

Contribution from the Departments of Chemistry, Kent State University, Kent, Ohio 44242, and Indiana-Purdue University at Fort Wayne, Fort Wayne, Indiana 46805

Electron Transfer. 99. Reductions of Oxyhalogens with Dimeric Molybdenum(V)¹

D. E. Linn, Jr.,^{*2a} S. K. Ghosh,^{2b} and E. S. Gould^{*2b}

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The bridged dimer of molybdenum(V) $\text{Mo}_2\text{O}_4^{2+}(\text{aq})$ (structure I) is readily oxidized to Mo(VI) by a number of oxyhalogen species in aqueous acidic media. Reactions of BrO_3^- , HBrO_2 , HClO_2 , and HOCl with excess reductant yield the corresponding halide ions, and reduction of ClO_3^- yields Cl^- , even when the oxidant is in large excess. The I(VII) acid H_5IO_6 is reduced very rapidly to IO_3^- , which undergoes further slow reduction, yielding I_2 . Reductions of the anions ClO_3^- and BrO_3^- are independent of $[\text{H}^+]$ in the range 0.05–1.0 M H^+ , but reductions of the acids HBrO_2 , HClO_2 , and H_5IO_6 are found to be inverse-first order in $[\text{H}^+]$. Acidity patterns are consistent with reaction through a $(\text{Mo}^{\text{V}})_2$ -anion complex, and the approaches to kinetic saturation in the ClO_3^- and BrO_3^- reductions allow estimates of the stability constants of such complexes in these instances. Hypochlorous acid appears to react via a $(\text{Mo}^{\text{V}})_2$ - ClOH adduct ($K = 800 \text{ M}^{-1}$), which undergoes deprotonation ($\text{p}K = 1$) prior to electron transfer. Reductions of IO_3^- at concentrations $<0.02 \text{ M}$ pass through an intermediate having a spectrum similar to that of the Mo(V) dimer used but exhibiting greatly enhanced reactivity. Both the formation and destruction of this intermediate are first order in IO_3^- . It is suggested that this intermediate is formed by substitution of iodate at a $\text{Mo}^{\text{V}}(\text{=O})$ site, yielding a species similar to cation III, and that electron transfer from $(\text{Mo}^{\text{V}})_2$ requires a second (external) unit of IO_3^- (reaction 6). None of the observed profiles indicates that transients formed by single-electron exchanges intervene in these systems. Kinetic behavior is thus consistent with an array of two-unit changes, possibly utilizing oxygen atom transfer. However, initiation by 1e transactions cannot be ruled out, especially since the order of oxyhalogen reactivity ($\text{ClO}_2^- \gg \text{BrO}_3^- > \text{IO}_3^- > \text{ClO}_3^-$) corresponds to that reported for 1e oxidations of the Co(II) center in cob(II)alamin. This question remains unresolved.

The recent surge of interest in the redox reactions of molybdenum has been sparked by an increased awareness of the richness of the solution chemistry of that element³ and by its recognized occurrence in an array of redox enzymes, most notably the nitrogenases, nitrate reductases, and xanthine dehydrogenases.^{3a,4} As with its congener, chromium, all oxidation states between 2+ and 6+ are prominently represented; and further variety arises from the ease with which each of these states forms dimeric and polymeric species.

Our initial contribution to this area dealt with the reduction of very low concentrations of Mo(VI) with vitamin B₁₂ (cob(I)alamin),⁵ but interpretation was complicated by the intrusion of autocatalytic behavior and uncertainty as to the identity of the reduced molybdenum species. In the present study, which treats the oxidation of dimeric molybdenum(V) with anionic oxyhalogen species, there is no ambiguity concerning oxidation states. We have, however, encountered some unexpected variations in kinetic patterns, with the reduction of iodate appearing to be unusually complex.

Experimental Section

Materials. Sodium chlorate (Baker and Adamson), sodium chlorite^{6,7}

(Aldrich), sodium bromite^{8,9} (Aldrich), sodium hypochlorite¹⁰ (Alfa), and sodium periodate (Alfa) were used as received. Sodium iodate (Baker and Adamson) was recrystallized three times before use in rate experiments to ensure that the unexpected kinetic peculiarities observed with this oxidant (vide infra) were not artifacts attributable to impurities. Solutions of hypiodous acid were prepared in situ as described by Chia.¹¹ Sodium perchlorate solutions (for use as the supporting electrolyte in kinetic experiments) were prepared by careful neutralization of NaHCO_3 and were then purged with N_2 to remove dissolved CO_2 . All solutions were prepared in distilled water that had been previously boiled for at least 1 h and then sparged with N_2 for 4 h.

The preparation of dimeric molybdenum(V) solutions, $\text{Mo}_2\text{O}_4^{2+}(\text{aq})$,¹² was carried out by aequation of $(\text{NH}_4)_2\text{MoCl}_5$.¹³ A deaerated column ($12 \times 1 \text{ cm}$) of Dowex W-X4 resin was washed with 12 M HClO_4 to remove ultraviolet-absorbing impurities and subjected to the Cr(II)-scrubbing procedure of Bowen¹⁴ to remove traces of O_2 . Typically, 0.13 g (0.40 mmol) of $(\text{NH}_4)_2\text{MoCl}_5$ in 100 mL of 0.05 M HClO_4 was adsorbed onto the cation-exchange resin and washed with 60 mL of 0.2 M HClO_4 to remove chloride, after which the orange-brown $\text{Mo}_2\text{O}_4^{2+}(\text{aq})$ was displaced with 25 mL of 2.0 M NaClO_4 under N_2 . Solutions of Mo(V) were standardized at 295 nm ($\epsilon_{295} = 3550 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁵ The preparations thus obtained (0.01–0.02 M in dimer) were stable for several weeks in the absence of O_2 . Gradual oxidation yielded the characteristic blue isopolymolybdate, which eventually precipitated.

Stoichiometric Studies. The stoichiometries of the five most rapid reactions were determined, taking $\text{Mo}_2\text{O}_4^{2+}$ in excess, by adding a measured deficiency of oxidant to $\text{Mo}_2\text{O}_4^{2+}$, waiting 30–80 min for completion of the reaction, and then measuring the decrease in absorbance at 295 nm (for conversion of Mo^{V} to Mo^{VI}). These changes were compared to those observed when the $\text{Mo}(\text{V})$ reductant was treated with excess

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- (4) See, for example: (a) Ochiai, E.-I. *Bioinorganic Chemistry*; Allyn and Bacon: Boston, MA, 1977; Chapter 11. (b) Rajagopalan, K. V.; Kramer, S.; Gardlek, S. *Polyhedron* **1986**, *5*, 573. (c) George, G. N.; Hawkes, T. R.; Jones, G. D.; Bray, R. C. *Polyhedron* **1986**, *5*, 587. (d) Kelley, B. C. *Polyhedron* **1986**, *5*, 597. (e) Wilson, G. L.; Kony, M.; Tiekink, E. R. T.; Pilbrow, J. R.; Spence, J. T.; Wedd, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 6923.
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- (6) The purity of this sample of NaClO_2 , as estimated by the method of Kolthoff and co-workers,⁷ was 78.0%, in agreement with the value of 80% given on the label. Attempted recrystallization did not improve its quality. Since the impurities were taken to be NaCl (which does not react with dimeric Mo^{V}) and NaClO_3 (which reacts much more slowly than NaClO_2), this oxidant was used as received and a correction was made for the estimated purity.
- (7) (a) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. *Quantitative Chemical Analysis*, 4th ed.; Collier-Macmillan: Toronto, 1969; p 852. (b) Balasubramanian, P. N.; Gould, E. S. *Inorg. Chem.* **1984**, *23*, 3689.

- (8) Analysis of this reagent⁹ indicated 0.4% NaOH and 1.7% NaBrO_3 but no detectable NaBr . Since BrO_3^- reacts much more slowly than BrO_2^- , it did not complicate our kinetic experiments with the latter, which were carried out with excess oxidant.
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Table I. Stoichiometries of the Reactions of Dimeric Molybdenum(V) with Oxyhalogen Species^a

| oxidant | [H ⁺], M | 10 ⁴ [(Mo ^V) ₂], M | 10 ⁴ [Ox], M | 10 ⁴ [(Mo ^V) ₂], M | 10 ⁴ Δ[Ox], M | Δ[(Mo ^V) ₂]/ Δ[Ox] |
|--------------------------------|-------------------------|--|----------------------------|--|-----------------------------|---|
| BrO ₃ ⁻ | 0.14 | 5.50 | 1.50 | 4.34 | | 2.90 |
| | 0.14 | 5.50 | 0.759 | 2.38 | | 3.13 |
| | 0.14 | 5.50 | 0.459 | 1.41 | | 3.07 |
| HBrO ₂ | 0.14 | 5.74 | 2.87 | 6.00 | | 2.08 |
| | 0.14 | 5.74 | 1.44 | 3.18 | | 2.20 |
| | 0.14 | 5.74 | 0.848 | 1.86 | | 2.20 |
| ClO ₃ ^{-b} | 0.10 | 18.7 | 1000 | | 6.25 | 2.99 |
| | 0.10 | 18.7 | 1000 | | 6.45 | 2.89 |
| HClO ₂ | 0.14 | 5.74 | 2.42 | 4.68 | | 1.93 |
| | 0.14 | 5.74 | 1.23 | 2.18 | | 1.77 |
| | 0.14 | 5.74 | 0.747 | 1.37 | | 1.84 |
| HOCl | 0.10 | 5.00 | 3.63 | 3.60 | | 0.99 |
| | 0.10 | 5.00 | 1.21 | 1.25 | | 1.03 |
| H ₃ IO ₆ | 0.10 | 2.40 | 0.578 | 0.565 | | 0.978 |
| | 0.10 | 2.40 | 0.168 | 0.165 | | 0.979 |
| IO ₃ ^{-c} | 0.10 | 4.00 | 60 | | 1.53 | 2.61 |
| | 0.10 | 4.00 | 60 | | 1.56 | 2.56 |

^aReactions with (Mo^V)₂ in excess were followed at 295 nm (see text). ^bReaction mixtures with ClO₃⁻ in excess were analyzed for Cl⁻ titrimetrically (see text). -Δ[ClO₃⁻] was taken as Δ[Cl⁻]. ^cReaction mixtures with IO₃⁻ in excess were analyzed for I₂ spectrophotometrically. -Δ[IO₃⁻] was taken as 2Δ[I₂].

oxidant. With ClO₃⁻ and IO₃⁻, both of which react slowly, an excess of oxidant was added, 40 min was allowed for complete reaction, and a Volhard titration for chloride¹⁰ or a spectrophotometric determination of iodine¹⁶ (λ_{max} = 461 nm; ε = 744 M⁻¹ s⁻¹) was carried out. Results are summarized in Table I.

Kinetic Studies. Rates were estimated from measurements of changes in absorbance at 295 nm, using a Beckman 5260 recording spectrophotometer or (for reactions exhibiting half-life periods less than 7 s) a Durrum-Gibson stopped-flow spectrophotometer. Since solutions of (Mo^V)₂ were found to exhibit turbidity at pH values above 1.7, [H⁺] was generally held between 0.050 and 1.0 M. Ionic strength was maintained at 1.0 M by adding NaClO₄. 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 oxidants except iodate yielded simple exponential (pseudo-first-order) curves. Conversions were followed for at least 4 half-lives. Rate constants were evaluated by using either semilogarithmic plots of absorbance differences vs reaction time or unweighted nonlinear least-squares fittings of data points to the relationship describing simple first-order decay. Specific rates for replicate runs using conventional mixing diverged by less than 10%, whereas stopped-flow experiments with each pair of master solutions were repeated until decay curves for three successive runs superimposed. Except for the IO₃⁻ reaction, examination of kinetic profiles gave no indication of intermediates formed or destroyed on a time scale comparable to that for the disappearance of the reductant. Moreover, no sharp drop in absorbance occurred immediately after addition of oxidant, thus ruling out the rapid formation of a partially reduced halogen species. Neither I₂ nor I₃⁻ was found to react with (Mo^V)₂ at a perceptible rate under our conditions.

The reactions of iodate, at oxidant concentrations below 0.015 M, did not yield the usual exponential kinetic traces. Instead, curves having a steadily increasing slope during the first 40% of the reaction were obtained, after which profiles became more nearly logarithmic (Figure 1). This behavior could not be attributed to autocatalysis, for when a fresh charge of reductant was added to the spent reaction mixture, the reaction proceeded as before with no evident acceleration. However, profiles were found to be of the type corresponding to the formation and destruction of an intermediate having a substantial molar absorptivity at the wavelength used.¹⁷ Such biphasic curves were separated into contributing pseudo-first-order processes in the sequence A → B → products, as described by Bose.¹⁸ Both components were found to be first order in iodate. Kinetic profiles from reactions carried out with [IO₃⁻] > 0.020 M were indistinguishable from straightforward exponential decay curves.¹⁹

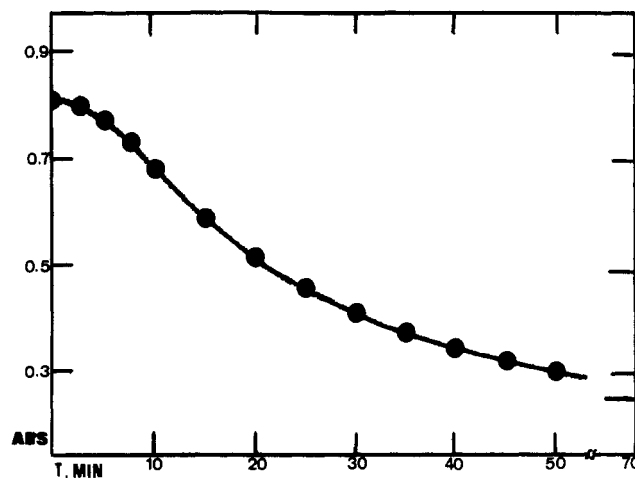
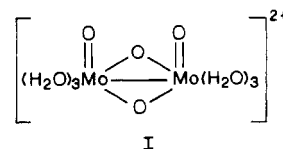


Figure 1. Kinetic profile at 295 nm for the oxidation of Mo₂O₄²⁺(aq) (2.5 × 10⁻⁴ M) with NaIO₃ (0.0125 M) at 25 °C and μ = 1.0 M (LiClO₄). The reaction was carried out under N₂ in a medium 0.2 M in HClO₄. The experimental curve (solid line) exhibits a delayed absorbance drop near the beginning of the reaction but an approach toward exponential behavior during the final half. This trace can be separated into contributing pseudo-first-order processes (ref 18, eq 2) in which an intermediate (ε₂₉₅ = 3.24 × 10³ M⁻¹ cm⁻¹) is formed at a specific rate of 2.52 × 10⁻³ s⁻¹ and decays at a rate of 1.04 × 10⁻³ s⁻¹. Circles represent absorbances calculated by using these parameters.

Results and Discussion

The Mo(V) species with which we are dealing has been shown to be a dinuclear cation having a +2 charge.^{15b} Its structure is represented as I, in accord with the ¹⁷O NMR spectrum reported



- (19) Attempts were made to study the oxidation of (Mo^V)₂ with hypiodite, generating the latter by the rapid reaction of iodide with hypochlorous acid.¹¹ With [H⁺] = 0.02 M, [HClO] = 0.002 M, [I⁻] = 0.0016 M, and [(Mo^V)₂] = 2 × 10⁻⁴ M, we observed exponential loss of (Mo^V)₂ proceeding at a specific rate near 1 s⁻¹ (25 °C, μ = 0.05 M). Although this decay was not noted in the absence of iodide, reproducibility was poor. The reaction of (Mo^V)₂ with excess Br₂ is relatively slow. Measurements at 295 nm yielded very shallow decay curves, reflecting increases in absorbance (by the product Br₃⁻), which partially offset the decreases resulting from loss of (Mo^V)₂. These curves led to an estimated specific rate of 0.39 M⁻¹ s⁻¹ (0.25 M H⁺, μ = 1.0 M, 25 °C).

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Table II. Kinetic Data for the Oxidation of Dimeric Molybdenum(V), $(\text{Mo}_2\text{O}_4)^{2+}$, with Bromate and Periodate^a

| oxidant | $10^3[\text{Ox}]$, M | $[\text{H}^+]$, M | k_{obsd} , s^{-1} | k_{calcd}^b , s^{-1} | |
|------------------|--------------------------|-----------------------|--|---|------|
| BrO_3^- | 2.50 | 0.100 | 0.0190 | 0.0170 | |
| | 5.00 | 0.100 | 0.036 | 0.034 | |
| | 12.5 | 0.100 | 0.083 | 0.081 | |
| | 50.0 | 0.100 | 0.27 | 0.28 | |
| | 100 | 0.100 | 0.42 | 0.48 | |
| | 150 | 0.100 | 0.70 | 0.63 | |
| | 200 | 0.100 | 0.79 | 0.75 | |
| | 5.0 | 0.050 | 0.028 | 0.034 | |
| | 5.0 | 0.250 | 0.037 | 0.034 | |
| | 5.0 | 0.75 | 0.037 | 0.034 | |
| | 5.0 | 1.00 | 0.038 | 0.034 | |
| | H_3IO_6 | 0.100 | 0.100 | 4.0 | 3.4 |
| | | 0.300 | 0.100 | 9.2 | 10.3 |
| 0.60 | | 0.100 | 22 | 21 | |
| 0.90 | | 0.100 | 28 | 31 | |
| 1.80 | | 0.100 | 60 | 62 | |
| 0.60 | | 0.50 | 5.0 | 4.1 | |
| 0.60 | | 1.00 | 2.0 | 2.1 | |

^a Reactions were carried out at 25 °C; the supporting electrolyte was NaClO_4 ($\mu = 1.0$ M). $[(\text{Mo}^V)_2] = 5.0 \times 10^{-4}$ M throughout.
^b Specific rates, calculated by using the relationships and parameters in Table III.

by Richens,^{3c} the EXAFS spectroscopic analysis by Gray and co-workers,^{20a} and the diamagnetism of its oxalato derivative.^{20bc}

Within the acidity range examined, both ClO_3^- and BrO_3^- exist preponderantly in their nonprotonated forms,²¹ whereas Cl(III) , Br(III) , Cl(I) , and I(VII) are converted very largely to the weak acids HClO_2 ($\text{p}K_A = 1.66$),²² HBrO_2 ($\text{p}K_A = 4.9$),²³ HOCl ($\text{p}K_A = 7.5$),²⁴ and H_5IO_6 (apparent $\text{p}K_A = 1.64$).²⁵ Partition between protonation levels is most evenly balanced for $\text{HIO}_3\text{-IO}_3^-$ ($\text{p}K_A$ 0.6).²⁶

Reactions of $(\text{Mo}^V)_2$ with BrO_3^- and ClO_3^- are seen (Table I) to consume very nearly 3 mol of dimer (6 equiv of Mo^V)/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 $(\text{Mo}^V)_2$. Each of these oxyhalogen species is thus reduced to the 1- state. A similar conclusion probably applies to the reaction with excess IO_3^- , but this reaction is complicated by the relatively rapid reaction between I^- and IO_3^- at low pH.²⁷ Formation of halide is not unexpected when the reductant is in excess, but determinations with ClO_3^- in very large excess are more informative, for they indicate that reductions of the intervening states, Cl(III) and Cl(I) , are much more rapid than reduction of Cl(V) , i.e., that the overall rate is determined by the initial attack on ClO_3^- . Such a conclusion is in accord with our kinetic measurements. Only with the very rapid oxidant H_3IO_6 does reduction clearly yield an intermediate state, for the I(V) product here is reduced so sluggishly that separate kinetic steps are readily discernible.

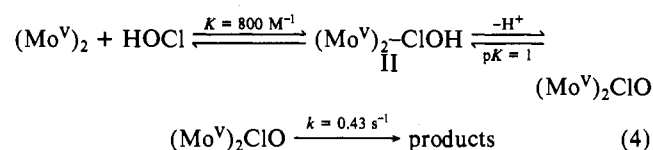
Kinetic data pertaining to two representative oxidants, BrO_3^- and H_3IO_6 , are given in Table II. Note that the rate of reduction of bromate is essentially independent of acidity in the range 0.05–1.0 M H^+ , whereas that for periodic acid is very nearly proportional to $[\text{H}^+]^{-1}$. With both oxyhalogens, rates are pro-

portional to [oxidant] at low concentrations of the latter, but there is a perceptible trend toward kinetic saturation at high concentrations of BrO_3^- , indicating association (in this case, ion-pairing) between molybdenum and oxyhalogen species. Rate laws for these systems, as well as for reactions with the remaining oxyhalogens, are listed in Table III. Also included are kinetic parameters resulting from least-squares refinements of observed rates in terms of these expressions. Specific rates calculated from these parameters are compared with observed values in Table II.

Monomial rate laws featuring inverse acid dependencies are observed for reductions of the uncharged oxyacids HClO_2 , HBrO_2 , and H_5IO_6 , pointing to an activated complex containing one unit each of $(\text{Mo}^V)_2$ and oxidant, formed with loss of a proton. The lack of such a $[\text{H}^+]^{-1}$ term for reductions of the negative BrO_3^- and ClO_3^- ions suggests that, in each case, the active oxidizing species is anionic. However, it is recognized that in the absence of bridging effects, deprotonation of an oxidant almost invariably converts it to a less effective electron acceptor. The implication here is then that oxyhalogen–molybdenum(V) complexation is preceding the redox process, an inference in accord with the recognized^{3c,12b} substitution lability associated with the coordinated water molecules about the reductant and with the rate law (1), which pertains to reduction of ClO_3^- and BrO_3^- . The approach to kinetic saturation observed for these anions allows evaluation of the association quotients (0.7 and 5 M^{-1}) for the respective $(\text{Mo}^V)_2$ -halate complexes, which may be taken as precursors in the redox sequences.

To place the relative reactivities of pentapositive and tripositive halogens on a common scale, the products kK pertaining to the halates (eq 1) should be compared to the quotients obtained by dividing the specific rates for the halous acids (eq 2) by their K_A values. The resulting "bimolecular specific rates" are 0.012 $\text{M}^{-1} \text{s}^{-1}$ for ClO_3^- , 8 $\text{M}^{-1} \text{s}^{-1}$ for BrO_3^- , $3 \times 10^4 \text{M}^{-1} \text{s}^{-1}$ for ClO_2^- , and $7 \times 10^7 \text{M}^{-1} \text{s}^{-1}$ for BrO_2^- . Such a comparison emphasizes the exceptional reactivity of Br(III) , the potency of which is partially masked by the unexpectedly high²³ $\text{p}K_A$ of HBrO_2 . An analogous calculation yields an effective specific rate of $1.5 \times 10^5 \text{M}^{-1} \text{s}^{-1}$ for the pair of equilibrating anions ($\text{IO}_4^- + \text{H}_4\text{IO}_6^-$) resulting from deprotonation of H_5IO_6 .^{25b}

The picture with hypochlorous acid is less straightforward. This oxidant follows a rate law (3) reflecting both a preassociation of redox partners and a deprotonation. The $\text{p}K_A$ near 1.0, consistent with the acidity pattern, does not correspond to that for HOCl (7.5)²⁴ 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.

Among the oxidants taken, only IO_3^- exhibits nonexponential kinetic behavior. Decay curves with oxidant in excess (e.g. Figure 1) feature increasing slopes during the first third of reaction but become more nearly logarithmic for the remainder. The profiles are not autocatalytic but instead are consistent with formation and destruction of an intermediate on a time scale comparable to that for the primary reaction. Separation of such curves into individual kinetic steps¹⁸ yielded the parameters listed in Table IV.

Although specific rates obtained from our refinement procedure must be considered less precise than those associated with simple exponential traces, it is nevertheless clear that both components are nearly first order in IO_3^- at concentrations of oxidant below 0.020 M. Rates of formation of the intermediate (k_1) are seen to increase with decreasing $[\text{H}^+]$ but approach a limiting value near 0.10 M H^+ . Values of k_1 conform to eq 5. Refinement

$$(k_1)_{\text{obsd}} = \frac{kK_A[\text{OX}]}{K_A + [\text{H}^+]} \quad (5)$$

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- (27) See, for example: Myers, O. E.; Kennedy, J. W. *J. Am. Chem. Soc.* **1950**, *72*, 897.

Table III. Rate Laws and Kinetic Parameters for the Oxidations of Dimeric Molybdenum(V) by Oxyhalogen Species^a

| oxidant (Ox) | rate law ^b | no. | parameters ^c |
|--------------------------------|--|-----|---|
| ClO ₃ ⁻ | $kK[\text{Ox}]/(1 + K[\text{Ox}])$ | 1 | $k = 0.018 \pm 0.003 \text{ s}^{-1}$; $K = 0.7 \pm 0.01 \text{ M}^{-1}$ |
| BrO ₃ ⁻ | $kK[\text{Ox}]/(1 + K[\text{Ox}])$ | | $k = 1.5 \pm 0.3 \text{ s}^{-1}$; $K = 5 \pm 1 \text{ M}^{-1}$ |
| HClO ₂ | $k[\text{Ox}][\text{H}^+]^{-1}$ | 2 | $k = 670 \pm 40 \text{ s}^{-1}$ |
| HBrO ₂ | $k[\text{Ox}][\text{H}^+]^{-1}$ | | $k = 880 \pm 20 \text{ s}^{-1}$ |
| HOCl | $kK K_A [\text{Ox}]/(K_A K [\text{Ox}] + [\text{H}^+] + K[\text{H}^+][\text{Ox}])$ | 3 | $k = 0.43 \pm 0.13 \text{ s}^{-1}$; $K = (7.7 \pm 2.3) \times 10^2 \text{ M}^{-1}$; $K_A = 0.11 \pm 0.05 \text{ M}$ |
| H ₃ IO ₆ | $k[\text{Ox}][\text{H}^+]^{-1}$ | | $k = 3440 \pm 150 \text{ s}^{-1}$ |

^aReactions were carried out at 25 °C; $\mu = 1.0 \text{ M}$ (NaClO₄-HClO₄). Experiments were monitored at 295 nm. ^bRate laws describe $-\ln[(\text{Mo}^{\text{V}})_2]/dt$ in s⁻¹. ^c K values pertain to (Mo^V)₂-Ox association quotient; K_A is a deprotonation quotient.

Table IV. Kinetic Data for Formation and Consumption of the Reaction Intermediate in the Oxidation of Dimeric Molybdenum(V) with Iodate^a

| [IO ₃ ⁻], M | [H ⁺], M | 10 ³ k_1 , s ⁻¹ ^b | 10 ⁴ k_2 , s ⁻¹ ^c | 10 ⁻³ ϵ_{int} , ^d M ⁻¹ cm ⁻¹ |
|---------------------------------------|-------------------------|---|---|---|
| 0.0032 | 0.100 | 0.90 (0.88) | 3.6 | 3.75 |
| 0.0063 | 0.100 | 2.02 (1.93) | 6.8 | 3.70 |
| 0.0125 | 0.100 | 3.6 (3.4) | 14.2 | 3.73 |
| 0.0250 | 0.100 | 10.2 (6.9) ^f | 34 | 3.56 |
| 0.0125 ^e | 0.100 | 3.6 (3.4) | 12.8 | 3.32 |
| 0.0125 | 0.025 | 4.3 (5.0) | 28 | 4.21 |
| 0.0125 | 0.038 | 4.2 (4.7) | 27 | 3.82 |
| 0.0125 | 0.050 | 4.4 (4.3) | 26 | 3.96 |
| 0.0125 | 0.075 | 3.9 (3.8) | 22 | 3.86 |
| 0.0125 | 0.100 | 3.7 (3.4) | 12.0 | 3.90 |
| 0.0125 | 0.150 | 3.0 (2.8) | 9.4 | 3.27 |
| 0.0125 | 0.200 | 2.5 (2.4) | 10.4 | 3.24 |
| 0.0125 | 0.30 | 2.4 (1.9) | 8.8 | 3.25 |
| 0.0125 | 0.40 | 1.15 (1.5) | 8.2 | 3.29 |

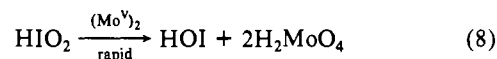
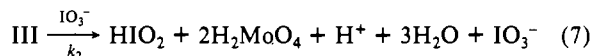
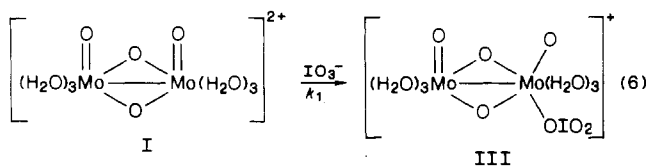
^aReactions were run at 25 °C; $\mu = 1.00 \text{ M}$ (LiClO₄); $[(\text{Mo}^{\text{V}})_2] = 2.5 \times 10^{-4} \text{ M}$ unless otherwise indicated; $\lambda = 295 \text{ nm}$. ^bPseudo-first-order specific rates for formation of the intermediate. Values in parentheses were calculated from eq 4, taking k as $0.47 \text{ M}^{-1} \text{ s}^{-1}$ and K_A as 0.14 M . ^cPseudo-first-order specific rates for consumption of the intermediate. ^dExtinction coefficient of the intermediate obtained from refinement of rate data.¹⁷ ^e $[(\text{Mo}^{\text{V}})_2] = 5.0 \times 10^{-4} \text{ M}$. ^fAt this concentration and above, a higher order in [IO₃⁻] was observed.²⁸

according to (5) yields a bimolecular specific rate (k) of $0.47 \pm 0.06 \text{ M}^{-1} \text{ s}^{-1}$ and an acidity quotient (K_A) of $0.14 \pm 0.04 \text{ M}$, the latter in agreement with the K_A for HIO₃ (0.16 M at $\mu = 0$) reported by Naiditch.²⁶ The intermediate is then formed from one unit each of (Mo^V)₂ and IO₃⁻, with the acidity dependence simply reflecting the distribution of I(V) between an inactive protonated form and an active deprotonated form.

The acidity pattern for k_2 values, pertaining to the disappearance of the intermediate, suggests the operation of two contributing paths, a slow protonated path prevailing at $[\text{H}^+] > 0.3 \text{ M}$ and a more rapid deprotonated path predominating at $[\text{H}^+] < 0.02 \text{ M}$. However, our data for this component are too few and are of insufficient precision to allow a refinement yielding reliable rate constants for the two component paths and the acidity constant by which they are related.²⁸

The calculated extinction coefficient of the intermediate, $(3.6 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ at 295 nm, lies very close to that for the (Mo^V)₂ reductant, and we find no region between 250 and 600 nm where the transient absorbs perceptibly more strongly than the reactant. It thus appears that conversion to the intermediate leaves the "chromophoric" system of dimeric Mo(V) unaltered, i.e., that the intermediate retains a pair of Mo(V) centers connected by oxy bridges, being neither a mononuclear species nor a Mo(V)-Mo(VI) dimer. Substitution of IO₃⁻, which presumably

coordinates through oxygen, for Mo(V)-bound water would not be expected to modify the electronic spectrum of the complex appreciably, but such replacement would take place much too rapidly ($t_{1/2} < 10^{-3} \text{ s}$)^{3c} to be detected in our kinetic experiments. However, Hinch and co-workers²⁹ have shown that the two nonbridging "-yl" oxygens of this dimer undergo exchange with solvent water at a specific rate near $4 \times 10^{-3} \text{ s}^{-1}$ under conditions similar to ours, whereas the bridging oxygens exchange only about 1/1000th as rapidly. It is then reasonable to attribute the initial step in the reduction to substitution of iodate at a Mo^V(=O) site, yielding a species similar to cation III. The coordinated I(V)



center in III does not undergo reduction directly, for conversion of this intermediate to Mo(VI) is also found to be first order in [IO₃⁻], thus requiring a second (external) unit of halate (reaction 7). Subsequent reduction of the I(III) species to I(I) (reaction 8) is expected to be rapid, as is conversion of the latter to I⁻. Our kinetic experiments yield no information concerning these follow-up steps. The manner in which (Mo^V)₂-IO₃⁻ ligation facilitates attack by an additional IO₃⁻ is not clear, but a closely allied effect is observed at high iodate concentrations where multiple reaction orders in oxidant are perceived.²⁸ Related synergisms have not been noted with the other oxyhalogens.

A vexing question concerning this reaction series is whether the individual redox steps are one- or two-electron transactions, i.e., whether odd-electron oxyhalogen species intervene. No facet of the observed rate behavior requires the operation of single-electron steps, nor do kinetic profiles suggest the formation and disappearance of possible molybdenum intermediates (e.g., monomeric Mo^V or a Mo^V-Mo^{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 outer-sphere transfers of two units have not yet been reported. In this respect, our evidence that these reactions involve (Mo^V)₂-oxyanion complexes is consistent with initiation by a two-unit transfer (although not demanding this). On the other hand, we note that the observed order of reactivity toward (Mo^V)₂, (ClO₂⁻ >> BrO₃⁻ > IO₃⁻ > ClO₃⁻), corresponds to that reported for the corresponding oxidations of vitamin B_{12r} (cob(II)alamin),^{7b} which is necessarily a single-electron reductant. We advise reservation of judgment on this key point.

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(28) Further complications are encountered at higher iodate concentrations. Although the biphasic kinetic behavior does not persist, between 0.025 and 0.15 M the [IO₃⁻] dependency becomes much steeper than that corresponding to a simple proportionality. Although rates at a single acidity are found to conform to the binomial function $a[\text{IO}_3^-]^2 + b[\text{IO}_3^-]^3$, we have been unable to formulate a rate law that is consistent with the known partition of iodate into protonated and nonprotonated forms.