whereas that periodic acid is very nearly proportional to [H⁺]⁻¹. With both oxyhalogens, rates are proportional to oxidant at low concentration of the latter, but there is a perceptible trend towards kinetic saturation at high concentration of BrO₃⁻, indicating association (in this case ion-pairing) between tungsten and oxyhalogen species. Rate laws for these system, as well as for reactions with remaining oxyhalogens, are listed in Table-3.

Monomial rate laws featuring inverse acid dependencies are observed for reductions of the uncharged oxyacids, HClO₂, HBrO₂, and H₃IO₆, pointing to an activated complex containing one

Table-2: Kinetic data for the oxidation of dimeric Tungsten(V), [(W₂O₄)]²⁺, with Bromate and Periodate^a.

Oxidant	10 ⁴ M[OX]	[H ⁺] M	k _{obsd} , s ⁻¹	k _{calcd} , ^b s ⁻¹
BrO ₃ ⁻	2.44	0.100	0.018	0.0165
	4.95	0.100	0.033	0.0334
	12.00	0.100	0.079	0.0809
	40.00	0.100	0.248	0.2588
	80.00	0.100	0.480	0.5100
	4.95	0.050	0.028	0.0334
	4.96	0.025	0.035	0.0334
	4.98	0.750	0.035	0.0334
	4.96	1.000	0.037	0.0334
	H ₃ IO ₆	0.10	0.100	4.00
0.25		0.100	7.80	8.5
0.50		0.100	16.50	17.0
0.75		0.100	23.56	25.50
1.00		0.100	32.00	34.00
2.00		0.100	64.00	68.00
0.50		0.50	4.58	3.89
0.50		1.00	2.25	1.95

^aReactions were carried out at 25°C; ionic strength 1.0M (NaClO₄), [(W^V)₂]=4.5 x 10⁻⁴M throughout, ^bSpecific rates calculated by using the relationships and parameters.

unit of each of (W^V)₂ and oxidant, formed with a loss of proton. The lack of such as [H⁺]⁻¹ term for reduction of negative BrO₃⁻ and ClO₃⁻ ions suggests that, in each case, the active oxidizing species is anionic.

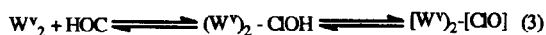
The picture with hypochlorous acid is less straight forward. This oxidant follows a rate law (3) reflecting both a pre-association of redox partners and a deprotonation. The pK_a near 1.0

Table-3: Rate Laws and Kinetic Parameters for the Oxidations of Dimeric Tungsten(V) by Oxyhalogen species^a.

Oxidant (Ox)	rate law ^b	No.	parameters ^c
ClO ₃ ⁻	$kK[Ox]/(1 + K[Ox])$	1	$k=0.021 \pm 0.004 \text{ S}^{-1}$; $K=0.8 \pm 0.01 \text{ M}^{-1}$
BrO ₃ ⁻	$kK[Ox]/(1 + K[Ox])$		$k=1.8 \pm 0.3 \text{ S}^{-1}$; $K=4.5 \pm 0.4 \text{ M}^{-1}$
HClO ₂	$k[Ox][H^+]^{-1}$	2	$k=650 \pm 40 \text{ S}^{-1}$;
HBrO ₂	$k[Ox][H^+]^{-1}$		$k=808 \pm 20.5 \text{ S}^{-1}$;
HOCl	$kK_A[Ox]/(K_A K[Ox] + [H^+])$	3	$k=0.45 \pm 0.13 \text{ S}^{-1}$; $K_A=(7.9 \pm 2.5) \times 10^3 \text{ M}^{-1}$; $K_A=0.14 \pm 0.05 \text{ M}$
H ₂ IO ₆	$k[Ox][H^+]^{-1}$		$k=3112 \pm 160 \text{ S}^{-1}$

Reactions were carried out at 25.0°C; I = 1.0M (NaClO₄ - HClO₄). Rate Laws -d [(W^v)₂]/dt in S⁻¹: K values pertain to (W^v)-Ox association quotient. K_A is a deprotonation quotient.

consistent with acidity pattern, does not correspond to that for HOCl (7.50) [16] but is instead assigned to the trinuclear precursor (II).



Attachment of HOCl in complex II may involve bonding to the chlorine atom, which is more electron-rich and much less hindered than the halogens in the higher oxyacids and their anions. Values of k conform to eq. 5.

$$(k) \text{ obsd} = \frac{kK_A [OX]}{K_A + [H^+]} \quad (5)$$

According to eq. 5, a bimolecular specific rate (k) of $0.45 \pm 0.07 \text{ M}^{-1}\text{S}^{-1}$ and an acidity quotient (k_A) of $0.12 \pm 0.05 \text{ M}$, the latter in agreement with the k_A for HIO₃ (0.16 M at I = O) reported by Naiditch [19].

An important question concerning this reaction series is whether the individual redox steps are one or two-electron transactions, i.e., whether odd-electron of oxyhalogen species intervene. No facts of the observed rate behaviours requires the operation of single electron steps, nor do kinetic profiles suggest the formation and disappearance of possible tungsten intermediates (e.g., tungsten monomeric, W, or a W^v-W^{VI} complex). However, sequences initiated by a single-electron change, followed by a very rapid second transfer between

intermediates within their solvent cage, cannot be ruled out. If all reactions involve 2e-changes, each must pass through a bridged intermediate, for outersphere transfers of two units have not yet been reported.

Experimental

Materials

Sodium cholrate (Baker and Adamson), sodium chlorite [6-7] (Aldrich) sodium bromate [8-9] (Aldrich), sodium hypochlorite (Alfa), sodium periodate (Alfa), were used as received. Sodium iodate (Baker and Adamson) was recrystallized three times before use in the experiments to ensure that the unexpected kinetic behaviour observed with the oxidant were not due to impurities. All solutions were prepared in distilled water that had been previously purged with nitrogen.

The preparation of dimeric tungsten(V) solutions, [W₂O₄]²⁺ (aqua) was done by dissolving (NH₄)₂ WOCl₅ (0.20 g) in O₂-free Hpts (100 cm³) (p-toluenesulphonic acid) working in a glove-bag conditions. After millipore filtration (pore size 8 cm) to remove a blue precipitate, the yellow-green solution was transferred (by syphoning) and loaded into an O₂-free, ice-cooled Dowex 50W-X2 cation-exchange column (10x15 cm), outside the glove-bag. The W^V binds as a compact yellow band with a blue impurity above it. The column was washed with (50 cm³) O₂-free 0.50M Hpts to remove chloro-complexes, and the W^V (1.0 x 10⁻²M) in 2M Hpts (ca. 20 cm³) were obtained. The solution could be stored for several hours in this form. More concentrated solution gave blue precipitates.

Stoichiometry studies

The stoichiometry of the reactions with oxyhalogens, including ClO₂⁻, ClO₃⁻, ClO⁻, BrO₃⁻, BrO₂⁻, IO₃⁻ were determined, taking [W₂O₄]²⁺ in excess, by adding a measured deficiency of oxidant to [W₂O₄]²⁺, waiting for 20-30 min. for completion of reaction, and then measuring the decrease in absorbance at 430 nm (for conversion of W^v to W^{VI}). These changes were compared to those observed when the W^v reductant was treated with excess oxidant. Reactions with ClO₃⁻, and IO₃⁻ took longer time for reaction (40 min) and reacted slowly, and a spectrophotometric determination of

iodine [10] (461 nm) was carried out. Results are summarized in Table-1.

Kinetic studies

Rates were estimated from measurements of changes in absorbance at 430 nm, using Shimadzu 120-02, recording spectrophotometer or (for reactions exhibiting half-lives periods less than 7 s) a Durrum-Gibson stopped-flow spectrophotometer. Ionic strength was maintained at 1.0M adding NaClO₄. The acid strength was generally kept between 0.05M and 1.0M. Reactions were usually carried out with the oxidant in excess, and concentrations were adjusted so that less than 10% of the oxidant was consumed during a run. All oxidant showed simple exponential (pseudo first-order) curves. Reaction was studied for at least 4 half-lives. Rate constants were evaluated by using either semilogarithmic plots of absorbance differences vs time or unweighted non-linear least-square fittings of data points to the relationship describing simple first-order decay. During the reactions no sharp drop in absorbance occurred immediately after addition of oxidant, thus ruling out the rapid formation of partially reduced halogen species.

The reactions of iodate, at oxidant concentration below 0.05M, did not yield the usual exponential kinetic traces. Instead, curves having a steadily increasing slope during the first 40% of the reaction were obtained. This behaviour could not be attributed to auto-catalysis, for when a fresh charge of reductant was added to the spent reaction mixture, the reaction proceeded as before with no evident acceleration.

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