Stoichiometric and Catalytic Oxidation of Organic Substrates with in-Situ-Generated Peracids

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Introduction

The replacement of hypochlorite and alkyl hydroperoxides as oxidants by hydrogen peroxide is being driven by environmental and economic considerations, respectively. The byproduct when peroxide behaves as an oxidant is water. Though peroxide is a potent oxidant, it is very slow reacting and needs to be activated.

One possible route to activation of H_2O_2 involves its conversion to peroxyacids. Organic peroxyacids are more effective oxidants than H_2O_2 and are reported to oxidize a variety of substrates under mild conditions.[1−5] Some of the peroxyacids used as oxidants include peroxyacetic acid, *m*-chloroperoxybenzoic acid, monoperoxyphthalic acid, peroxymaleic acid, and trifluoroperoxyacetic acid. As the electron-withdrawing nature of the substituent increases, the peracid becomes more reactive. Peroxyacids have been used exclusively as stoichiometric oxidants.

Organic sulfides are important substrates to oxidize. One important application involves oxidation of bis(2-chloroethyl) sulfide, HD, or mustard for decontamination and stock pile destruction.[6] When less reactive organic peroxyacids are used, thioethers are converted to sulfoxides, and the further oxidation of sulfoxides to the corresponding sulfones occurs at a slower rate.[7−9] Peroxymaleic acid, prepared by the reaction of maleic anhydride and 90% H_2O_2 in an inert solvent, oxidized[10] diallyl sulfoxide to the corresponding sulfone in an 87% yield in methylene chloride at 0 °C.

The oxidation of *p,p*-dichlorobenzyl sulfide[11] and diphenyl sulfide[12] using a series of para-substituted peroxybenzoic acids[11] showed an increased oxidation rate when electron-withdrawing groups were used on the peracid and a decreased oxidation rate with electron-donating groups. In both acidic and alkaline media, substitution of electron-withdrawing groups on the oxidant led to an increase in the rates of oxidation of *p*-tolyl methyl sulfoxide.[13] These substituent variations and kinetic studies have led to a mechanism[5] involving nucleophilic attack on the peracid by the sulfide or sulfoxide with simultaneous proton transfer to the carbonyl.

The oxidation of thioethers using a polymer-supported peroxyacid has been reported.[14] A 1:1 ratio of tetrahydrothiophene or L-methionine and oxidant yielded both the corresponding sulfoxides and sulfones. Higher yields of the sulfones were obtained when a 2:1 oxidant-to-substrate ratio was used.

Transition metal-catalyzed oxidations by peroxyacids have received little attention. Thioethers are oxidized to the corresponding sulfones in the presence of a catalytic amount of $Mn(acac)_3$ using H_2O_2 in acetic acid.[15] The reactive oxidant was suggested to be peroxyacetic acid. In the presence of a catalytic amount of the catalyst, $[Fe(CH_3CN)_4[ClO_4]_2$, *m*-chloroperoxybenzoic acid oxidized diphenyl sulfide and diphenyl sulfoxide to the corresponding sulfoxide and sulfone, with 51−71% efficiencies in peroxyacid utilization.[16]

Reactions of peroxy acids with alkenes result in epoxidation and hydroxylation reactions.[17] The mechanism for epoxidation reactions has been discussed in detail recently.[18] The epoxide, formed by nucleophilic attack by the alkene, may react with the carboxylic acid formed from the peroxyacid to yield the monocarboxylate of the diol, which forms the diol upon hydrolysis. Acid-catalyzed ring-opening of epoxides also yield diols. Perbenzoic acid gives good yields of epoxide with octenes and other high molcular weight olefins.[4] Monoperphthalic acid has also been used to epoxidize alkenes, but reactions are generally slower. The use of peracetic acid in epoxidation reactions generally is carried out in acetic acid and produces diols and their monoacetates. Good yields of epoxides are obtained[2,3] in inert solvents. Subsequently, it was shown that good yields of epoxides resulted if the reaction was carried out at 20−25 °C, short reaction times were employed, and strong acids were avoided.

This work is concerned with the in-situ generation of organic peroxyacids from carboxylic acids and anhydrides with aqueous H_2O_2 in the solvent 1-methyl-2-pyrrolidinone. Conditions are examined to make peracid formation catalytic in the carboxylic acid. This oxidant system is studied for the oxidation of both sulfides and alkenes with and without transition metal cocatalysts.

Results and Discussion

Sulfide Oxidations. When maleic anhydride (MAnh) (1.6×10^{-2} mol) and 30% aqueous H_2O_2 are added to 10 mL of *N*-methylpyrrolidinone (NMP), a very efficient oxidant is produced for sulfide oxidation. A 0.2 M solution of *n*-butyl sulfide is completely oxidized in 1 h at ambient temperature, as shown in Table 1. By using a 10-fold excess of maleic anhydride and varying the

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Table 1. *n*-Butyl Sulfide Oxidations Using Maleic Anhydride and H_2O_2[a]

amt of substrate (mol)	amt of H_2O_2 (mol)	time (min)	product (%)
1.6×10^{-3} [b]	1.6×10^{-3}	5	R_2SO (12)
		30	R_2SO (21)
		60	R_2SO (29)
		240	R_2SO (62)
		360	R_2SO (79)
		600	R_2SO (94)
		720	R_2SO (97)
		840	R_2SO (100)
1.6×10^{-3} [b]	4.9×10^{-3}	5	R_2SO (35) R_2SO_2 (57)
		30	R_2SO (10) R_2SO_2 (88)
		60	R_2SO_2 (95)
3.2×10^{-2} [b,d]	3.2×10^{-2}	5	R_2SO (73) R_2SO_2 (27)
5.0×10^{-2} [b,d]	5.0×10^{-2}	5	R_2SO (67) R_2SO_2 (33)
3.2×10^{-2} [b]	3.2×10^{-2}	5	R_2SO (75) R_2SO_2 (11)

[a] The amount of MAnh in all experiments was 1.6×10^{-2} mol; 30% aqueous H_2O_2 was used. The reactions were studied under N_2 at 25 °C unless otherwise indicated. [b] 10 mL of NMP was used. [c] 4 mL of NMP was used. [d] Run under air instead of N_2.

amount of H_2O_2, selective production of sulfoxide or sulfone can result. In the first reaction listed in Table 1, a 1:1 ratio of H_2O_2 to sulfide is used, resulting in 100% conversion to sulfoxide and 100% efficiency in the utilization of peroxide. In an analogous reaction in which maleic anhydride is omitted, only a 7% conversion to sulfoxide occurred. This result demonstrates the involvement of a much stronger oxidant than H_2O_2, i.e., the peroxyacid, in the previous reaction. The use of a 3:1 excess of H_2O_2 to sulfide results in the complete conversion of the sulfide to sulfone in 1 h.

Using a 3:1 H_2O_2-to-substrate ratio, the less nucleophilic thioether, diphenyl sulfide, also reacts with the maleic anhydride/H_2O_2 system, leading to the complete oxidation of the substrate to sulfoxide (14%) and sulfone (84%) in 1 h. No oxidation products were observed in an analogous reaction containing no maleic anhydride.

It should be emphasized that conversion of the diphenyl sulfide to sulfone requires the peracid formed to be a strong enough electrophile to oxidize the sulfur of the weak nucleophile diphenyl sulfoxide.

Catalytic Sulfide Oxidation. In order for the reaction to be catalytic in maleic anhydride, the maleic acid formed after oxygen atom transfer from the peracid would have to react with H_2O_2 to regenerate the peracid, as illustrated in Scheme 1 and eqs 1−3. To evaluate this

$$(RCO)_2O + H_2O_2 \rightarrow RC(O)OH + RC(O)OOH \quad (1)$$

$$RC(O)OOH + S \rightarrow \text{products} + RC(O)OH \quad (2)$$

$$RC(O)OH + H_2O_2 \rightarrow RC(O)OOH + H_2O \quad (3)$$

possibility, a 20-fold increase in *n*-butyl sulfide concentration over that in Table 1 was oxidized using a 1:1 H_2O_2-to-substrate molar ratio at ambient conditions. This produces reactant molarities that are 2 times that of maleic anhydride. After 5 min of reaction, complete oxidation of the substrate had occurred. A similar result was obtained when a 3:1 reactant-to-maleic anhydride ratio was employed. The results obtained for these experiments show >100% efficient use of H_2O_2. The addition of the H_2O_2 to these solutions, containing the acid anhydride and the substrate, results in a very exothermic reaction, with temperatures of >75 °C being observed. Since the reaction vessels were open to the atmosphere, it is most likely that the solvent, 1-methyl-2-pyrrolidinone, reacted with atmospheric oxygen to form the corresponding *N*-alkylamide hydroperoxide, which would result in the further oxidation of the sulfide and/or sulfoxide. Under an N_2 atmosphere, an analogous reaction showed a 97% efficient use of the H_2O_2 (Table 1). A blank run with no maleic anhydride was carried out under air. Butyl sulfide (3.2×10^{-2} mol) was reacted with H_2O_2 (1:1 ratio) at room temperature using 4.1 mL of NMP as solvent. This reaction produced only 9% sulfoxide in 5 min and 16% in 30 min.

Scheme 1

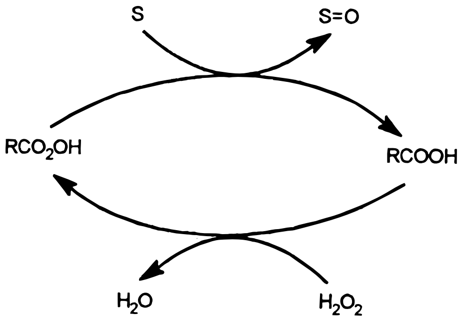

Table 2. Transition Metal-Catalyzed *n*-Butyl Sulfide Oxidations Using Maleic Anhydride and H_2O_2[a]

cocatalyst	time (min)	products (%)
none	5	R_2SO (35) R_2SO_2 (57)
	30	R_2SO (10) R_2SO_2 (88)
	60	R_2SO_2 (95)
$RuCl_3 \cdot 3H_2O$	5	R_2SO (2) R_2SO_2 (93)
	30	R_2SO (1) R_2SO_2 (98)
	60	R_2SO_2 (100)
$Mo(O)_2(acac)_2$	5	R_2SO_2 (100)
$ReCl_3$	5	R_2SO (2) R_2SO_2 (92)
	30	R_2SO (1) R_2SO (99)
	60	R_2SO_2 (100)
$NiCl_2 \cdot 6H_2O$	5	R_2SO_2 (100)

[a] Reaction conditions: substrate (1.6×10^{-3} mol), 1.6×10^{-4} mol of metal compounds, H_2O_2 (4.9×10^{-3} mol, 30% aqueous solution), MAnh (1.6×10^{-2} mol), NMP (10 mL), run under N_2 at ambient conditions.

Effect of Transition Metal Catalysts. The activation of H_2O_2 in the solvent, 1-methyl-2-pyrrolidinone, was pursued using maleic anhydride in the presence of transition metal cocatalysts. The addition of 5×10^{-3} mol of H_2O_2 and 1.6×10^{-2} mol of maleic anhydride to 10 mL of 1-methyl-2-pyrrolidinone led to ~90% oxidation of 1.6×10^{-3} mol of *n*-butyl sulfide to the sulfone in 30 min (Table 2). Several transition metal compounds increased the activity of this system. The addition of $Mo(O)_2(acac)_2$ to the above reaction led to complete oxidation of the sulfide to the sulfone in 5 min (Table 2). An analogous reaction containing $Mo(O)_2(acac)_2$ but no maleic anhydride required 48 h to oxidize the sulfide to the sulfone.

Complete oxidation of the sulfide to the sulfone also occurred in 5 min when $NiCl_2·6H_2O$ was added to the peroxyacid system. The use of H_2O_2 as the oxidant in an analogous reaction with $NiCl_2·6H_2O$ but with no maleic anhydride led to only 10% substrate conversion to the sulfone in 48 h. The reaction was accompanied by nonproductive peroxide decomposition.

The catalysts $RuCl_3·3H_2O$ and $ReCl_3$ enhanced the activity but were less effective than the molybdenum(VI) and nickel(II) catalysts. No increase in activity was observed with $V(O)(acac)_2$, $CoCl_2·6H_2O$, and $FeCl_3·6H_2O$, and metal-catalyzed peroxide decomposition becomes a factor.

Epoxidation of Alkenes. In view of the excellent reactivity observed for sulfide oxidations, the maleic anhydride/H_2O_2 system of Table 1 was used to attempt the epoxidation of olefins. The liquid olefin 1-octene was selected as the substrate because of its similarity to propene but greater ease of handling. Terminal olefins tend to be difficult to selectively epoxidize. When the same conditions used for the noncatalytic thioether oxidations were used for the 1-octene epoxidation, only a small consumption of olefin (9%) was observed after 16 h. The epoxide peak could not be observed in this run because the maleic anhydride has similar retention times. Phthalic anhydride was used in the place of maleic anhydride under similar conditions, and after 3 h, no consumption of olefin or formation of epoxide was observed.

Phthalic anhydride was used for the epoxidation of 1-octene under the conditions used for the catalytic sulfide oxidations. A biphasic system resulted, and no products could be observed in either of the phases after 3 h of reaction. When reacting 5 mmol of the olefin, 3 mmol of 50% aqueous hydrogen peroxide, and 1 mmol of phthalic anhydride at 65 °C, only one phase was observed. After 3 h, very little olefin disappeared, and no epoxide could be found by GC. Addition of $NiCl_2$ did not increase the rate of epoxidation to the extent required to react at the peracid concentrations in this system.

Commercial magnesium monoperphthalate (MgMMP, 2 mmol) was employed as the oxidant for 1-octene (5 mmol) with 3 mmol of 50% H_2O_2 in 10 mL of NMP. In this reaction, 26% of the initial olefin was consumed, and a 23% yield of epoxide was obtained after 1 h of reaction. The olefin consumption corresponds to utilization of 65% of the MgMPP used. None of the hydrogen peroxide reacts with the phthalate anion to regenerate the peracid at these conditions.

The poor reactivity of 1-octene in contrast to sulfide and sulfone is attributed to the poor nucleophilicity of 1-octene. Accordingly, the epoxidation of *cis*-cyclooctene was tried next at 65 °C. Cyclooctene (3 mmol) was reacted with phthalic anhydride (2 mmol) and 50% aqueous hydrogen peroxide (5 mmol) in 10 mL of NMP. After 1 h, 20% of the initial olefin was converted to the epoxide, with a selectivity of 85%.

To increase reactivity, aqueous 50% hydrogen peroxide was substituted by the urea hydrogen peroxide adduct (UHP) in the same reaction to increase the equilibrium concentration of peracid by decreasing the excess water in the system (eq 3). In this reaction, 2 mmol of phthalic anhydride was added to a solution containing 5 mmol of UHP and 3 mmol of *cis*-cyclooctene in 10 mL of NMP. After 1 h at 65 °C, 37% of the initial olefin was converted to the epoxide, with a selectivity of 93%.

Phthalic acid (2 mmol) was used instead of the anhydride in the oxidation of cyclooctene (3 mmol), using UHP (5 mmol) as the oxidant and 10 mL of NMP as solvent. After 1 h at 65 °C, little consumption of the olefin (<5%) and no epoxide were observed. This result indicates that the epoxidation reaction would not be catalytic in anhydride.

A series of experiments were carried out in *N*-methylpyrrolidinone using benzoic acid, 3-chlorobenzoic acid, and 3,5-dichlorobenzoic acid. The purpose of these experiments was to study the regeneration step with increasingly electron-withdrawing substituents. In all instances, the decrease in octene in 3 h at 65 °C was 5% or less.

Since UHP provides a good and safe source of anhydrous hydrogen peroxide[18] and increases the conversion of cyclooctene, attempts were made to oxidize 1-octene with this system. First, 40 mmol of UHP was reacted with 10 mmol of phthalic anhydride in 25 mL of NMP at 40 or 80 °C. After 30 min, 4 mmol of 1-octene was added. The reaction at 40 °C gave an 18% decrease on the olefin and a similar amount of epoxide after 3 h. The reaction at 80 °C, run 10, gave a 38% decrease of the olefin but only 13% epoxide after 3 h. This difference is due to the reaction of phthalic acid and epoxide to form the carboxylate of the diol.

The more facile reaction of sulfides than alkenes with the peracid generated in this system is readily understood in terms of their nucleophilicity. Much higher concentrations of peracid are needed for epoxidation than for sulfide oxidation. These concentrations are not produced at room temperature with phthalic anhydride and 50% aqueous H_2O_2, so little or no reaction occurs. Attempts to facilitate peracid formation by acid catalysis also catalyze ring-opening hydrolysis.

Conclusions

Thioethers, such as *n*-butyl sulfide, can be oxidized to the corresponding sulfoxides and sulfones in the solvent 1-methyl-2pyrrolidinone using maleic anhydride to activate H_2O_2 under ambient conditions. When compared with the analogous thioether oxidations using H_2O_2, the addition of maleic anhydride to these reactions resulted in a very pronounced increase in activity. The use of a catalytic amount of the acid anhydride in reactions employing 1:1 molar ratios of H_2O_2 to substrate led to nearly complete oxidation of the sulfide in minutes, demonstrating the regeneration of the organic peroxyacid from the carboxylic acid formed from the reaction.

Catalytic amounts of transition metal complex catalysts showed an increase in the activity of the peroxyacid. These systems were considerably more active than the analogous metal-catalyzed reaction using the oxidant H_2O_2.

The amount of peracid existing in solutions of H_2O_2 and carboxylic acid is low in the absence of strong acids. For the strong sulfide nucleophile, this amount is enough for reaction, and as the peracid is consumed, this small amount is replenished via eq 3. In the epoxidation reactions, this small concentration leads to a very slow reaction. Since the epoxide production is slow, secondary reactions of the epoxide can occur. If an acid is added to catalyze the peracid formation, it also catalyzes the ring-opening of the epoxide product. When a buffer is added to protect the epoxide from solvolysis, the concentration of the peracid in solution is decreased.

Increasing the temperature to increase the rate and concentration of peracid in solution generated from the carboxylic acid also leads to an increase in rate of the competing epoxide reactions. Conditions can be found that lead to good yields and selectivities for the stoichiometric reaction in which peracids are generated from anhydrides reacting with H_2O_2.

Experimental Section

Reagents and Equipment. The *n*-butyl sulfide, *n*-butyl sulfoxide, *n*-butyl sulfone, diphenyl sulfide, diphenyl sulfoxide, diphenyl sulfone, and 1-methyl-2-pyrrolidinone (HPLC grade) were obtained from Aldrich Chemical Co. and used as received. The metal complexes $Mo(O)_2(acac)_2$, $C(O)(acac)_2$, $ReCl_3$, and $RuCl_3{\cdot}3H_2O$ were received from Aldrich Chemical Co. as well. All other reagents and solvents were obtained from Fisher Scientific and used as received.

Product Analysis. A Varian 3700 GC with an FID and Hewlett Packard 3390A integrator was used to analyze the products of the sulfide reactions, using a 6 ft stainless steel column packed with Carbowax 20M (10%) on Chromosorb WHP (80/100 mesh) for the *n*-butyl sulfide oxidations and a 6 ft stainless steel column packed with SE-30 (3%) on Gas Chromosorb Q (80/100 mesh) for the diphenyl sulfide oxidations. All olefin reactions were carried out using *o*-dichlorobenzene as an internal standard. Reaction products were analyzed using an HP 5890 GC. The substrate(s) and product(s) were identified and quantified using known standards.

Peroxymaleic Acid Stability. Maleic anhydride, 30% aqueous H_2O_2, and the solvent 1-methyl-2-pyrrolidinone produce peroxymaleic acid, a potent oxygen atom transfer agent. This conversion is enhanced by the hydrogen-bonding of the product water to the solvent. The solvent 1-methyl-2-pyrrolidinone is readily oxidized by O_2 at 75 °C, so its oxidative stability to peroxy acids was investigated.

Maleic anhydride (1.6 g, 1.6×10^{-2} mol) and 1-methyl-2-pyrrolidinone (10 mL) were placed in a 100 mL round-bottom flask equipped with magnetic stirring. After 5 min of stirring, H_2O_2 (4.9×10^{-3} mol, 30% aqueous solution) was added dropwise to the acid anhydride solution. After 1 h of stirring, the colorless solution was stored under ambient conditions. The peroxyacid solution was analyzed periodically. Under ambient conditions, 1.6×10^{-2} mol of maleic anhydride and 4.9×10^{-3} mol of H_2O_2 showed <5% loss of oxidation titer over a period of 168 h. The peracid content in the solutions was determined as the difference of the total oxidant content and the hydrogen peroxide content. These were determined in separate titrations as follows. The total oxidant content was determined using an iodomeric titration. Samples were withdrawn and diluted in 2-propanol. A saturated solution of NaI in 2-propanol and acetic acid were added, and the mixture was heated to reflux for 30 s. The iodine was titrated with a standard sodium thiosulfate solution. The H_2O_2 content was determined using a redox titration with Ce^{4+}, using ferroin as an indicator. Samples were withdrawn and diluted in 1 M H_2SO_4 that was cooled to 0 °C. They were then titrated quickly with a standardized solution of $Ce^{IV}(NH_4)_4(SO_4)_4$ in 2.5 M H_2SO_4.

Sulfide Oxidations. Maleic anhydride (1.6 g, 1.6×10^{-2} mol) and 1-methyl-2-pyrrolidinone (5.0 mL) were placed in a 100 mL round-bottom flask equipped with magnetic stirring and an N_2 atmosphere. After 5 min of stirring, the appropriate amount of H_2O_2 was added dropwise to the acid anhydride solution. The resulting colorless solution was stirred for 1 h to ensure formation of the peroxyacid.

1-Methyl-2-pyrrolidinone (5.0 mL) and n-butyl sulfide (0.23 g, 1.6×10^{-3} mol) were placed in a 100 mL round-bottom flask equipped with magnetic stirring and an N_2 atmosphere. After 30 min of stirring, the previously prepared peroxyacid solution was added dropwise to the reaction solution. Samples were analyzed periodically by GC.

Catalytic Maleic Anhydride. For the catalytic maleic anhydride experiment, maleic anhydride, n-butyl sulfide, and 1-methyl-2pyrrolidinone were placed in a 100 mL round-bottom flask equipped with magnetic stirring and stirred for 5 min. Samples were analyzed periodically by GC.

Metal-catalyzed sulfide oxidations were carried out by stirring maleic anhydride (1.6 g, 1.6×10^{-2} mol) and 1-methyl-2-pyrrolidinone (5.0 mL) in a 100 mL round-bottom flask equipped with magnetic stirring and an N_2 atmosphere for 5 min. H_2O_2 (4.9×10^{-3} mol, 0.5 mL of a 30% aqueous solution) was added dropwise to the solution and stirred for 1 h. 1-Methyl-2-pyrrolidinone (5.0 mL), *n*-butyl sulfide (0.23 g, 1.6×10^{-3} mol), and the appropriate catalyst (1.6×10^{-4} mol) were placed in a 100 mL round-bottom flask equipped with magnetic stirring and an N_2 atmosphere. After 30 min of stirring, the previously prepared peroxyacid solution was added dropwise to the reaction solution. When 30% H_2O_2 was the oxidant, it was added dropwise to the sulfide−metal complex solution in NMP. Samples were analyzed periodically by GC.

Epoxidation of Olefins by Peracids. Epoxidation reactions were carried out either on a Parr pressure bottle or in a round-bottom flask equipped with a cold water condenser. Care must be taken when using hydrogen peroxide solutions with 50% or greater content. In general, anhydrides (1.0×10^{-3} mol) were allowed to react with hydrogen peroxide 50% (3.0×10^{-3} mol) in 10 mL of NMP for 0.5 h at room temperature. 1-Octene (5.0×10^{-3} mol) was then added, and the reaction flask was placed in a silicon oil bath at 65 °C. The reaction was monitored by collecting samples periodically and analyzing by GC using an internal standard. Solutions of known concentration were prepared and used to construct calibration curves to permit quantitative determination of octene and the corresponding epoxide.

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