Oxidations of Cyclic β-Diketones Catalyzed by Methylrhenium Trioxide

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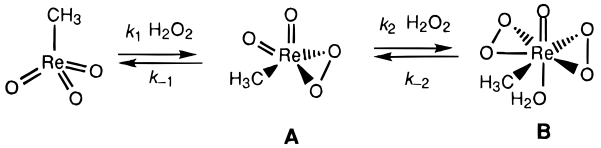
Received May 13, 1996[⊗]

Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes the oxidation of β-diketones by hydrogen peroxide. The kinetics of the initial oxidation step have been investigated in CH_3CN/H_2O (1:1 v/v) at 25 °C for a group of cyclic β-diketones. The initial oxidation step features the enol form, the majority species, as the reactant. Its rate responds to substituents in the "normal" manner: electron-donating groups accelerate the reaction. We suggest that the double bond of the enol attacks a peroxo oxygen of a peroxorhenium complex **A** = $CH_3Re(O)_2(O_2)$ or **B** = $CH_3Re(O)(O_2)_2(H_2O)$. This reaction affords a 2-hydroxy-1,3-dicarbonyl intermediate, which in some instances was detected by ^1H NMR. This hydroxy intermediate is susceptible to cleavage via a Baeyer−Villiger oxidation to yield carboxylic acids as final products. In contrast to the first reaction, this step may feature the peroxorhenium complexes **A** and **B** as nucleophiles rather than their customary electrophilic behavior; perhaps the trend is reversed by substrate binding to rhenium. Time profiles for the different stages of the reaction were also determined. The mechanistic aspects of these multistep catalytic oxidations are discussed in terms of the electronic nature of the activated rhenium-bound peroxo ligands.

Introduction

Selective oxidations with hydrogen peroxide offer the potential for reducing wastes and byproducts as compared to metal-based reagents such as permanganate and chromate, in that only water is produced.[1−3] Hydrogen peroxide, however, suffers from its kinetic inertness and from the involvement of radical pathways that lead to mixtures of products. The desirable reactions of hydrogen peroxide are those in which an oxygen atom from peroxide is transferred to the substrate. An efficient catalyst for hydrogen peroxide reactions can both overcome the kinetic barriers thus reducing the tendency for multiple reaction pathways.

Methylrhenium trioxide (CH_3ReO_3 or MTO) was first prepared in 1979,[4] but only much later did Herrmann and co-workers recognized its potential in catalysis.[5−7] MTO has been shown to be a catalyst for certain types of peroxide reactions. This catalyst possesses other desirable characteristics such as stability toward air and acid and solubility in both organic and aqueous media. MTO catalysis involves in the first instance reactions with hydrogen peroxide to form monoperoxo- and diperoxorhenium complexes, **A** and **B**, respectively. They are formed in equilibrium reactions (K_1 = 13 L mol^{-1} and K_2 = 132 L mol^{-1} at 25 °C and μ 0.10 M in 1:1 CH_3CN/H_2O v/v solution),[8−10] but the equilibria are not instantaneously established. Thus, in some instances, the steps in eq 1 participate as a part of the overall kinetic scheme in the catalyzed reactions.



(1)

Principally, although not exclusively, MTO catalyzes oxygen atom transfer from hydrogen peroxide (but not from alkyl hydroperoxides or oxygen) to certain acceptors. They are often nucleophiles that can accept an oxygen atom: phosphines,[8] sulfides,[11] amines,[12] halide ions,[13,14] etc. or other electron-rich centers such as alkenes that are catalytically converted to epoxides.[6,10]

The kinetic data in each of these instances point to a mechanism in which the nucleophile attacks a peroxide atom of **A** or **B**, this having been electrophilically activated by coordination to rhenium(VII), a strong Lewis acid. Indeed, certain predictions that follow from this mechanism have been verified: electron-donating substituents on a given substrate increase the reaction rate, and isotopic labeling showed that $PhSCH_3$ reacts with $H_2{}^{16}O_2$ in the presence of $MeRe^{18}O_3$ in $H_2{}^{18}O$ to yield only $PhS(^{16}O)CH_3$.[11] The nucleophilic step leads to the regeneration of MTO, which then recycles as in eq 1.

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1996.

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S0276-7333(96)00353-6 CCC: $12.00

It is appreciated, however,[15−18] that peroxide systems have open to them just the opposite possibility: that peroxide will react as a nucleophile toward substrates that are sufficiently electron poor. Instances in which the alternative is operative are, however, poorly documented for MTO−**A**−**B** systems. In this research, the catalytic reactions of the MTO−H_2O_2 system have been extended to β-dicarbonyl compounds. The β-diketones investigated in this study are present mainly in the enolic form, which is electron deficient owing to the conjugation of the double bond with the electron-withdrawing carbonyl group.[19] Therefore, β-diketones can be used to examine the ability of **A** and **B** to oxidize electron-deficient substrates by a mechanism different from that which has been recognized for more electron-rich systems. Further interest in the oxidations of β-diketones stems from their use in the synthesis of natural products,[20] such as naturally-occurring antibiotics.[21]

Data will be presented to show that β-diketones are slowly cleaved with MTO−H_2O_2, in some instances via an intermediate that could be detected directly in the ^{1}H NMR spectrum, prior to further oxidation to a carboxylic acid. We have found that the enol initially gives rise to an intermediate that is susceptible to cleavage via a Baeyer−Villiger oxidation in which the peroxorhenium complexes **A** and **B** may act as nucleophiles rather than their already-recognized electrophilic behavior. MTO has been reported as an effective catalyst for the Baeyer−Villiger oxidations of cyclic ketone to give the corresponding lactones.[22,23] These catalytic oxidations show that MTO can change mechanisms according to substrate demand. Kinetic studies were completed for the initial step of oxidation of β-diketones, and time-resolved concentration profiles were obtained for the different stages of the reactions.

Experimental Section

Materials. HPLC grade acetonitrile (Fisher) was used, and high-purity water was obtained by passing laboratory distilled water through a Millipore-Q water purification system. Hydrogen peroxide (30%, Fisher) was used to prepare peroxide solutions. Methylrhenium trioxide and the diketones (Aldrich) were reagent grade chemicals. The purity of the starting reagents was checked by ^{1}H NMR. Stock solutions of MTO were prepared in water, protected from light, stored at −5 °C, used within few days, and standardized spectrophotometrically before each use.[9,24] The reaction products were characterized by ^{1}H and ^{13}C NMR. The spectra matched those of authentic samples purchased from Aldrich.

Kinetic studies were performed at 25.0 ± 0.2 °C in 1:1 (v/v) CH_3CN-H_2O, containing 0.10 M perchloric acid. The acid was added to stabilize the MTO−H_2O_2 system against decomposition.[25] All manipulations were performed without exclusion of air, since the same results were obtained regardless. Conventional spectrophotometry (Shimadzu UV-2101PC or UV-3101PC) was used to monitor the kinetics. The temperature was maintained by a thermostated water-filled cuvette holder. The absorbance loss of the enolic tautomer of the β-diketones was recorded. The enolic form of a β-diketone absorbs intensely in the near UV region (230−290 nm) with an extinction coefficient ca. 10^4 L mol^{-1} cm^{-1}.[19] Quartz cuvettes with short optical paths (0.10−0.01 cm) were used. Figure 1 displays a typical kinetic trace for the reaction of 2-chloro-5,5-dimethyl-1,3-cyclohexanedione (monochlorodimedone or MCD, for short).

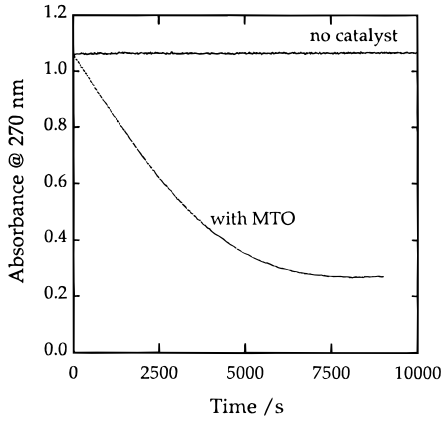

Figure 1. MTO-catalyzed oxidation of monochlorodimedone (MCD) compared to the uncatalyzed reaction. The enolic form (major species in solution, >95%) was monitored spectrophotometrically at 270 nm (optical path, 0.010 cm). Conditions: 5.5 mM MCD, 1.0 M H_2O_2, and 0.10 M $HClO_4$ in CH_3CN−H_2O (1:1 v/v) at 25 °C with 9.0 or 0 mM MTO.

With the exception of one substrate, MCD, the reactions followed first-order kinetics under these conditions. The pseudo-first-order rate constants (k_ψ) were evaluated by nonlinear fitting of the absorbance−time profiles to a single-exponential rate equation

$$\mathrm{Abs}_t = \mathrm{Abs}_\infty + (\mathrm{Abs}_0 - \mathrm{Abs}_\infty)\exp(-k_\psi t)$$

The MCD reaction required the use of the method of initial rates, however, owing to the involvement of chloride ions, a byproduct, later in the reaction cycle, as described subsequently. The absorbance change over the initial 5% of the reaction was used to evaluate the initial rate.

Synthetic Procedure. The MTO-catalyzed oxidation of 5,5-dimethyl-1,3-cyclohexanedione (dimedone) by H_2O_2 was also carried out on a larger scale. We give the results of a typical experiment, to illustrate both the practicalities of the matter and the identification of the products. Dimedone (0.94 g, 6.74 mmol) in 150 mL of acetonitrile was treated with 30% H_2O_2 (2.70 mL, 27 mmol) and then MTO (57 mg, 0.23 mmol). The mixture was allowed to stir at room temperature for approximately 4.5 h. The reaction mixture was tested for formic acid with $Ag(NH_3)_4^+$, Tollen's reagent.[26,27] Formation of a silver mirror indicated the presence of HCO_2H in the products. The mixture was then concentrated by rotary evaporation and extracted with diethyl ether. The organic layer was dried over magnesium sulfate, filtered, and finally evaporated to give 3,3-dimethylglutaric acid as a white solid (0.70 g, 4.4 mmol, 65% yield). This product had ^{1}H and ^{13}C

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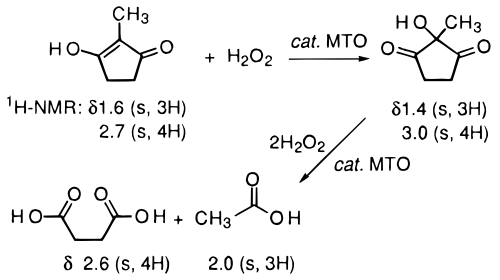
Scheme 1

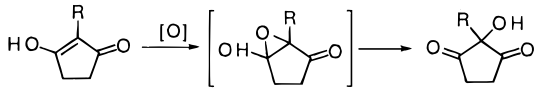


NMR spectra and a melting point that matched those of the authentic compound.

Results

General Observations. β-Diketones react slowly with MTO−H_2O_2. The initial oxidation step affords a 2-hydroxy-1,3-dicarbonyl intermediate, which could be detected in the ^{1}H NMR for the 2-methyl-substituted dicarbonyls. This intermediate is then oxidized further to yield the final products which are the corresponding organic acids. These general observations are summarized in Scheme 1 for 2-methyl-1,3-cyclopentanedione.

The β-diketones investigated in this study were present to more than 95% in the enolic form in solution. The 2-hydroxy-1,3-diketone intermediate arises from the rearrangement of the product of an initial epoxidation step:



(2)

The next step involves oxidative cleavage of the C−C bond, possibly via a Baeyer−Villiger mechanism. MTO is a known catalyst for the Baeyer−Villiger oxidations of cyclic ketones to the corresponding lactones.[22,23] Also, 2-hydroxy-1,3-diketones easily undergo cleavage with oxidizing agents such as IO_4^- and HOO^-.[28,29] The lactone in this case rearranges due to the hydroxyl group on C-2. This affords an α-diketone intermediate (not observed) that is easily oxidized further by hydrogen peroxide to yield the final products, which are the carboxylic acids. α-Diketones are oxidized by hydrogen peroxide to organic acids, catalyzed by both acid and base.[15,29] Therefore, we propose this sequence: epoxidation of the enolic tautomer (major species in solution) initially, followed by oxygen insertion into C−C bond, and finally rupture of the α-diketo intermediate to afford organic acids. This mechanism is illustrated for the case of 2-methyl-1,3-cyclopentanedione in Scheme 2. The different β-diketones that we investigated are listed in Table 1 alongside the final products and yields obtained from catalytic oxidations with the MTO−H_2O_2 system.

Kinetics. The strong UV absorption of the enols was used to follow their reactions with **A** and **B**, the rhenium peroxides. The initial epoxidation of the enol destroys the conjugation responsible for the intense UV absorption of these species. Therefore, spectrophotometric techniques enabled us to study the kinetics of the initial oxidation step only. Figure 1 displays a typical kinetic trace for the MTO-catalyzed reaction of MCD with H_2O_2. The results from a control experiment lacking MTO are also shown; clearly, the uncatalyzed reaction is insignificant.

The solvent used for these studies was 1:1 acetonitrile−water (v/v). This was chosen in light of the lack of solubility of most of the cyclic diketones in organic solvents and the fact that the rates of formation of **A** and **B** are much faster in semi-aqueous media than in dry organic solvents.[8,10,25] This latter fact simplifies the kinetic treatment since the peroxide reactions of MTO can be regarded as rapid prior equilibria. An aqueous or semi-aqueous medium, however, necessitates the addition of acid for catalyst stability.[25] Although acid alone catalyzes the oxidation of β-diketones by hydrogen peroxide without MTO, this effect is not appreciable;

Scheme 2

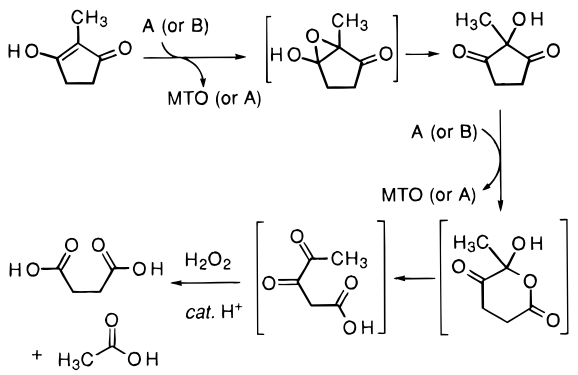
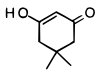
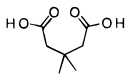
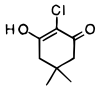
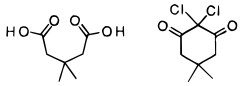
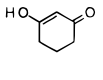
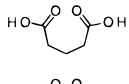
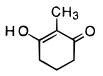
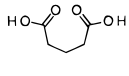
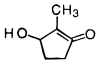
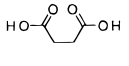
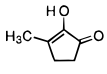
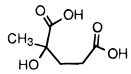
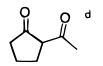
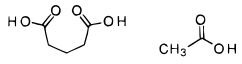
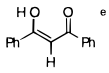
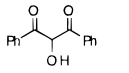


Table 1. Products and Yields from the MTO-Catalyzed Oxidations of β-Diketones by Hydrogen Peroxide[a]

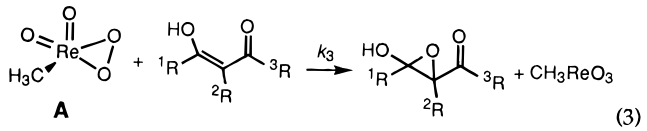
Compound	Products	% Conversion[b]	% Yield[c]
		66	100
		95	74, 26
		85	100
		95	100
		100	100
		95	100
		90	100
		62	85

[a] Conditions: MTO:β-diketone:H_2O_2 = 1:12:70 at 25 °C, in 1:1 CD_3CN/D_2O and pD 1. [b] Based on starting material. [c] By NMR based on conversion. [d] In CD_3CN at 25 °C. [e] In $CDCl_3$ at 25 °C, MTO:β-diketone:H_2O_2 = 1:10:50.

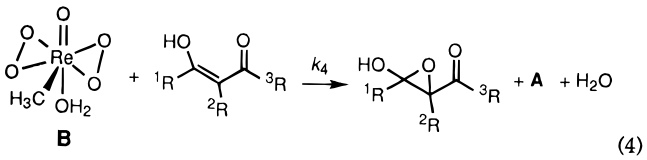
(28) Wolfrom, M. L.; Bobbitt, J. M. *J. Am. Chem. Soc.* **1956**, *78*, 2489.
(29) Ogata, Y.; Sawaki, Y.; Shiroyama, M. *J. Org. chem.* **1977**, *42*, 4061.

the MTO-catalyzed oxidations have been found in all instances to be much faster than those of acid alone.

The different reactions involved in the catalytic cycle are described in eqs 1, 3, and 4. The complete form of



(3)



(4)

the steady-state rate law is shown in eq 5, in which [β]

$$-\frac{d[\beta]}{dt} = v = \frac{k_1k_3[Re]_T[H_2O_2][\beta] + \dfrac{k_1k_2k_4[Re]_T[\beta][H_2O_2]^2}{k_4[\beta] + k_{-2}}}{k_{-1} + k_3[\beta] + k_1[H_2O_2] + \dfrac{k_1k_2[H_2O_2]^2}{k_4[\beta] + k_{-2}}} \quad (5)$$

is an abbreviation for [β-diketone] and v symbolizes its consumption rate. This equation results from the application of the steady-state approximation to the entire reaction scheme. Depending on the concentrations and values of k_3 and k_4, the interplay of eqs 1, 3, and 4 in defining the experimental kinetics will differ. For example, one set of conditions under which the MTO−peroxide reactions of eq 1 are rapid with respect to the oxidation steps (eqs 3 and 4) are as follows: [β-diketone] = [MTO] = 5×10^{-4} M; 0.006−0.10 M H_2O_2. Since the equilibria in eq 1 are established much faster than the oxidation of β-diketones at these higher peroxide levels, the concentrations of **A** and **B** remain constant throughout the reaction in these circumstances. In that case, the complex form of eq 5 reduces to a simpler form, eq 6, with the concentrations of **A**

$$v = k_\psi[\beta] = k_3[\beta][\mathbf{A}] + k_4[\beta][\mathbf{B}] \quad (6)$$

and **B** given by the values at equilibrium in eq 1. Both eqs 5 and 6 were applied to the case of 2-methyl-1,3-cyclopentanedione. The results are shown in Figure 2a,b, respectively. Both fits yield the same values for k_3 and k_4, in each case with the use of values of the rate constants k_1, k_{-1}, k_2, and k_{-2} for eq 1 that had been determined previously.[8−10] The second-order rate constants for the reactions of cyclic β-diketones with **A** (k_3) and **B** (k_4) are presented in Table 2.

Detection of an Intermediate. In some instances an intermediate 2-hydroxy-1,3-diketone (Scheme 1) was detected by its NMR spectrum prior to the production of organic acids, the final products. The concentration−time profiles for reactant, intermediate, and product are shown in Figure 3 for 2-methyl-1,3-cyclohexanedione. Such intermediates were observed only for 2-methyl-substituted cyclic β-diketones. On the other hand, the buildup and decline of an intermediate were not observed for cyclic β-diketones that had H or Cl in place of methyl on C-2. Since MCD (Cl on C-2) reacts 10 times more slowly than the methyl-substituted β-diketone (Table 2), one cannot conclude that the 2-hydroxy intermediate for MCD was not observed owing to its greater reactivity in comparison to the 2-methyl-substituted β-diketone. Nevertheless, 1,3-cyclohexanedione and 2-methyl-1,3-cyclohexanedione have compa-

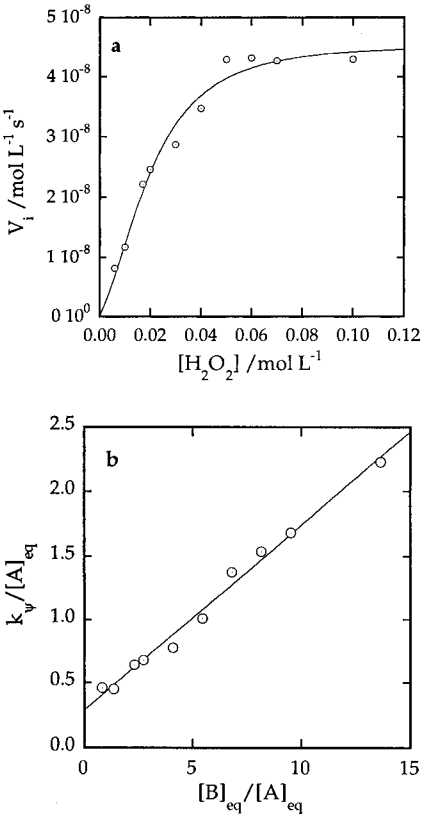
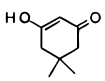
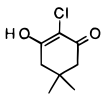
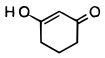
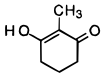
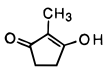
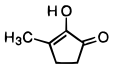


Figure 2. Kinetic data for the oxidation of 2-methyl-1,3-cyclopentanedione fitted to (a) eq 5 and (b) eq 6. Conditions: 0.60 mM 2-Me-1,3-cyclopentanedione, 0.50 mM MTO, and 0.006−0.10 M H_2O_2 in CH_3CN-H_2O (1:1 v/v) containing 0.10 M $HClO_4$ at 25 °C.

Table 2. Rate Constants for the Oxidation of Cyclic β-Diketones by the Rhenium Peroxides A and B[a]

Compound	k_3/L mol^{-1} s^{-1}	k_4/L mol^{-1} s^{-1}
	0.19 ± 0.03	0.11 ± 0.01
	–	0.018 ± 0.001
	0.28 ± 0.06	0.11 ± 0.01
	0.86 ± 0.02	0.17 ± 0.02
	0.28 ± 0.04	0.15 ± 0.01
	–	0.12 ± 0.01

[a] At 25 °C in CH_3CN-H_2O (1:1 v/v) containing 0.10 M $HClO_4$.

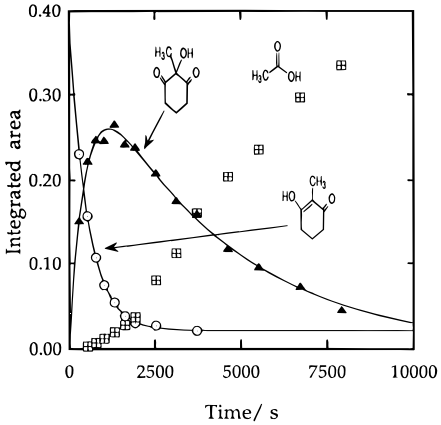
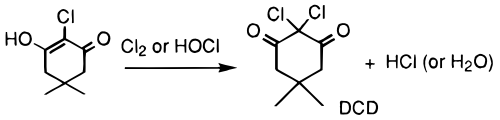


Figure 3. Concentration−time profiles from ^{1}H NMR data for reactant, intermediate, and product for the oxidation of 2-methyl-1,3-cyclohexanedione. Conditions: 0.080 M 2-Me-1,3-cyclohexanedione, 0.010 M MTO, and 0.50 M H_2O_2 in CD_3CN-D_2O containing 0.10 M $DClO_4$ at 25 °C. The decay of the starting β-diketone is fitted to a single-exponential decay equation and the intermediate, to a biexponential model as in R → I → P.

rable k_4 values (Table 2), and 2-methyl-substituted cyclic ketones exhibit reactivities similar to the unsubstituted ones in Baeyer−Villiger oxidations.[18] Therefore, it is reasonable to assume that the Baeyer−Villiger oxidation (oxygen insertion) of this intermediate proceeds more rapidly for the substrates with H or Cl substituents.

Perhaps the mechanism changes at this stage of the reaction. The 2-hydroxy-1,3-dicarbonyl intermediate behaves like an electrophile in the oxygen insertion step and not like a nucleophile. It is worth noting that the kinetics of formation and disappearance of the 2-hydroxy-1,3-dicarbonyl intermediate are dependent on the rhenium concentration. Therefore, oxygen insertion into C−C bond is accelerated by MTO. Since the intermediate was observed only for cyclic β-diketones having a methyl substituent on C-2, the kinetics of this oxygen insertion step could be determined only for these compounds. Table 3 presents the second-order rate constants for the reaction of the 2-hydroxy-1,3-dicarbonyl intermediate with the diperoxorhenium complex **B.**

Monochlorodimedone. In the case of MCD two products were observed, 3,3-dimethylglutaric acid (70%) and 2,2-dichloro-5,5-dimethyl-1,3-cyclohexanedione (dichlorodimedone or DCD) (25%). The dichlorodimedone product was verified by utilizing the MTO-catalyzed reaction between chloride ions and hydrogen peroxide; this process yielded HOCl and Cl_2 that convert MCD to DCD.[14] In one experiment with 0.05 M MCD,



(7)

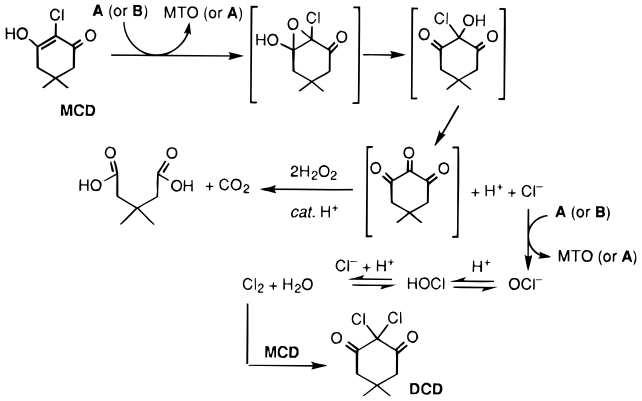
1.0 M Cl^-, 0.010 M MTO, 0.10 M H_2O_2, and 1.0 M $DClO_4$ in D_2O/CD_3CN, DCD was the only product observed [90% yield; ^{1}H-NMR δ 1.00 ppm (s, 6H) and 3.03 ppm (s, 4H)]. These signals for DCD matched those of the second product observed for the MCD oxidation by MTO−H_2O_2 in the absence of Cl^-. The chlorine lost from one MCD must be incorporated into a second, by way of the Cl_2/HOCl reaction. The sequence of events we envisage for monochlorodimedone oxidation is shown in Scheme 3.

Table 3. Rate Constants for the Baeyer−Villiger Oxidation of the 2-Hydroxy-1,3-dicarbonyl Intermediate by B[a]

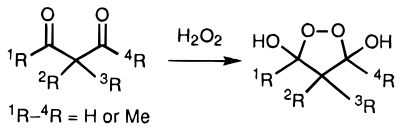
Intermediate	k_5/L mol^{-1} s^{-1}
	0.02
	0.02

[a] At 25 °C in CD_3CN/D_2O (1:1 v/v) containing 1.0 M $DClO_4$; measured by ^{1}H-NMR.

Scheme 3

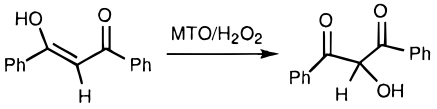


Aliphatic β-Diketones. Since nonhindered simple aliphatic dicarbonyl compounds such as pentane-2,4-dione and its derivatives form cyclic peroxo compounds with hydrogen peroxide,[30] eq 8, the MTO-catalyzed



(8)

oxidations could not be studied independently. However, when bulky substituents were present, hydrogen peroxide and the hindered diketone do not react without a catalyst. MTO catalyzes this oxidation, giving dibenzoylmethanol, eq 9. Since MTO catalyzes the Baeyer−



(9)

Villiger oxidation of cyclic but not aliphatic ketones,[23] dibenzoylmethanol is not appreciably oxidized to carboxylic acids by MTO−H_2O_2. In contrast, cyclic β-diketones are cleaved by MTO−H_2O_2 via a Baeyer−Villiger oxidation step that yields organic acids as the final products.

Discussion

The rhenium peroxides **A** and **B** show similar reactivities toward a given β-diketone, as much as they do

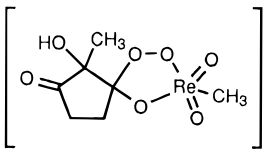
(30) Cocker, W.; Grayson, D. H. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1347.

toward most substrates.[8,10−14,24] This initial oxidation step is characterized by kinetic trends that suggest nucleophilic attack of the substrate on oxygen atom of a peroxide coordinated to the rhenium atom of **A** and **B**. This trend is most pronounced by MCD and dimedone. For dimedone, k_4 is 0.11 L mol^{-1} s^{-1}, and that for MCD, 0.018 L mol^{-1} s^{-1}. The rate retardation by substitution of Cl for H in the 2-position of the diketone supports rate-controlling nucleophilic attack by the enol, as does the further enhancement for the 2-methyl derivative, with $k_4 = 0.17$ L mol^{-1} s^{-1}.

A and **B** are equilibrated more rapidly in eqs 3 and 4 than the oxidation of β-diketones. The concentrations of **A** and **B** therefore remained constant throughout the reaction, given the substantial excess of hydrogen peroxide. In the limit of moderate peroxide concentrations (0.006−0.04 M), [**A**] and [**B**] are of a similar magnitude and each contributes to the overall reaction in proportion with its relative abundance and intrinsic reactivity. Under these conditions the rate is given by eq 6. At higher [H_2O_2], **B** becomes the dominant rhenium species in solution and the rate law simplifies further to $v = k_4$[β-diketone][**B**]. The above statement is true only if **A** is not much more reactive than **B** (i.e., k_3 is comparable to k_4); since k_3 and k_4 are indeed comparable (see Table 2), the simpler form holds at high [H_2O_2]. In such cases, k_4 follows simply from the initial rates: $k_4 = v_i$[β-diketone]$^{-1}$[**B**]$^{-1}$.

The kinetic trends exhibited by the variation of the subsistent at the 2-position of cyclic β-diketones were helpful in recognizing the operative mechanism. From them, we infer that the double bond of the enol acts as a nucleophile, attacking the rhenium-bound peroxides **A** and **B**. The difference in reactivities between **A** and **B** is minor, Table 2: k_3 and k_4 differ by less than 1 order of magnitude. This trend is not at all uncommon, being found for other nucleophilic substrates.[8,10−14]

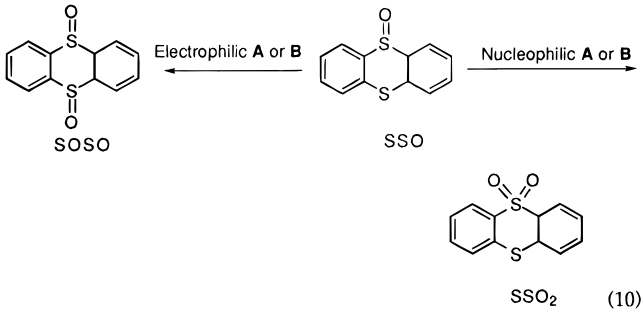
Oxygen insertion into a C−C bond, the Baeyer−Villiger oxidation step, implicates a cyclic Re−peroxo intermediate, illustrated as follows for **A**:



Analogous intermediates have been proposed for the rhenium-catalyzed Baeyer−Villiger oxidations of cyclic ketones,[23] as well as for the enzyme catechol dioxygenase,[31,32] which catalyzes the oxygenation of catechol to 2,4-hexadienedioic acid.

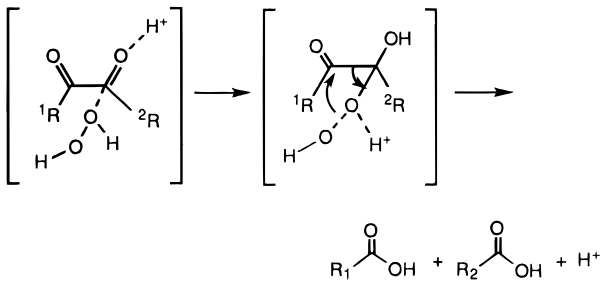
The Baeyer−Villiger oxidation of the 2-hydroxy intermediate follows a trend different from the usual, signaling a change in mechanism. For example, the 2-hydroxy-1,3-dicarbonyl intermediate was sustained at a detectable level only for the cyclic β-diketones with a C-2 methyl group but not for those with H or Cl in place of the methyl. This finding establishes that the 2-hydroxy intermediate disappeared more rapidly for the more electrophilic compounds. Perhaps the rhenium peroxides **A** and **B** behave as nucleophiles in this oxygen insertion step, as observed previously in the MTO-catalyzed oxidations of cyclic ketones to lactones[23] as well as in the Dakin reaction of benzaldehydes with H_2O_2 catalyzed by MTO to give phenols.[33] The changeover between electrophilic and nucleophilic character of the rhenium-bound peroxides in **A** and **B** can be illustrated in reactions of thianthrene 5-oxide (SSO). This substance is an established mechanistic probe for oxygen transfer reagents, eq 10.[34,35] The oxygen transfer parameter was found[23] to have an intermediate value. However, it has been suggested that SSO is not an ideal probe for the character of peroxo metal complexes.[36] Nevertheless, it appears reasonable in light of the results here and those reported previously[23,33] to suggest that **B** exhibits both nucleophilic and electrophilic reactivity. Therefore, **B** (and **A**) is able to adapt its reactivity as necessitated by the substrate involved. This feature allows **A** and **B** to be versatile oxidation catalysts since they are able to react with a wider range of substrates.

$$X_{SO} = \frac{n_{SSO_2}}{n_{SSO_2} + n_{SOSO}}$$



(10)

In our case the lactone formed from the oxygen insertion step rearranges to the α-diketone owing to the presence of a hydroxyl group on C-2. The resulting α-diketone is then oxidized by H_2O_2, this step being catalyzed by the acid present in solution, eq 11.



(11)

MTO does not catalyze the Baeyer−Villiger oxidations of aliphatic ketones.[23] Similarly, oxidative cleavage of aliphatic β-diketones is not catalyzed by methylrhenium trioxide; for example, acacH_2 and its derivatives form

(31) Que, L. *J. Chem. Educ.* **1985**, *62*, 938.
(32) Lippard, S. J.; Berg, J. M. *Principles of Bioinorganic Chemistry*; University Science Books: Mill Valley, CA, 1994; pp 111−112.
(33) Yamazaki, S. *Chem. Lett.* **1995**, 127−128.
(34) Adam, W.; Haas, W.; Lohray, B. B. *J. Am. Chem. Soc.* **1991**, *113*, 6202.
(35) Adam, W.; Lohray, B. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 188.
(36) Ballistreri, F. P.; Tomaselli, G. A.; Toscano, R. M.; Conte, V.; Furia, F. D. *J. Am. Chem. Soc.* **1991**, *113*, 6209.

organic peroxo compounds, eq 8, and dibenzoylmethane yields dibenzoylmethanol, eq 9. MTO does, however, catalyze oxygen insertion into C−C bond of cyclic β-diketones, resulting in complete cleavage products, organic acids.

Why should the postulated reversal in the mechanism be found for these special cases? In these and other such cases, the substrate has a lead-in oxygen atom capable of coordination to rhenium.[37] A situation would then arise where the substrate and peroxide were both bound to rhenium, but the substrate, less nucleophilic than O_2^{2-}, would be polarized to a greater extent. The peroxide in such cases would be a better nucleophile than coordinated substrate. This situation appears to dominate the reactivity of thiophene-based sulfoxides.[38] Indeed, some otherwise puzzling data for thianthrene 5-oxide derivatives may be reconciled in this manner.

Acknowledgment. J.H.E. is grateful to Prof. Charles E. Castro for helpful discussions and suggestions. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82 and by a U.S. Department of Education Fellowship awarded to M.M.A.-O.

OM9603530

(37) Brown, K. N. Private communication.

(38) Brown, K. N.; Espenson, J. H. Submitted for publication.