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Facile Abstraction of Successive Oxygen Atoms from Perchlorate Ions by Methylrhenium Dioxide

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Perchlorate ions are notoriously sluggish oxidizing agents.[1−5] We have found that methylrhenium dioxide (CH_3ReO_2, or MDO),[6−10] prepared in situ from CH_3ReO_3 (MTO)[11−15] and H_3PO_2, reacts efficiently with ClO_4^- in aqueous solution at pH 0 (1.0 M HOTf, trifluoromethanesulfonic acid). The occurrence of this reaction was established by the following experiments. (a) Addition of ClO_4^- to a solution of MDO caused the regeneration of the UV and ^1H spectra of MTO, at the same concentration that existed prior to the formation of MDO, with due allowance for the dilution. (b) Aged solutions of MDO turned blue as the dinuclear species $MeO_2Re{-}O{-}ReO_2Me$ was formed from MDO and MTO, and eventually a black precipitate deposited, this being the dimer and oligomers of MDO; addition of ClO_4^- at either stage restored MTO quantitatively, showing that the methyl−rhenium bond remained intact in these species. (c) Tests for chloride in the final solutions were positive: both a qualitative test, precipitation of AgCl, as well as quantitative detection by ion chromatography. (d) MTO was also regenerated by adding ClO_3^- to the MDO solutions, more rapidly than with ClO_4^-. (e) Conduct of the $MTO{-}H_3PO_2$ reaction in 0.1 M perchloric acid gave, by UV and ^1H-NMR, the appearance that no reaction had occurred; in fact, these methods were unresponsive to the conversion of ClO_4^- to Cl^- as the cycle of reactions caused MTO to remain at a constant concentration. (f) Nevertheless, when the reaction in (e) was monitored by ^{31}P-NMR, clear evidence was obtained for the formation of H_3PO_3.

The stoichiometry, based on the Cl^- found, on the extent to which the dinuclear rhenium(VI) species $MeO_2Re{-}O{-}ReO_2{-}Me$ was formed from MDO and MTO concurrent with the reaction between MDO and ClO_4^-, and on kinetic tests to be described subsequently, allows us to write this overall reaction:

$$4MDO + ClO_4^- \rightarrow 4MTO + Cl^- \qquad (1)$$

Kinetic studies of reaction 1 showed, to no surprise, that oxygen atom abstraction is a stepwise process, the initial step being

$$MDO + ClO_4^- \rightarrow MTO + ClO_3^- \ (k_1) \qquad (2)$$

The kinetic data were based on the buildup of MTO, followed spectrophotometrically at 270 nm (λ_{max} for MTO, ϵ 1300 L mol^{-1} s^{-1}). Both conventional and stopped-flow techniques were used, depending on the concentrations, which determined the time scale. These data required more than the usual care in their analysis, however, because it was not evident at the outset whether the three successive oxygen atoms would be abstracted so rapidly that the immediate, and not only the eventual, resultant would be reaction 1, having reaction 2 as its rate-controlling step, with a rate given by

$$-\frac{d[MDO]}{dt} = 4k_1[MDO][ClO_4^-] \qquad (3)$$

In some of the experiments $[ClO_4^-]_0 \gg [MDO]_0$, and k_ψ represents the pseudo-first-order rate constant. When the concentrations were comparable, k_ψ represents the product $4k_1\Delta_0$, where $\Delta_0 = [ClO_4^-]_\infty = ([ClO_4^-]_0 - [MDO]_0/4)$. This treatment follows from the following rearrangement of the integrated rate law for mixed-second-order kinetics, in terms of concentration (eq 4) or absorbance (eq 5).

$$[MDO]_t = \frac{\Delta_0}{([ClO_4^-]_0/[MDO]_0)\exp(4k_1\Delta_0 t) - 1} \qquad (4)$$

$$Abs_t = Abs_\infty + \frac{(\Delta_0/[MDO]_0)(Abs_0 - Abs_\infty)}{([ClO_4^-]_0/[MDO]_0)\exp(4k_1\Delta_0 t) - 1} \qquad (5)$$

The 4:1 stoichiometry represented by eq 1, and implied in the definition of Δ_0, was verified because the substitution of $[ClO_4^-]_t = ([ClO_4^-]_0 - [MDO]_0/4) + [MDO]_t/4$ into eqs 3−5 gave values of k_1 that were satisfactorily constant when the concentrations of ClO_4^- and MDO were varied, whereas the alternative substitution for $[ClO_4^-]_t$ without the divisors of 4 (which would hold had only reaction 2 occurred on the kinetic time scale) gave poor fits within the runs and widely discrepant values of k_1.

The kinetic data are displayed in Figure 1 as a plot of k_ψ (the pseudo-first-order rate constant for the reaction) vs Δ_0, which as explained represents the effective concentration of ClO_4^- in each experiment. From the slope, $4k_1 = 29 \pm 1$ L mol^{-1} s^{-1} at 25.0 °C in aqueous trifluoromethane sulfonic acid with $[H_3O^+] = \mu = 1.0$ M.

The rapidity of the next step, reaction 6, was confirmed by direct stopped-flow measurements. The value of k_2, defined

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[1] Taube, H. In *ACS Symposium Series*; American Chemical Society: Washington, DC, 1982; Vol. 198; pp 151−171.
[2] Duke, F. R.; Quinney, P. D. *J. Am. Chem. Soc.* **1954**, *76*, 3800. The units of time did not appear in this article or in the thesis of P.D.Q. found in the library of this university but were inferred from the description of the experimental protocol.
[3] Endicott, J. F.; Taube, H. *Inorg. Chem.* **1965**, *4*, 437.
[4] King, W. R.; Garner, C. S. *J. Phys. Chem.* **1954**, *58*, 29.
[5] Kallen, T. W.; Earley, J. E. *Inorg. Chem.* **1971**, *10*, 1153.
[6] Felixberger, J. K.; Kuchler, J. G.; Herdtweck, E.; Paciello, R. A.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 946−948.
[7] Herrmann, W. A.; Wang, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1641.
[8] Herrmann, W. A.; Roesky, P. W.; Wang, M.; Scherer, W. *Organometallics* **1994**, *13*, 4531.
[9] Zhu, Z.; Espenson, J. H. *J. Mol. Catal.*, in press.
[10] Under previous circumstances MDO is coordinated by triphenylphosphine. Here, however, there are no potential ligands other than the solvent itself, since at pH 0 the anions of H_3PO_2 and H_3PO_3, which would be weakly coordinating in any event, are present at low concentration. We presume but have not verified that one or more water molecules is coordinated to the rhenium atom of MDO in this medium.
[11] Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.
[12] Herrmann, W. A.; Ramao, C. C.; Kiprof, P.; Behm, J.; Cook, M. R.; Taillefer, J. *J. Organomet. Chem.* **1991**, *413*, 11.
[13] Herrmann, W. A.; Kühn, F. E.; Fischer, R. W.; Thiel, W. R.; Ramao, C. C. *Inorg. Chem.* **1992**, *31*, 4431.
[14] Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683.
[15] Huston, P.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1993**, *32*, 4517.
[16] Gordon, G.; Tewari, P. *J. Phys. Chem.* **1966**, *70*, 200.
[17] Thompson, R. C.; Gordon, G. *Inorg. Chem.* **1966**, *5*, 561.
[18] Hahn, M.; Wieghardt, K. *Inorg. Chem.* **1984**, *23*, 3977; L = 1,4,7-trizazcyclononane.
[19] Liu, B.; Wagner, P. A.; Earley, J. E. *Inorg. Chem.* **1984**, *23*, 3418.
[20] Adin, A.; Sykes, A. G. *J. Chem. Soc A* **1966**, 1230.

0020-1669/95/1334-6239$09.00/0

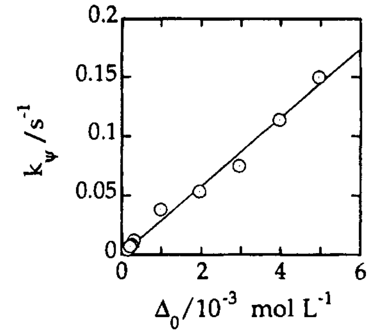

Figure 1. Plot of k_ψ vs Δ_0 for the reduction of perchlorate ions from both pseudo-first-order and mixed-second-order conditions. This plot depicts the data at low concentrations of ClO_4^-. The parameter Δ_0 represents the effective concentration of ClO_4^- in second-order as well as pseudo-first-order kinetics (see text), and its use allows the results from experiments of both types to be displayed together.

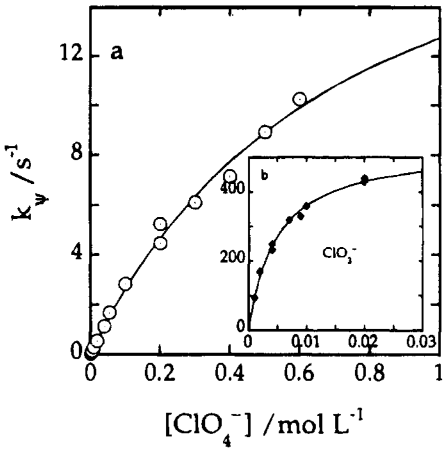

Figure 2. Plot of k_ψ vs (a) $[ClO_4^-]$ and (b) $[ClO_3^-]$ showing a plateau pattern at higher concentrations of the anions.

as in eq 7, is 3.8×10^4 L mol^{-1} s^{-1} at 25.0 °C, showing that chlorate ions are indeed much more reactive than perchlorate. The stoichiometry of 3:1 for this reaction was also verified kinetically as described above.

$$\mathrm{MDO} + \mathrm{ClO_3^-} \rightarrow \mathrm{MTO} + \mathrm{ClO_2^-} \ (k_2) \tag{6}$$

$$-\frac{\mathrm{d[MDO]}}{\mathrm{d}t} = 3k_2[\mathrm{MDO}][\mathrm{ClO_3^-}] \tag{7}$$

Table 1. Summary of Kinetic Parameters[a] for Reactions of Solvated CH_3ReO_2 with Oxoanions

XO_n^-	k_{bi}/L mol^{-1} s^{-1}	k/s^{-1}	K/L mol^{-1}
ClO_4^-	$k_1 = 7.3$	5.5 ± 0.5	1.3 ± 0.2
ClO_3^-	$k_2 = 3.8 \times 10^4$	177 ± 5	212 ± 17

[a] In aqueous 1.0 M triflic acid at 25 °C. [b] Kinetic parameters are defined as in eqs 3, 7, and 9.

Table 2. Rate Constants for the Reduction of Perchlorate and Chlorate Ions by Transition Metal Complexes

reduced form	oxidized form	T/ °C	k/L mol^{-1} s^{-1} ClO_4^-	ClO_3^-	ref
CH_3ReO_2	CH_3ReO_3	25	7.3	3.8×10^4	this work
$Ti(H_2O)_6^{3+}$	$(H_2O)_5TiO^{2+}$ (1e)	50	1.5×10^{-3}		2
$Ru(NH_3)_5(OH_2)^{2+}$	$(NH_3)_5RuO^{2+}$	25	2.7×10^{-2}	3.2×10^{-2}	3
$Ru(H_2O)_6^{2+}$	$(H_2O)_5RuO^{2+}$ (?)	25	3.2×10^{-3}	3×10^{-2}	5
$Ru(NH_3)_6^{2+}$	$(NH_3)_5RuO^{2+}$ (?)	25	3.0×10^{-4}	3.2×10^{-2}	3
$V(H_2O)_6^{2+}$	$(H_2O)_5VO^{2+}$	50	2.2×10^{-5}		4
$V(H_2O)_6^{2+}$	$(H_2O)_5VO^{2+}$	20		1.82×10^1	16
$V(H_2O)_6^{3+}$	$(H_2O)_4VO^{2+}$	50	2.8×10^{-6}		4
$Fe(H_2O)_6^{2+}$			no reaction	2×10^{-2}	17
$Cr(H_2O)_6^{2+}$	$(H_2O)_5CrO^{2+}$ (?)		no reaction	3.9×10^1	17
$[L_2Mo_2(H_2O_2(\mu\text{-}OH)_2]^{4+}$	$[L_2Mo_2O_2(\mu\text{-}O)_2]^{2+}$	21	2.0×10^{-3}		18
Ti(Hedta)	$Ti(Hedta)^+$ (1e)	25	2×10^{-3}		19
Eu_{aq}^{2+}	Eu_{aq}^{3+} (1e)	28	$\sim 10^{-8}$		20

Both of these reactions exhibit rates that plateau at still higher concentrations of the anions. The data are shown in Figure 2. The onset of curvature in the case of perchlorate occurs at a high enough concentration as to invite the question of whether this might be a medium effect: perchlorate is not a perfect substitute for triflate at high concentration; might not the reaction really follow second-order kinetics throughout? The curvature for chlorate, on the other hand, is evident at low concentrations, and the alternative explanation for it would be untenable. We thus argue that the curvature reflects a genuine kinetic phenomenon for both, which provides direct evidence for the proposed O-atom abstraction, in that it signals the existence of an intermediate. For both perchlorate and chlorate ions, we can write this scheme and the accompanying rate expression derived with the prior-equilibrium assumption:

$$\mathrm{ClO}_n^- + \mathrm{MDO} \overset{K}{\rightleftharpoons} [\mathrm{Me(O)_2ReOClO}_{n-1}^-] \xrightarrow{k} \mathrm{MeReO_3} + \mathrm{ClO}_{n-1}^- \tag{8}$$

$$k_1 \ (\text{or } k_2) = \frac{k[\mathrm{ClO}_n^-]}{K^{-1} + [\mathrm{ClO}_n^-]} \tag{9}$$

Nonlinear least-squares fitting gave the parameters that are summarized in Table 1. It should be noted that a mechanism involving a steady-state intermediate common to ClO_4^- and ClO_3^- cannot be valid since the two anions attain different kinetic plateaus in the high-concentration limit. Values of the second-order rate constants for the reduction of these anions by different metal complexes are given in Table 2.

Efforts are underway to define the kinetic parameters in terms of the inherent oxophilicities of the metal complexes, to detect and characterize the intermediates more fully, to examine other potential oxygen atom donor reagents, and to explore the mechanism of the H_3PO_2–MTO reaction from which MDO is formed.

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