J. Org. Chem. **1999,** *64,* 1191−1196

Bromide Ions and Methyltrioxorhenium as Cocatalysts for Hydrogen Peroxide Oxidations and Brominations

James H. Espenson,* Zuolin Zhu, and Timothy H. Zauche

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received August 24, 1998

Oxidation of alcohols by hydrogen peroxide is negligible; even when catalyzed by methyltrioxorhenium (MTO), the process requires a long reaction time. The addition of a catalytic quantity of bromide ions, as HBr or NaBr, greatly enhances the rate. Some of the reactions were carried out on a larger scale in glacial acetic acid, and others at kinetic concentrations. The data establish that Br_2 is the active oxidizing agent in the system, because the catalytic rates under suitable circumstances match those for the independently measured Br_2 reaction with alcohol (benzyl alcohol, in particular). At much lower levels of MTO, however, Br_2 formation plays a role in the kinetics. Certain other reluctant transformations are conveniently carried out with the $MTO/H_2O_2/Br^-$ combination: aldehydes to methyl esters; 1,3-dioxolanes to glycol monoesters; and ethers (with cleavage) to ketones (mostly), but in fair yield only. When Br^- was used in stoichiometric quantity, certain bromination reactions occur. Thus, phenyl acetylenes (PhC_2R, R = H, Me, Ph) are converted to dibromoalkenes that are entirely or largely formed as the trans isomer, and phenols are brominated. The latter reaction shows the preference para > ortho > meta. Kinetic studies of benzyl alcohol oxidation with $MTO/H_2O_2/Br^-$ were carried out in aqueous solution. With sufficient (normal) levels of MTO, the rate constant for the formation of benzaldehyde agreed with the independently determined value for $Br_2 + PhCH_2OH$, $k = 4.3 \times 10^{-3}$ L mol^{-1} s^{-1} at 25.0 °C; for *sec*-phenethyl alcohol, $k = (9.8 \pm 0.4) \times 10^{-3}$ L mol^{-1} s^{-1}. Bromine is formed from the known oxidation of Br^- with H_2O_2, catalyzed by MTO. This reaction results in $BrO^-/HOBr$, which is then rapidly converted to Br_2. However, with substantially lower concentrations of MTO, the buildup of benzaldehyde is ca. 4-fold slower, reflecting the diminished rate of Br^- oxidation.

Introduction

Reactions of hydrogen peroxide for which MTO is an efficient catalyst are nearly always those in which one oxygen atom can be added immediately to the substrate.[1−3] A rare exception is alcohol oxidation, which occurs quite slowly even with MTO present.[4,5] Alcohols show an appreciable C−H/C−D kinetic isotope effect, which is one reason to suggest a mechanism involving C−H activation and, in particular, hydride abstraction.[5]

Because MTO catalyzes the peroxide oxidation of bromide to hypobromite,[6] we chose to examine whether Br^- would promote hydrogen peroxide oxidations that occur by hydride ion abstraction. Catalytic functionalization of organic compounds by mimicking metalloenzymes is one of the important methods for mild and highly selective syntheses.[7] Haloperoxidases are enzymes that catalyze the oxidation of halide ions by hydrogen peroxide.[8] Certain of their reactions have been mimicked by ammonium metavanadate.[9−11] In the case of MTO, the active oxidizing agents for Br^- are the two peroxorhenium species **A**, $CH_3Re(O)_2(\eta^2\text{-}O_2)$, and **B**, $CH_3Re(O)(\eta^2\text{-}O_2)_2(H_2O)$.

The oxidation of organic compounds by hypohalite salts or halogens is an important method in organic synthesis.[12−15] Halogenation reactions are widely used in the synthesis of flame retardants, pharmaceuticals, agrochemicals, and specialty chemicals.[16] Because they are high-risk oxidants, it is useful to develop catalytic routes that minimize the introduction of halogens and the production of halogenated wastes.[17] The development of regiospecific reactions is one area needing investigation.

Alcohols were one target for oxidations, in that the reactions without bromide ions are so sluggish despite the acceleration provided by MTO. We also sought to discover the conditions under which alcohols would be oxidized, to evaluate bromide vs chloride as cocatalyst, and to examine the oxidations of 1,3-dioxolanes and ethers. In a separate aspect of this research, we set out

---

[1] Espenson, J. H.; Abu-Omar, M. M. *Adv. Chem. Ser.* **1997**, *253*, 99−134.

[2] Herrmann, W. A.; Kühn, F. E. *Acc. Chem. Res.* **1997**, *30*, 169−180.

[3] Gable, K. P. *Adv. Organomet. Chem.* **1997**, *41*, 127−161.

[4] Murray, R. W.; Iyanar, K.; Chen, J.; Wearing, J. T. *Tetrahedron Lett.* **1995**, *36*, 6415.

[5] Zauche, T. H.; Espenson, J. H. *Inorg. Chem.*, **1998**, *37*, 6827.

[6] Espenson, J. H.; Pestovsky, O.; Huston, P.; Staudt, S. *J. Am. Chem. Soc.* **1994**, *116*, 2869.

[7] Barton, D. H. R.; Doller, D. *Acc. Chem. Res.* **1992**, *25*, 504−512.

[8] Butler, A.; Walker, J. V. *Chem. Rev.* **1993**, *93*, 1937−1944.

[9] Dinesh, C. U.; Kumar, R.; Pandey, B.; Kumar, P. *J. Chem. Soc., Chem. Commun.* **1995**, 611.

[10] Conte, V.; Furia, F. D.; Moro, S. *Tetrahedron Lett.* **1994**, *35*, 7429.

[11] Conte, V.; Furia, F. D.; Moro, S.; Rabbollini, S. *J. Mol. Catal.* **1996**, *113*, 175.

[12] Stevens, R. V.; Chapman, K. T.; Weller, H. N. *J. Org. Chem.* **1980**, *45*, 2030.

[13] Katritzky, A. R.; Meth-Cohn, O.; Rees, C. W. In *Comprehensive Organic Functional Group Transformations*; Pergamon Press: New York, 1995; Vol. 5.

[14] Larock, R. C. *Comprehensive Organic Transformations*; VCH Publishers, Inc.: New York, 1989.

[15] Palou, J. *Chem. Soc. Rev.* **1994**, 357−361.

[16] Taylor, R. *Electrophilic Aromatic Substitution*; John Wiley & Sons: New York, 1990.

[17] Nelson, D. W.; Gypser, A.; Ho, P. T.; Kolb, H. C.; Kondo, T.; Kwong, H.-L.; McGrath, D. V.; Rubin, A. E.; Norrby, P.-O.; Gable, K. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 1840.

10.1021/jo9817164 CCC: $18.00

Table 1. Comparison of Bromide to Chloride Ions as Cocatalysts in Oxidative Transformations with Hydrogen Peroxide Catalyzed by MTO

Reactant	Products	Yields	
		NaBr	NaCl
$PhCHO^a$	PhCOOMe	>99	87
	PhCOOH		13
$n\text{-}C_7H_{15}CHO^a$	$C_7H_{15}COOMe$	81	56
	$C_7H_{15}COOH$	19	44
$PhCH_2OH^b$	PhCHO	89	32
	$PhCH_2O_2CMe$	11	68
$PhCH(OH)Me^b$	PhC(O)Me	>99	92
	$PhCH(Me)O_2CMe$		8
$EtCH(OH)\text{-}Am^{n\,b}$	EtC(O)-Am	94	64
	EtCH(Am)OOCMe	6	20^c
$c\text{-}C_6H_{11}OH^b$	cyclohexanone	91	58
	$c\text{-}C_6H_{11}OOCCH_3$	9	34^c

[a] In MeOH. [b] In HOAc. [c] All halide ions were consumed and organic halides were formed.

to learn whether phenols and acetylenes could be brominated, which of course requires a stoichiometric and not a catalytic level of bromide. The experimental effort was divided between synthetic and mechanistic investigations. Several "active bromine" intermediates, including BrO^-, HOBr, and Br_2, as well as $^1O_2$, have been identified as a part of the reaction sequence when bromide is oxidized by hydrogen peroxide with MTO catalyst.[6] Our results point to Br_2 as the only active species under the conditions employed.

Results and Interpretation

Net Oxidations. Acetic acid was chosen as the solvent for certain experiments because acidic conditions prolong the lifetime of the catalyst against irreversible decomposition.[18] The overall reactions of secondary and primary alcohols can be represented by this chemical equation:

$$RCH_2OH/R_2CHOH + H_2O_2 \xrightarrow[\text{HOAc}]{\text{MTO/NaBr (5 mol \%)}} RCHO/R_2CO + 2H_2O \quad (1)$$

Hydrogen peroxide is consumed in stoichiometric amounts. Both bromide[6] and chloride[19] ions were tried as cocatalysts. The former reacted more efficiently and gave a purer product, as presented in Table 1. The products from a representative sampling of secondary alcohols with the cocatalysts $NaBr/CH_3ReO_3$ are given in Table 2. In all of the cases examined, the conversions and selectivities were nearly quantitative.

Data for primary alcohols are given in Table 3. The conversions in 10 h ranged from 32% to 100%, the lower values being found for aliphatic alcohols. Benzylic alcohols reacted satisfactorily, giving aldehydes; they are all known compounds and were identified by their ^1H NMR spectra. The one exception to a high yield of oxidation is the highly activated substrate $p\text{-}CH_3OC_6H_4CH_2OH$, which gave 1% yield of the aldehyde and 99% of the bromide $p\text{-}CH_3OC_6H_4CH_2Br$ as more Br^- was added; with Br^- maintained at the catalytic level, the reaction stopped completely once the Br^- had been converted to the benzyl bromide. This is an example of a bromination reaction, which is the subject of the next section.

Table 2. Yields and Conversions Obtained for the Oxidation of Secondary Alcohols with Hydrogen Peroxide with Methyltrioxorhenium and Bromide Ions as Cocatalysts

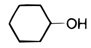
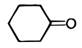
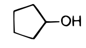
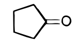
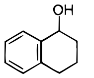
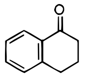
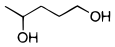
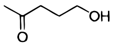
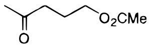
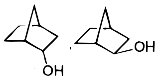
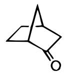
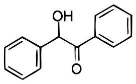
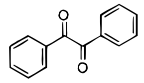
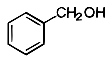
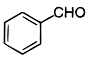
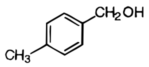
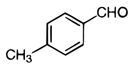
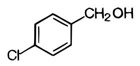
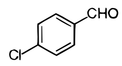
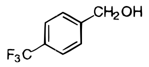
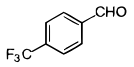
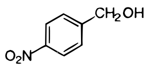
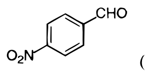
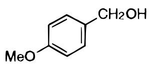
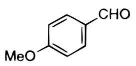
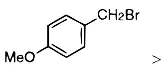
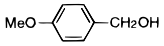
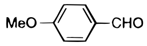
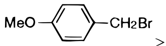
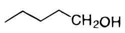
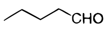
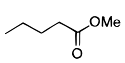
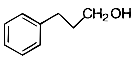
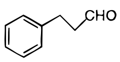
Substrate	Main Product (Yield)	Other Products
PhCH(OH)Me	PhC(O)Me (99%)	
	 (91%)	$C_6H_{11}O_2CMe$ (9%)
	 (92%)	$C_5H_9O_2CMe$ (8%)
PhCH(OH)Et	PhC(O)Et (91%)	$PhCH(Et)O_2CMe$ (9%)
	 (99%)	
	 (94%)	 (6%)
	 (>95%)	
	 (99%)	

Table 3. Oxidation of Primary Alcohols with Hydrogen Peroxide Using Methyltrioxorhenium and Bromide Ions as Cocatalysts

Substrate	Aldehyde (Yield)	Other Product
	 (89%)	$PhCH_2O_2CCH_3$ (11%)
	 (99%)	
	 (90%)	$p\text{-}Cl\text{-}C_6H_4CH_2O_2CCH_3$ (10%)
	 (99%)	
	 (>99%)	
	 (<1%)	 >99
	 (<1%)	 >99
	 (21%)	 79
	 (12%)	$Ph(CH_2)_3O_2CMe$ (88%)

The reaction time of 10 h was chosen as the uniform standard. The larger primary aliphatic alcohols gave lower yields because of the concurrent decomposition of MTO and hydrogen peroxide at longer times: CH_3ReO_3

---

[18] Abu-Omar, M.; Hansen, P. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1996**, *118*, 4966–4974.

[19] Hansen, P. J.; Espenson, J. H. *Inorg. Chem.* **1995**, *34*, 5839.

Table 4. Conversion of Aldehydes to Methyl Esters with Hydrogen Peroxide Using Methyltrioxorhenium and Bromide Ions as Cocatalysts

Aldehyde	Ester (Yield)[a]
PhCHO	$PhCO_2Me$ (100%)
n-$C_7H_{15}CHO$	$C_7H_{15}CO_2Me$ (81%)
c-$C_6H_{11}CHO$	c-$C_6H_{11}CO_2Me$ (92%)
4-MeC_6H_4CHO	4-$MeC_6H_4CO_2Me$ (89%)
4-ClC_6H_4CHO	4-$ClC_6H_4CO_2Me$ (94%)

[a] The balance is the carboxylic acid.

+ $H_2O_2 \rightarrow CH_3OH + HReO_4$.[18] Direct detection of CH_3ReO_3, **A**, and **B** by ^1H NMR allowed us to monitor catalyst stability. Most of the alcohols had been largely oxidized during the time in which catalyst deactivation had occurred. The oxidation of the secondary alcohols, on the other hand, was complete while most of the CH_3-Re bonds still remained intact.

Further Oxidations: Aldehydes, Dioxolanes, and Ethers. The further oxidation of aldehydes to carboxylic acids and, in acetic acid, to acetate esters, signals complications. The other products found in Tables 2 and 3 indicate the extent to which the side reactions constitute a major difficulty. When the reactions are run in methanol, the aldehydes can be further oxidized to their methyl esters. A minor amount of carboxylic acid is also found. Table 4 summarizes the findings. Unlike the literature method[20] that uses >1.5 equiv of NaOCl at 0−5 °C to attain an acceptable yield, this method with only 5% NaBr gives an excellent yield of the esters.

The oxidation of 1,3-dioxolanes is of some interest, given the importance of glycol monoesters. Existing methods that start with the diol require a tedious separation.[21] Alternatively, the oxidative cleavage of cyclic acetals by *tert*-butyl hydroperoxide with a Pd(II) catalyst can be used.[22] The $MTO/H_2O_2/Br^-$ combination, under the same conditions as for the alcohols, was used for three 1,3-dioxolanes. A palladium-catalyzed acetal hydrolysis/oxidation leads to similar products.[22] These results are reported in Table 5.

Ethers, generally quite difficult to cleave oxidatively, can be cleaved in fair yield by this combination. The yields, however, are <60%, as summarized in Table 6. These results are presented only because this is an unusual transformation.

Catalytic Brominations. MTO catalyzes the bromination of alkynes by the combination of H_2O_2 and Br^-. Diphenylacetylene, methyl phenylacetylene, and phenylacetylene were brominated. As presented in Table 7, the *trans*-dibromoalkene is favored, increasingly so as the group R increases in size. The products were identified by ^1H NMR and MS, and the isomer ratio was determined by ^1H integration.[23−25] The literature reports that bromination of methylphenyl acetylene in acetic acid with bromine itself gives a 42:58 trans:cis ratio, which increases to (an extrapolated) 100% trans at higher bromide concentrations, where the mechanism has changed. The bulk of these oxidations were carried out with bromide present at fairly high concentration, resulting in the predominance of the trans product.[25]

Table 5. Oxidative Cleavage of 1,3-Dioxolanes to Glycol Monoesters by $MTO/H_2O_2/Br^-$ in Glacial Acetic Acid

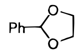
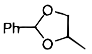
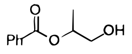
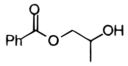
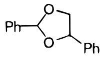
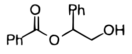
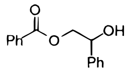
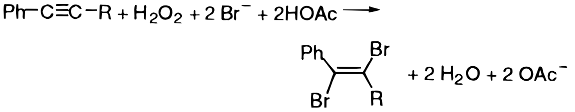
1,3-Dioxolane	Product	Yield
	$PhCO_2CH_2CH_2OH$	85%
		79%
		1:1.5 ratio
		83%
		1:2 ratio

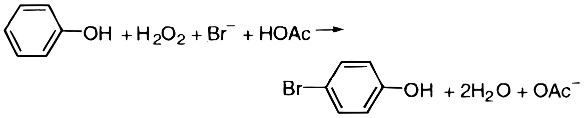
Table 6. Oxidative Cleavage of Ethers with Hydrogen Peroxide Using Methyltrioxorhenium and Bromide Ions as Cocatalysts

Ether	Product	Yield
$PhCH_2-O-CH_2Ph$	PhCHO, $PhCO_2H$	42%, 17%
PhCH(Me)–O–CH(Me)Ph	PhC(O)Me	53%
PhCH(Et)–O–CH(Et)Ph	PhC(O)Et	49%
$Ph_2CH-O-CHPh_2$	Ph_2CO	60%
n-$C_6H_{13}-O-C_6H_{13}$	$C_5H_{11}CHO$, $C_5H_{11}CO_2H$	30%, 19%

The trans configuration of dibromostilbene, a compound that had not been well-characterized previously, was confirmed by an X-ray determination. The structure is displayed in Figure 1. The stoichiometry of the net transformation is given in eq 2.


(2)

Phenols are brominated *rapidly* by H_2O_2, Br^-, and MTO. These reactions (Table 8) exhibit a preference for bromination at the para position. Bromination did occur, however, when only the meta position was available. The selectivity in general follows the order para > ortho > meta. This ordering is sufficiently pronounced that only a single product was obtained *in every case* when competing sites were available. The stoichiometry of the overall reaction is


(3)

Kinetics and Mechanism. The steps in this catalytic process are presumed to be as follows. MTO binds

---

(20) Stevens, R. V.; Chapman, K. T.; Stubbs, C. A.; Tam, W. W.; Albizati, K. F. *Tetrahedron Lett.* **1982**, *23*, 4647.

(21) Babler, J. H.; Coghlan, M. J. *Tetrahedron Lett.* **1979**, 1971.

(22) Hosokawa, T.; Imada, Y.; Murahashi, S.-I. *J. Chem. Soc., Chem. Commun.* **1983**, 1245.

(23) Berthelot, J.; Fournier, M. *Can. J. Chem.* **1986**, *64*, 603.

(24) Uemura, S.; Okazaki, H.; Okano, M. *J. Chem. Soc., Perkin Trans. 1* **1978**, 1278.

(25) Pincock, J. A.; Yates, K. *Can. J. Chem.* **1970**, *48*, 3332.

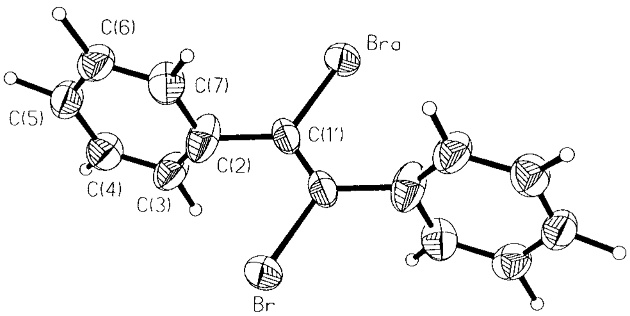


Figure 1. Molecular structure of *trans*-α,α′-dibromostilbene prepared from the MTO-catalyzed bromination of diphenylacetylene with hydrogen peroxide; this provides definite proof for the exclusive formation of the trans isomer.

Table 7. Products of the MTO-Catalyzed Bromination of Phenylacetylenes by Hydrogen Peroxide and Sodium Bromide

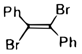
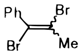
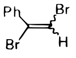
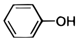
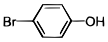
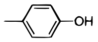
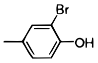
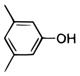
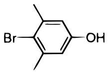
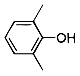
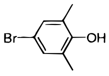
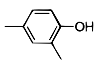
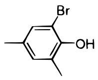
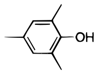
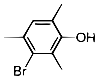
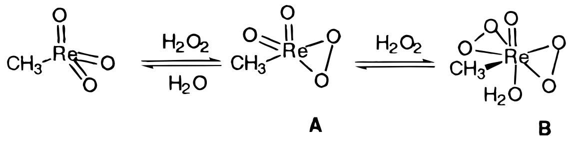
Alkyne $Ph{-}C{\equiv}C{-}R$	Products	Trans/Cis Yield	MS ($m/e = M^{\bullet+}$)	^1H NMR ($CDCl_3$, Me_4Si)
$Ph{-}C{\equiv}C{-}Ph$	 mp 215–216 °C	>99:1 100%	340, 338, 336	7.47 (m, 4H), 7.35 (m, 6H)
$Ph{-}C{\equiv}C{-}Me$		~99:1 100%	278, 276, 274	*trans:* 7.30 (m, 5H), 2.60 (s, 3H); *cis:* 7.28 (m, 5H), 2.26 (s, 3H)
$Ph{-}C{\equiv}C{-}H$		7:1 100%	264, 262, 260	*trans:* 7.42 (m, 5H), 6.80 (s, 1H); *cis:* 7.33 (m, 5H), 7.04 (s, 1H)

Table 8. Products of the MTO-Catalyzed Bromination of Phenols by Hydrogen Peroxide and Sodium Bromide[a]

Phenol	Product	Reaction Time	mp °C	MS ($m/e = M^+$)	^1H NMR ($CDCl_3$, Me_4Si)
	 99%[b]	<10 min		174, 172	7.00 (2, 2H), 6.49 (d, 2H), 5.11 (s, 1H)
				188, 186	7.23–6.88 (m, 3H); 5.21 (s, 1H), 2.23 (s, 6H)
			114–115	202, 200	6.57 (s, 2H), 2.33 (s, 6H)
			79–80	202, 200	7.08 (s, 2H), 4.55 (s, 1H), 2.18 (s, 3H)
			6–7	202, 200	7.25 (s, 1H), 7.01 (s, 1H), 5.53 (s, 1H), 2.41 (s, 3H), 2.38 (s, 3H)
			83–84	216, 214	6.87 (s, 1H), 4.54 (s, 1H), 2.33 (s, 3H), 2.29 (s, 2H), 2.16 (s, 3H)

[a] Yields were quantitative. [b] 2,4-Dibromophenol was also formed after ~1 h.

Scheme 1. Reactions in the Cycle of Alcohol Oxidation by Hydrogen Peroxide with Methyltrioxorhenium and Bromide Ions as Cocatalysts



$$\mathbf{A}\ (\text{or } \mathbf{B}) + Br^- \rightarrow CH_3ReO_3\ (\text{or } \mathbf{A}) + BrO^- \quad k_3\ (k_4)$$

$$BrO^- + 2H^+ + Br^- \rightarrow Br_2 + H_2O$$

$$R^1R^2CHOH + Br_2 \rightarrow R^1R^2C{=}O + 2Br^- + 2H^+ \qquad (k_5)$$

hydrogen peroxide[11] in two reversible and reasonably rapid equilibria.[13,17] Each peroxorhenium species, **A** and **B**, converts Br^- to BrO^-.[6] This, too, is reasonably rapid. In an acidic medium, BrO^-/HOBr then becomes Br_2 nearly instantly. The alcohol is subsequently attacked by species that are known to abstract hydride from the OH-bearing carbon. That reagent is probably bromine[15,26] or, less likely, hypobromite.[27,28] This sequence of reactions is depicted in Scheme 1.

Bromide ions are central to this process. Without Br^-, the peroxorhenium complexes are unable to proceed further. Although numerous examples can be cited in which peroxorhenium complexes are efficient donors of an oxygen atom,[1] they are for the most part unable to abstract hydride. Thus, the synergistic effect of the cocatalysts: the one excises an oxygen atom from peroxide, and the other, after accepting that oxygen, in turn is converted to a species capable of abstracting hydride ion from the alcohol, which is the key to its oxidation.

The only rate constant in Scheme 1 that was not previously known in this medium is k_5. Our determinations for benzyl alcohol were carried out with $[Br_2]_0 = 1.58$ mM and $[PhCH_2OH]_0 = 64-450$ mM. The absorbance increase accompanying benzaldehyde formation was monitored. The data were fit by nonlinear least squares to first-order kinetics. The resulting second-order rate constant is $k_5 = (4.3 \pm 0.3) \times 10^{-3}$ L mol^{-1} s^{-1}; for *sec*-phenethyl alcohol, $k_5 = (9.8 \pm 0.4) \times 10^{-3}$ L mol^{-1} s^{-1}.

Two series of experiments were performed, each with these initial concentrations: 0.296 M benzyl alcohol, 4.7 mM H_2O_2, and 1.0 M $HClO_4$. In the first set of four determinations, [MTO] and $[Br^-]$ were varied in the ranges 2.1−5.0 mM and 2.5−9.9 mM, respectively. With this fairly high level of MTO, it seemed that Br_2 formation would be considerably faster than its consumption. The formation of benzyldehyde was again monitored. The data from each experiment fit first-order kinetics. The average value of k_ψ was divided by $[PhCH_2OH]$. The resulting quotient was a constant, with the average value $(4.6 \pm 0.5) \times 10^{-3}$ L mol^{-1} s^{-1}. This agrees with the value directly determined for k_5, thus confirming that the reaction between Br_2 and $PhCH_2OH$ was indeed rate-controlling under these circumstances. It further con-

---

(26) March, J. *Advanced Organic Chemistry*; 4th ed.; Wiley: New York, 1992.

(27) Puttaswamy; Mahadevappa, D. S.; Made Gowa, N. M. *Int. J. Chem. Kinet.* **1991**, *23*, 27−35.

(28) Wolfe, S.; Hasan, S. K.; Campbell, J. R. *Chem. Commun.* **1970**, 1420.

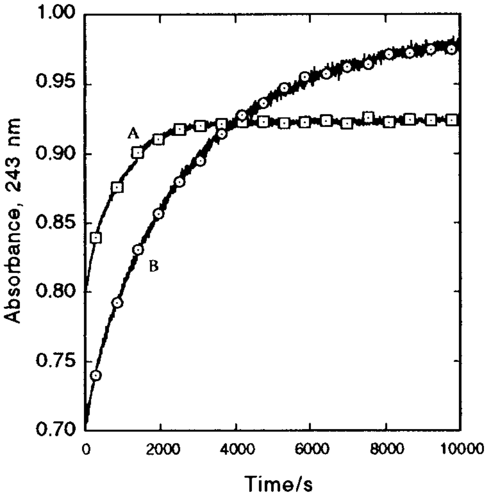
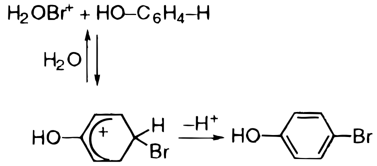


Figure 2. Absorbance-time recordings for the oxidation of $PhCH_2OH$ (0.296 M) with hydrogen peroxide (4.7 mM) in solutions containing the cocatalysts Br^- (4.94 mM) and MTO (A, 5.02 mM; B, 0.05 mM). The experiments were carried out in aqueous solution at 25.0 °C.

firms, of course, that Br_2 is the active catalytic intermediate responsible for alcohol oxidation. Under these reaction conditions, no further oxidation of benzaldehyde occurred; this was confirmed by an experiment with independent aldehyde that confirmed no reaction in >4000 s.

The second set of experiments was performed with much lower concentration of MTO, 50−100 μM. This was done deliberately to reduce the rate of Br^- oxidation by **A**, thus making Br_2 formation more competitive with its consumption. The rate constants in this series were much less, about 25% of the values of those cited previously, substantiating the contribution of the k_3 reaction to the kinetic barrier. Figure 2 shows the catalytic buildup of benzaldehyde in two experiments with different levels of MTO. The two curves vary somewhat in shape, but the effect of catalyst variation is not very great because MTO is not involved in the step between bromine and alcohol.

Is There a Role for HOBr? One might ask whether HOBr or a protonated species H_2OBr^+ is an active brominating agent. The relative electrophilicities of the species H_2OBr^+, Br_2, and HOBr have been found to be in the ratio ca. 10^6:$10^{3.8}$:1.[16] Clearly, HOBr is an unattractive candidate. The protonated reagent appears a feasible candidate:



The presence of bromine is indicated by a red coloration that rapidly develops in the reaction solutions for the bromination of both the alkynes and phenols. However, Br_2 may not be the reactive species; it may simply exist in labile equilibrium with H_2OBr^+. On the other hand, bromine is itself a perfectly competent brominating agent and the more likely reactant. The correspondence between the rate constants for benzaldehyde formation and for the independently determined reaction between Br_2 and benzyl alcohol support this assignment.

The mechanism by which Br_2 oxidizes alcohols involves hydride abstraction. The considerable body of evidence for a hydride abstraction mechanism has been summarized.[29]

Discussion

The use of hydrogen peroxide with a molybdenum catalyst has been reported: secondary alcohols reacted, primaries did not, and aldehydes were converted to carboxylic acids.[10,11] The principle evinced here, however, is entirely different because of the involvement of bromide, hypobromite, and bromine. One report has appeared concerning the oxidation of benzylic alcohols by hydrogen peroxide with an HBr catalyst; as in our work, the active intermediate was shown to be Br_2.[30] This is consistent with the known fact that H_2O_2 and Br^- react to generate Br_2, even in the absence of MTO.[31,32] The use of a somewhat higher level of Br^- and an elevated temperature (60 °C) allowed the net conversion even without MTO. Oxygen is not effectively activated by methylrhenium peroxide and cannot be substituted for hydrogen peroxide. These features are just those presented by vanadium bromoperoxidase.[8]

Experimental Section

The experiments on alcohol oxidations entailed the use of 15 mL of acetic acid, to which were added 2 mmol of alcohol, 4 mmol of hydrogen peroxide, 0.1 of mmol sodium bromide, and (in three portions over 10 h) 0.1 mmol of MTO. The solution was stirred at room temperature over this time.

For the conversion of an aldehyde to an ester, the aldehyde (2 mmol) was dissolved in 15 mL of methanol containing HOAc (3 mmol), sodium bromide (0.1 mmol), and hydrogen peroxide (>4 mmol). A solution of MTO (0.1 mmol in all) was added over 10 h, while the solution was stirred at room temperature. The reaction products were checked by GC−MS before separation.

A typical procedure for the cleavage of an ether is as follows, using dibenzyl ether as the example. Acetic acid (25 mL) was added to a solution of $(PhCH_2)_2O$ (19 mmol), followed by NaBr (1.9 mmol) and hydrogen peroxide (38−45 mmol). The solution was maintained at room temperature while the MTO (2 mmol) was added in three portions over 12 h with stirring. The solvent was removed by distillation, and the product was extracted with diethyl ether and dried over anhydrous sodium sulfate.

The bromination of the alkynes was carried out as follows. The alkyne (10 mmol), sodium bromide (21 mmol), and MTO (0.2 mmol, 2 mol %) were dissolved in 20 mmol of acetic acid and cooled to 10 °C. The hydrogen peroxide (>50 mmol) was infused over 20 min with a syringe pump under vigorous stirring. The low temperature was adopted to minimize catalyst decomposition.[18] Each reaction was finished within 20 min and gave a nearly quantitative yield of product. The products were isolated by vacuum distillation (with the exception of α,α′-dibromostilbene, a solid that was recrystallized from acetone).

The bromination of phenols was carried out with phenol (10 mmol), sodium bromide (10.5 mmol), MTO (0.2 mmol), and H_2O_2 (>30 mmol, added by syringe pump). The reactions were finished within 30 min and proceeded in nearly quantitative yield. The products were isolated by simple vacuum distillation (entries 1 and 2) or filtration, after removing the solvent by

---

(29) Stewart, R. In *Oxidation Mechanisms: Applications to Organic Chemistry*; W. A. Benjamin, Inc.: New York, 1964.

(30) Dakka, J.; Sasson, Y. *Bull. Soc. Chim. Fr.* **1988**, 756.

(31) Bray, W. C. *Chem. Rev.* **1932**, *10*, 161.

(32) Bray, W. C.; Livingston, R. S. *J. Am. Chem. Soc.* **1928**, *50*, 1654.

rotary evaporation, followed by recrystallization from acetone. The bromophenols were identified by ^{1}H and MS data.[33–36]

Kinetics experiments on the oxidation of $PhCH_2OH$ by MTO/H_2O_2/Br^- were carried out by UV–visible methods. The reaction progress was monitored by the buildup of PhCHO at 243 nm, an absorption maximum with ϵ 1.1 × 10^4 L mol^{-1} cm^{-1}.

Acknowledgment. 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. We are grateful to Professor P. J. Stang for alerting us to references on the bromination of acetylenes.

Supporting Information Available: Summary of the crystallographic information (data collection, structure solution, refinement details, and bond distances and angles) for *trans*-dibromostilbene. This material is available free of charge via the Internet at http://pubs.acs.org.

JO9817164

---

(33) Berthelot, J.; Guette, C.; Desbène, P.-L.; Basselier, J.-J.; Chaquin, P.; Masure, D. *Can. J. Chem.* **1989**, *67*, 2061.

(34) Fischer, A.; Henderson, G. N. *Can. J. Chem.* **1982**, *61*, 1045.

(35) Brittain, J. M.; de la Mare, P. D. B.; Newman, P. A.; Chin, W. S. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1193.

(36) Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra*; Aldrich Chemical Co.: Milwaukee, 1993.