until colorless. The resulting solutions were worked up as in the iron(III) experiments.

Dependence of Isomers Ratio in the Oxidation of 1, 2, and Fe(III). Two stock solutions were made: (a) **1g** (563 mg, 2.24 mmol), 1-octene (518 mg, 6.62 mmol), and biphenyl (293 mg) in MeCN (10 mL); (b) $Fe(ClO_4)_3 \cdot 9H_2O$ (23 mmol) in MeCN (31 mL). Solution a, acetonitrile, and solution b were mixed together under N_2 in the following proportions, respectively: (1) 1.5, 1.44, and 0.45; (2) 1.5, 0.53, and 1.37; (3) 1.5, 0.1, and 1.8; (4) 1.5, 0, and 2.22. The resulting solutions were stirred at 20 °C for 1–24 h, stopped at different times, worked up as before, and analyzed by GC for the determination of the conversion, yield, and isomers ratio. The results are plotted in Figure 1 as ratios of ortho/para isomers against **1g** conversion. From these data the following slopes (correlation coefficient) were obtained: (1) 0.57 (0.9991), (2) 0.42 (0.9993), (3) 0.28 (0.9989), (4) 0.23 (0.9996). A linear correlation with a slope of –1.1 ($r = 0.9988$) of these data against Fe(III) concentration can be deduced.

Dependence of Isomers Ratio in the Oxidation of 1, 2, and $Mn(OAc)_3$. A stock solution was made from compound **1g** (500 mg, 1.99 mmol) and 1-octene (447 mg, 3.98 mmol) in AcOH (5 mL). $Mn(OAc)_3$ dihydrate (95% purity) was weighed in four two-necked flasks (117 mg, 218 mg, 326 mg, 429 mg, respectively); acetic acid (3 mL) was added, and the mixtures were flushed with N_2 for 5 min. The stock solution (1 mL) was added at 20 °C to the resulting mixtures, each flask was introduced in a thermostated bath at 70 °C, and the reactions were followed by withdrawing at different time samples, which were worked up and analyzed as before. The results are reported in Figure 2 as dependence of $R_{o/p}$ against the substrate conversion. The following slopes (correlation coefficient) were obtained, respectively: 0.41 (0.9988), 0.31 (0.9992), 0.19 (0.9996), 0.02 (0.9991). A linear correlation of these data against Mn(III) concentration can be deduced with a slope of –1.4 ($r = 0.9992$).

Dependence of Isomers Ratio in the Oxidation of 1, 2, and CAN. Two stock solutions were made: (a) compound **1g** (513 mg, 2.04 mmol), 1-octene (463 mg, 4.13 mmol) and biphenyl (286 mg) in MeOH (5 mL); (b) $Ce(NH_4)_2(NO_3)_4$ (2.886 g, 5.26 mmol) in MeOH (31 mL). Solutions a, methanol, and solution b were mixed together under N_2 in the following proportions, respectively: (1) 0.9, 2.1, and 0.70; (2) 0.9, 1.40, and 1.40; (3) 0.9, 0.7, and 2.1; (4) 0.9, 0 and 2.8. The resulting solutions were stirred at 20 °C for 1–6 h, stopped at different times, and worked up as before. The results are reported in Figure 3 as dependence of $R_{o/p}$ against the substrate conversion. The following slopes (correlation coefficient) were obtained: (1) 0.05 (0.9986), 0.04 (0.9992), 0.05 (0.9984), 0.05 (0.9992).

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Registry No. **1a**, 3243-01-4; **1b**, 134208-95-0; **1c**, 134208-96-1; **1d**, 101585-29-9; **1e**, 101829-74-7; **1f**, 134208-97-2; **1g**, 57477-12-0; **2a**, 111-66-0; **2b**, 100-42-5; **2c**, 108-05-4; **2d**, 15870-10-7; **2e**, 140-88-5; **2f**, 107-13-1; **3a**, 629-05-0; **3b**, 536-74-3; **3c**, 623-47-2; **3d**, 1070-71-9; **4a**, 134208-75-6; **4b**, 134208-76-7; **4c**, 134208-77-8; **4d**, 134208-78-9; **5e**, 134208-79-0; **5f**, 134208-80-3; **6a**, 134208-81-4; **6b**, 134208-82-5; **6c**, 134237-91-5; **6d**, 134208-85-8; **6e**, 134208-87-0; **6f**, 134208-89-2; **7a**, 134237-90-4; **7b**, 134208-83-6; **7c**, 134208-84-7; **7d**, 134208-86-9; **7e**, 134208-88-1; **7f**, 134208-90-5; **8a**, 134208-91-6; **8b**, 134208-93-8; **8c**, 134609-10-2; **9a**, 134208-92-7; **9b**, 134208-94-9; ethyl propiolate, 623-47-2.

Supplementary Material Available: Analytical data of compounds **1a–g** (Table IV) and mass spectral data of compounds **4a–d**, **5e–f**, **6a–e**, **7a–e**, **8a–e**, and **9a–b** (Table V) (4 pages). Ordering information is given on any current masthead page.

The Oxidation of Alcohols by Permanganate. A Comparison with Other High-Valent Transition-Metal Oxidants

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The results obtained from a study of the oxidation of mandelic acid and cyclobutanol by permanganate in 1.0 M KOH are best accommodated by a mechanism in which the initial reaction is the addition of a manganese–oxo bond to the α-C–H bond of the alcohol, followed by homolytic cleavage of the resulting Mn–C bond to give free-radical intermediates. A comparison with other high-valent transition-metal oxidants suggests that it is possible to systematically classify the way in which these reagents react with alcohols on the basis of the initial reaction (C–H or O–H addition) and the cleavage mode of the metal–oxygen or metal–carbon bond (homolytic or heterolytic). The approach provides a framework for understanding these reactions that is less chaotic than the current situation where distinctive mechanisms have been proposed for each individual oxidant.

Introduction

Transition-metal oxides have been widely used for the conversion of alcohols into carbonyl compounds. Permanganate,[1] manganate(VI),[2] chromic acid,[3] chlorochromate,[4] chromyl chloride,[5] molybdenum(VI) complexes,[6] pentavalent vanadium,[7] ruthenium tetroxide,[8] osmium tetraoxide,[9] perruthenate,[10] ruthenate,[11] and ferrate[12] have all proven to be useful oxidants for specific alcohols.

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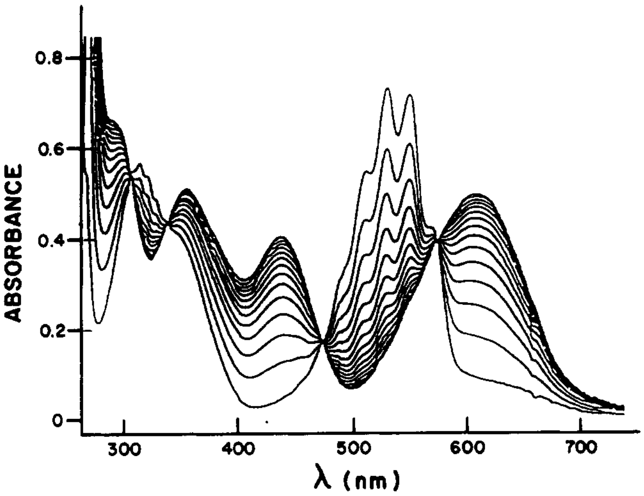

Figure 1. Successive scans obtained at intervals of 50 s during the oxidation of mandelic acid (1.80×10^{-3} M) by permanganate (3.02×10^{-4} M) in 1.0 M KOH at 25.0 ± 0.1 °C.

Although these oxidation reactions are all quite similar, somewhat different mechanisms have been proposed for each reagent. For example, it has been firmly established that chromic acid reacts with alcohols by formation of chromate esters that subsequently undergo oxidative decomposition.[13] Alternatively, it has been suggested that the reactions of ruthenium tetroxide,[14] and certain ruthenium(IV) complexes[15] with alcohols involve hydride transfers, while hydrogen atom transfers have been implicated in permanganate[1] and perruthenate[16] oxidations. In several instances it has also been noted that oxidation appears to be preceded by complex formation.[6,9,12,17]

Despite this apparent diversity, it seems reasonable to expect that there should be certain features of the mechanism for all oxidants that are universally applicable. In particular, it would be surprising if the initial interaction between alcohols and all high-valent transition-metal oxides would not be very similar.

In this paper the results of a kinetic study of the oxidation of mandelic acid by permanganate in 1.0 M KOH are presented and a new mechanism based partly on experimental results and partly on previously published molecular orbital calculations[18] is proposed. The applicability of this mechanism to the reactions of other high-valent transition-metal oxides with alcohols is also considered.

Experimental Section

Materials. Potassium permanganate and potassium hydroxide were obtained from Fisher Scientific. Potassium manganate(VI) was obtained from the Carus Chemical Co. Mandelic acid was obtained from the Aldrich Chemical Co. and recrystallized from benzene before use. Mp: 119–120 °C (lit.[19] mp 121.3 °C). The mandelic acids were prepared by reacting substituted benzaldehydes with chlorotrimethylsilane and potassium cyanide in refluxing acetonitrile to give the corresponding trimethylsilyl ethers.[20] Hydrolysis in refluxing aqueous HCl then gave the substituted mandelic acids in yields of about 90%. Mandelic acid-*α*-*d* was prepared starting from benzaldehyde-*α*-*d* that had been obtained from Merck, Sharp and Dohme Canada Limited. All substituted mandelic acids exhibited consistent NMR and IR spectra and had sharp melting points that were in agreement with literature values.

Reaction Products. When the reaction was monitored spectrophotometrically (Figure 1) it was apparent from the spectrum of the product that permanganate had been reduced to manganate(VI) under these conditions.

In an attempt to identify the organic product, mandelic acid (3.75 g, 0.025 mol) was added to a 100 mL of 1.0 M KOH solution and stirred in an ice–water bath for about 15 min. Then a portion of finely ground potassium permanganate (8.3 g, 0.053 mol) was added over a period of 15 min. The mixture was stirred for 0.5 h during which time the temperature was held below 0 °C. On completion of the reaction, sodium sulfite (29 g, 0.224 mol) was introduced and concentrated HCl was carefully added until all of the oxidant had been reduced to colorless manganese(II). Extraction with 4 × 50 mL portions of ether, followed by drying of the combined extracts over anhydrous $MgSO_4$ for a few minutes, and evaporation of the ether gave an oily residue that solidified on cooling in a refrigerator (1.80 g, 50%). IR (Nujol): 3100–3300 (vs), 2922.1 (vs), 2854 (s), 1738.9 (m), 1659.6 (s), 1593 (m), 1452.4 (s). Proton NMR (DMSO-d_6): 7.41 (m, 2 H), 7.74 (m, 1 H), 7.90 (m, 2 H). After recrystallization from carbon tetrachloride its melting point was 66–68 °C. The reported melting point of the expected product, benzoylformic acid, is 66 °C.[21]

The products of the reactions of MnO_4^- and MnO_4^{2-} with cyclobutanol were determined as follows:

Cyclobutanol (1.0 g, 13.6 mmol) in 100 mL of 6.0 M KOH was allowed to react with aqueous sodium manganate(VI) (0.155 M, 200 mL) in an ice water bath. After 5 min sodium sulfite (10 g, 79.3 mmol) was introduced and concd HCl was carefully added until the solution was colorless. The solution was saturated with NaCl, made slightly basic, and extracted with 5 × 100 mL portions of ether. The etheral extracts were dried over anhydrous magnesium sulfate and evaporated to give a liquid product that was identified as cyclobutanone from its GLC retention time (12% carbowax on 20 M column) and magnetic resonance spectra. ^{1}H NMR (200 MHz, $CDCl_3$): 1.94 (m, 2 H), 3.04 (t, 4 H). ^{13}C NMR (200 MHz, $CHCl_3$) 9.6, 47.6, 209.2. The yield was 85% with 7% starting material recovered.

Cyclobutanol (0.98 g, 13.5 mmol in 100 mL of 1.0 M KOH) was allowed to react for 2–3 min with aqueous potassium permanganate (5.00 g, 31.6 mmol in 100 mL of water) under magnetic stirring and in an ice–water bath. An excess of sodium sulfide (34 g, 0.27 mol) was then introduced and concentrated HCl carefully added until all higher oxidation states of manganese had been reduced to colorless manganese(II). The solution was saturated with sodium chloride, made slightly basic, and extracted with 2 × 100 mL portions of ether. The etheral extract was dried over anhydrous magnesium sulfate for a few minutes and evaporated to give a liquid product (0.08 g, 8.5%) that was determined to be cyclobutanone as described above.

The residual aqueous solution was acidified to pH 2 and extracted with 4 × 100 mL portions of ether. The combined extracts were dried over anhydrous magnesium sulfate for a few minutes and concentrated by rotary evaporation to give a white solid product. It was identified as malonic acid (8.0 g, 57%). Mp: 134–136 °C (lit.[22] mp 134.8 °C). ^{1}H NMR (200 MHz, CD_3COCD_3): 3.45 (s). ^{13}C NMR (200 MHz, CD_3COCD_3): 168.6, 206.9.

Stoichiometry. Solutions (1.0 mL) containing various concentrations of mandelate ion in 2.0 M KOH were mixed with aqueous solutions (1.0 mL) containing constant concentrations

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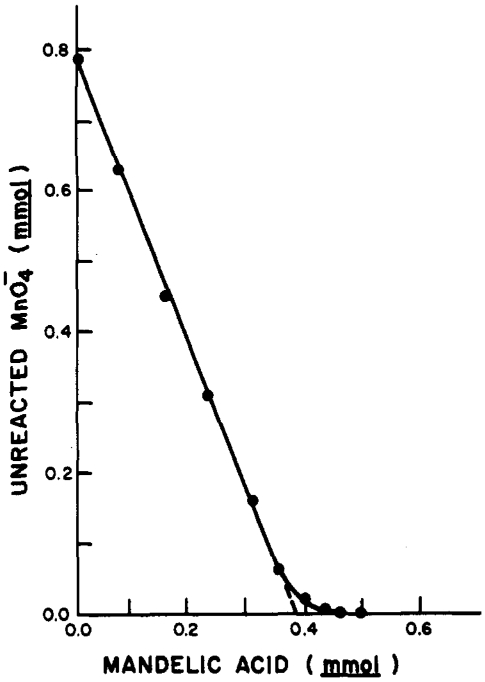

Figure 2. Determination of the stoichiometry for the oxidation of mandelic acid by permanganate in 1.0 M KOH solutions.

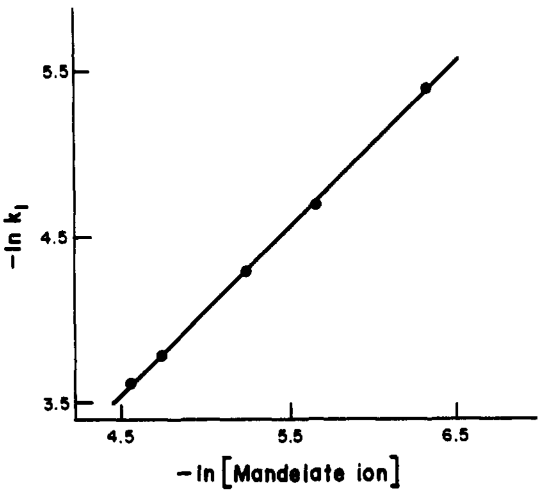

Figure 3. Dependence of the pseudo-first-order rate constants on the concentration of mandelate ion in 1.00 M KOH. $[MnO_4^-]$ = 2.98×10^{-4} M. $T = 25.0 \pm 0.1$ °C. Slope = 1.00 ± 0.01. r = 0.999.

of permanganate and held in the dark for 5 h. The amount of unreacted permanganate was then determined and plotted against the amount of mandelate ion present as in Figure 2.

Kinetic Method. Standardized solutions of permanganate and mandelate ion, each in 1.0 M KOH, were thermostated for 15 min in a water bath. Aliquots (1.0 mL) of each solution were then mixed in a 1.0-cm cuvette located in the thermostated cell compartment of an HP 8450A spectrophotometer, and the reaction was monitored by following the decrease in absorbance at 546 nm.

Results

When an excess of mandelate ion is present, plots of ln $(A - A_t)$ vs time are linear with high correlation coefficients, thus confirming that the reaction is first-order in oxidant. The pseudo-first-order rate constants so obtained are directly dependent on the concentration of mandelate ion (Figure 3), thereby showing that the rate of reaction is also first order in reductant.

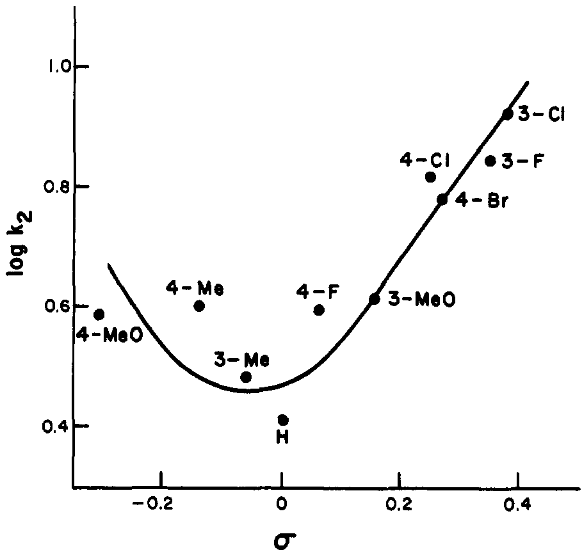

Figure 4. Hammett plot for the oxidation of substituted mandelate ions by permanganate in 1.0 M KOH solutions at 25.0 °C.

Table I. Reaction Rate Constants for the Oxidation of Substituted Mandelate Ions by Permanganate in 1.0 M KOH Solutions[a]

substrate	k_2[b] (M^{-1} s^{-1})	substrate	k_2[b] (M^{-1} s^{-1})
4-MeO	3.67 ± 0.03	3-MeO	4.02 ± 0.03
4-Me	4.04 ± 0.03	4-Br	5.94 ± 0.10
3-Me	3.06 ± 0.08	4-Cl	6.54 ± 0.07
H	2.55 ± 0.03	3-F	6.87 ± 0.17
4-F	4.09 ± 0.03	3-Cl	8.35 ± 0.43

[a] [Substrate] = 8.8×10^{-3} M; $[MnO_4^-]$ = 3.98×10^{-4} M; [KOH] = 1.0 M; temperature = 25.0 ± 0.1 °C. [b] Average of three or more experiments.

The products and stoichiometry studies (which indicate an oxidant/reductant ratio of 2/1) demonstrate that the reaction under consideration may be summarized as in eq 1.

$$PhCHOHCO_2^- + 2MnO_4^- \rightarrow PhCOCO_2^- + 2HMnO_4^- \tag{1}$$

A primary kinetic isotope effect (k_H/k_D = 3.90 ± 0.05) was observed when the rate of oxidation of mandelate-α-*d* was compared with unlabeled mandelate in 1.0 M KOH at 25 °C.

Discussion

The observation that the oxidation of cyclobutanol produces primarily acyclic products is good evidence that the reaction intermediates are free radicals.[23-25] This conclusion is also consistent with the scattered, slightly concave Hammett plot (Figure 4) obtained from a study of the effect of substituents on the rate of reaction (Table I).[26]

The primary deuterium isotope effect indicates that the α-C–H bond is substantially stretched and possibly broken in the transition state[27] and the large negative entropy of activation values ($-\Delta S^\ddagger$ = 25–35 eu)[28] are consistent with a bimolecular reaction in which the transition state is well

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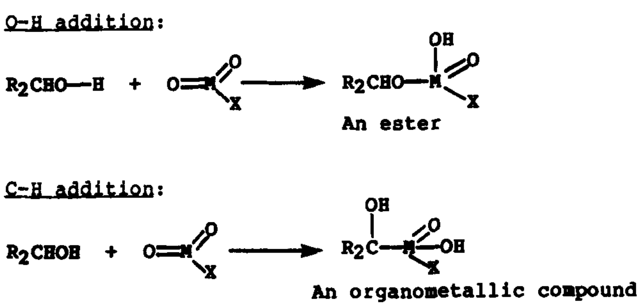
Scheme I

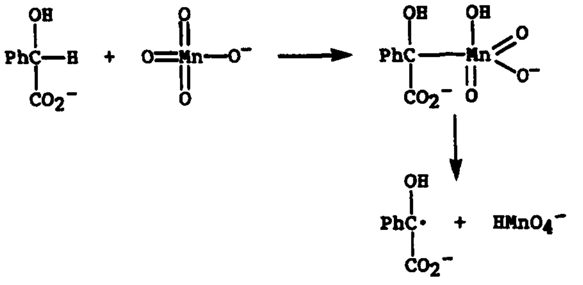


organized and possibly highly solvated.

Molecular orbital calculations, reported by Rappe and Goddard,[18] indicate that transition-metal oxides react with alcohols by addition of a metal oxo double bond to a C–H or an O–H bond. Assuming that the α-C–H bond would be more reactive, these two possibilities can be illustrated by the reactions in Scheme I, where M represents a high-valent transition metal.

Addition to an O–H bond results in the formation of an ester; addition to a C–H bond gives an organometallic compound. Experimental distinction between these two possibilities can be made by comparing the rates of oxidation of alcohols and ethers. Although ethers contain an activated α-C–H bond, they obviously cannot react by O–H addition. Therefore, oxidants such as chromic acid that react by way of ester formation do not oxidize ethers as rapidly as alcohols,[29] whereas oxidants such as ruthenium tetraoxide that attack C–H bonds react at approximately equal rates with both alcohols and ethers.[30]

Because alcohols and ethers are both readily oxidized by permanganate,[28] it is most probable that the reaction involves C–H addition. Homolytic cleavage of the Mn–C bond (eq 2) would then result in the formation of free radicals as demanded by the results reported above. Subsequent oxidation of the free radicals would give the observed product, benzoylformic acid, as in eq 3.

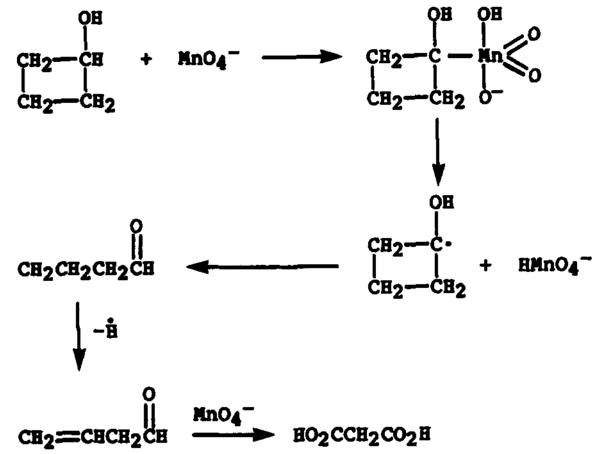

(2)

$$\text{Ph}\dot{\text{C}}\text{OHCO}_2^- + \text{MnO}_4^- \xrightarrow{\text{fast}} \text{PhCOCO}_2^- + \text{HMnO}_4^- \quad (3)$$

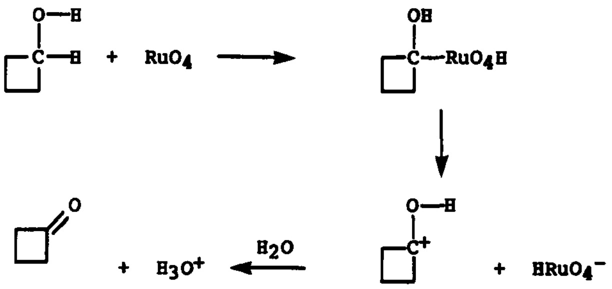
Similarly, the reaction of permanganate with cyclobutanol would produce a cyclic, strained free radical that would undergo ring opening to give noncyclic free radicals (Scheme II) in accordance with the experimentally observed products. The small amount of cyclobutanone obtained (8.5%) is likely due to oxidation by manganate(VI), which has been shown to convert cyclobutanol to the corresponding ketone in high yields.

In summary, it is apparent that C–H addition is involved because permanganate reacts readily with both alcohols and ethers, and it is likely that the intermediate organometallic compound breaks down homolytically because acyclic products are obtained from the oxidation of cyclobutanol. Heterolytic cleavage of the Mn–C bond would have produced a carbocation that would react by proton loss to give cyclobutanone.

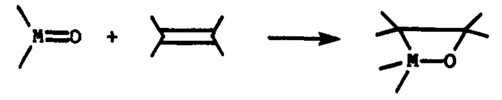
Scheme II



Other oxidants are known that react rapidly with both alcohols and ethers, but without formation of free radicals. For example, although ruthenium tetraoxide reacts with 2-propanol and THF at approximately equal rates,[30] it oxidizes cyclobutanol to cyclobutanone in quantitative yields,[31] thereby suggesting that cleavage of the Ru–C bond must occur heterolytically[32] to produce a cation that readily loses a proton to form the ketone as in eq 4. The overall consequence of this reaction is transfer of a hydride ion as opposed to the hydrogen atom transfer that occurs with permanganate.


(4)

This mechanism is also consistent with the reactions of high-valent transition-metal oxides with carbon–carbon double bonds where it has been shown that the initial reaction involves 2 + 2 addition to a metal oxo bond as in eq 5.[33]


(5)

It is also very probable that the oxidation of hydrocarbons is initiated by addition of an M=O bond to a reactive C—H bond as in eq 6.[18,34]

$$R_3CH + MnO_4^- \rightarrow R_3C{-}MnO_4H^- \rightarrow R_3C\bullet + HMnO_4^- \quad (6)$$

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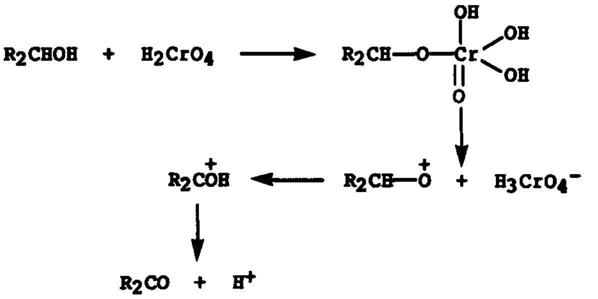
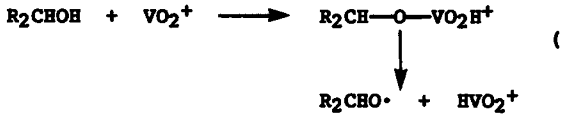
Oxidants that react with alcohols by O–H addition can also be classified from an analysis of the products obtained when cyclobutanol is oxidized.[23-25] In terms of the proposed mechanism, formation of acyclic products corresponds to a homolytic cleavage of the metal–oxygen bond while production of cyclobutanone results from heterolytic cleavage.[32] For example, chromic acid, which reacts slowly with ethers[29] and gives a good yield of cyclobutanone, can be considered to react with alcohols as in eq 7—the overall result being hydride transfer.[35]



$$R_2CHOH + H_2CrO_4 \longrightarrow R_2CH{-}O{-}Cr(OH)_3{=}O \longrightarrow R_2CH{-}\overset{+}{O} + H_3CrO_4^- ;\quad R_2CH{-}\overset{+}{O} \longrightarrow R_2\overset{+}{C}OH \longrightarrow R_2CO + H^+ \tag{7}$$

Alternatively, pentavalent vanadium, which reacts about 10^4 times more rapidly with alcohols than ethers[24] and yields only acyclic products from the oxidation of cyclobutanol,[24] appears to be an example of an oxidant that reacts by O–H addition to form an ester,[37] which subsequently decomposes by homolytic cleavage of the V–O bond as in eq 8.



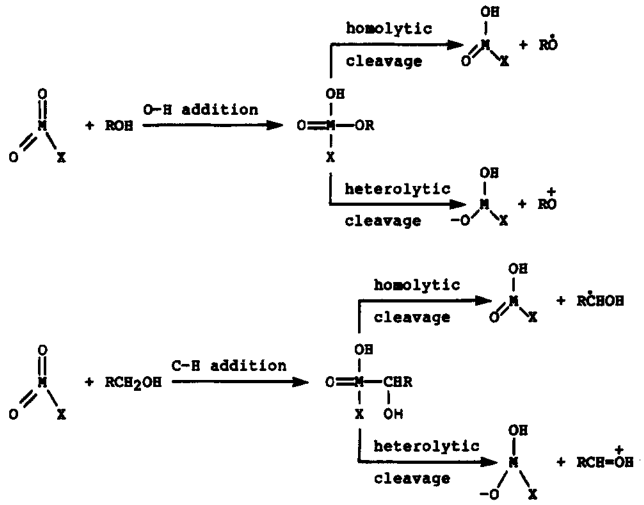
$$R_2CHOH + VO_2^+ \longrightarrow R_2CH{-}O{-}VO_2H^+ \longrightarrow R_2CHO\cdot + HVO_2^+ \tag{8}$$

The free radical so formed may undergo further oxidation to a carbonyl or rearrange with C–C bond cleavage to give more stable products.[25,38]

Similarly it can be shown that the reactions of osmium tetraoxide,[9] ruthenate,[39] and manganate(VI)[40] can also be understood in terms of this mechanism.

The mechanism followed by a particular oxidant would be dependent on a number of factors, chief among them the relative strengths of the metal–oxygen and metal–carbon bonds. Because of the lack of reliable bond dissociation energies,[41] it is difficult to predict which reactions will involve C–H and which O–H addition. However, the experimental tests described above appear to be satisfactory in several cases; for others more evidence is required to make a definitive classification.

Scheme III



Summary

The results obtained from a study of the oxidation of cyclobutanol and substituted mandelic acids by permanganate have been explained in terms of a mechanism that involves initial addition of a carbon–hydrogen bond to a manganese oxo double bond. The resulting orgonometallic compound then decomposes by homolytic cleavage of the manganese–carbon bond to give manganate(VI) and a free radical. A concave Hammett plot and the formation of acyclic products from the oxidation of cyclobutanol support the intermediacy of free radicals.

The assumption that alcohols react with all high-valent transition-metal oxides by addition of either C–H or O–H bonds to metal–oxo double bonds, as predicted by molecular orbital calculations,[18] provides the basis for a unified mechanism that is generally applicable to reactions of this type. It is consistent with the observation that most of these reactions are known to proceed by way of intermediate complexes[6,9,12,17,39,42,43] and with the way in which transition-metal oxides are known to react with carbon–carbon double bonds.[33]

The addition reactions are followed by either homolytic or heterolytic cleavage[32] of the metal–oxygen or metal–carbon bonds and the reactions between alcohols and transition-metal oxides can therefore be classified as belonging to one of four categories as summaried in Scheme III.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support and to the Carus Chemical Company for a gift of potassium manganate(VI).

Registry No. Cyclobutanol, 2919-23-5; cyclobutanone, 1191-95-3; malonic acid, 141-82-2; sodium manganate(IV), 10101-50-5; potassium permanganate, 7722-64-7; mandelic acid, 90-64-2; benzoylformic acid, 611-73-4.

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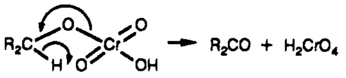
(35) It has also been proposed[13,36] that hydride transfer could occur in a cyclic mechanism:



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