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Metal Catalysis in Oxidation by Peroxides.[1] Kinetics and Mechanism of the Molybdenum-Catalyzed Oxidation of Sulfoxides to Sulfones with Hydrogen Peroxide

O. Bortolini, S. Campestrini, F. Di Furia,* and G. Modena

Centro C.N.R di Studio sui Meccanismi di Reazioni Organiche, Dipartimento di Chimica Organica dell'Università, Università di Padova, 35131 Padova, Italy

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The rates of oxidation to sulfones of three model sulfoxides, di-*n*-butyl, phenyl methyl, and diphenyl, with hydrogen peroxide, in the presence of catalytic amounts of $MoO_2(acac)_2$, have been measured in ethanol solvent, at 40 °C, both in acid and basic solutions. The comparison of the behavior observed with those of the *m*-chloroperbenzoic oxidation of the same substrates, either in acid or basic solutions, and of the oxidation of the parent sulfides provides an useful mechanistic tool for differentiating electrophilic oxygen transfers from the nucleophilic ones.

In the oxidation of organic substrates with peroxycarboxylic acids both homolytic and heterolytic mechanisms may operate.[2] Heterolytic processes involve either the oxidation of nucleophilic substrates, e.g., organic sulfides or alkenes,[2] via a formal electrophilic oxygen transfer or the oxidation of electrophilic substrates, e.g., ketones,[2,3a] via a formal nucleophilic attack by the peroxy oxygen.

The aim of the presence investigation has been a comparison of the oxidative behavior of peroxycarboxylic acids with that of molybdenum–peroxo complexes[4] and, in particular, a quantitative evaluation of the reactivity of anionic Mo(VI)–peroxo species. As recently pointed out,[5] the Baeyer–Villiger oxidation of ketones, owing to the very low rates observed even when a highly reactive oxidant such as trifluoroperacetic acid is used,[3a] may not be a good model reaction. Consequently, the oxidation of alkyl- or arylboronic acids as a probe of nucleophilic reactivity has been recently suggested.[5] Here we employ an alternative model reaction, i.e., the oxidation of sulfoxides to sulfones, which was proposed and investigated several years ago by one of us.[3b] In fact, sulfoxides are rather peculiar substrates which may be oxidized via either a electrophilic or a nucleophilic oxygen transfer.[6]

The results obtained indicate that the oxidation of sulfoxides with *m*-chloroperbenzoate anion proceeds via a nucleophilic mechanism, whereas neutral MCPBA and both neutral and anionic molybdenum–peroxo complexes behave as electrophilic oxidants toward sulfoxides. The implications of these findings on the nature of Mo(VI)–peroxo anions are also discussed.

Results and Discussion

Di-*n*-butyl sulfoxide (**1**), phenyl methyl sulfoxide (**2**), and diphenyl sulfoxide (**3**), were used a model substrates.

A one-to-one stoichiometry of the catalyzed oxidation of **2** with H_2O_2 was determined (see Experimental Section) both in acid and basic solutions.

The kinetic study has been carried out under pseudo-first-order conditions by employing an excess of the substrate over hydrogen peroxide.

The rate law of the oxidation in acid media (CH_3SO_3H, 1×10^{-4} M) has been determined by employing **2** as model substrate (eq 1). The pertinent data are collected in Table I.

$$R_o = -d[H_2O_2]/dt = k_2[\text{substrate}][\text{Mo(VI)}] \quad (1)$$

The linearity of plots of $[H_2O_2]$ vs time up to 80–90% reaction indicates a zero-order dependence of rates on hydrogen peroxide initial concentration, resulting from the large value of the association constant of H_2O_2 to the metal in forming the peroxometal complexes[7] which is the actual oxidant in solution. As far as the nature of the peroxometal species is concerned, previous investigations have shown that, in ethanol solvent, independently of the molybdenum species added, an oxo–diperoxo complex, $MoO(O_2)_2(EtOH)_n$, is formed.[2b]

Although k_2 should depend on the concentration of the acid, the data reported in Table I show that a 10-fold increase of the acid concentration causes only a small enhancement (ca. 1.5-fold) of k_2. This may be taken as evidence that at 1×10^{-4} M CH_3SO_3H the peroxomolybdenum species is almost completely present in its un-ionized, neutral form. Consequently, an increase of the acidity of the medium should not affect the acid–base equilibria involving the oxidant. It must be mentioned that potentiometric experiments indicated that $MoO(O_2)_2(EtOH)_n$ behaves in ethanol as a monobasic acid of medium strength according to the general equilibrium in eq 2.

$$MoO(O_2)_2(EtOH)_n + EtOH \rightleftarrows [MoO(O_2)_2(EtO)(EtOH)_{n-1}]^- + EtOH_2^+ \quad (2)$$

On the other hand, no direct evidence is available on the structure of the metal–peroxo anion and, in particular, on the localization of the negative charge. The results obtained in this study may, as discussed below, shed some light on this point.

The rate law of the oxidation of **2** in alkaline (EtONa, 1×10^{-3} M) solution has been determined. The data are reported in Table I. Also in basic media the association constant of hydrogen peroxide to molybednum appears to be large. A plot of R_o vs [substrate] shows an intercept. This should be attributed to the slow oxidation of the solvent carried out by anionic molybdenum–peroxo com-

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[1] Metal Catalysis in Oxidation by Peroxides. 27. Part 28: Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G.; Valle, G. *J. Org. Chem.*, in press.

[2] (a) *The Chemistry of Peroxides*; Patai, S., Ed.; Wiley: New York, 1982. (b) Di Furia, F.; Modena, G. *Pure Appl. Chem.* **1982**, *54*, 1853. (c) Curci, R.; Edwards, J. O. *Organic Peroxides*; Swern, D., Ed.; Wiley, New York, 1970; Vol. 1, pp 199–264 and references therein.

[3] (a) House, H. O. *Modern Synthetic Reactions*; Benjamin: New York, 1972. (b) Curci, R.; Modena, G. *Gazz. Chim. Ital.* **1964**, *94*, 1257 and references cited therein.

[4] (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981. (b) Di Furia, F.; Modena, G. *Rev. Chem. Intermed.* **1985**, *6*, 51.

[5] Brauchaud, B. P.; Walsh, C. T. *J. Am. Chem. Soc.* **1985**, *107*, 2153.

[6] (a) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020. (b) Akasaka, T.; Ando, W. *J. Chem. Soc., Chem. Commun.* **1983**, 1203 and references therein.

[7] Di Furia, F.; Modena, G.; Curci, R.; Bachofer, S. J.; Edwards, J. O.; Pomerantz, M. *J. Mol. Catal.* **1982**, *14*, 219.

0022-3263/87/1952-5093$01.50/0

Table I. Oxidation of Phenyl Methyl Sulfoxide to the Corresponding Sulfone with H_2O_2, Catalyzed by $MoO_2(acac)_2$, in EtOH–H_2O (0.04 M) at 40.0 ± 0.02 °C[a]

$[PhS(O)CH_3]$, M	$10^4[MoO_2(acac)_2]$, M	$10^4[CH_3SO_3H]$, M	10^4[EtONa], M	10^7R_0,[b] M s^{-1}	10^2k_2,[c] M^{-1} s^{-1}
0.05	1.25	1		2.1	3.36
0.05	2.5	1		4.3	3.44
0.05	5.0	1		8.6	3.44
0.05	5.0	1		8.6	3.44[d]
0.02	5.0	1		3.5	3.50
0.10	5.0	1		17.8	3.56
0.025	5.0	10		4.3	3.45
0.05	5.0		10	3.2	0.88
0.10	5.0		10	5.5	0.90
0.20	5.0		10	9.8	0.88
0.35	5.0		10	15.9	0.85
0.50	5.0		10	22.0	0.84
0.05	10.0		10	6.5	0.90

[a] In all esperiments $[H_2O_2]_0$ = 0.01 M. [b] Slope of plots of $[H_2O_2]$ vs time, linear up to 80% reaction; duplicate runs agree within 3–5%. [c] Calculated as R_0/[substrate] [catalyst] in acid solution and as $(R_0 - R_S)$/[substrate] [catalyst] in basic solution. R_S values (1×10^{-7} M s^{-1} at [catalyst] = 5×10^{-4} M and 2×10^{-7} M s^{-1} at [catalyst] = 10×10^{-3} M) were obtained by experiments run in the absence of $PhS(O)OH_3$ as slopes of plots of $[H_2O_2]$ vs time. [d] $[H_2O_2]_0$ = 0.005 M.

Table II. Relative Rates of Oxidation of Sulfoxides to Sulfones and of Sulfides to Sulfoxides with Various Oxidizing Systems

		H_2O_2/Mo(VI)[b]		MCPBA[c]	
substrate	H_2O_2/H^+[a]	acid	alkaline	acid	alkaline
n-Bu_2SO		3.2	3.1	4.1	0.66
$PhS(O)CH_3$		1.9	1.9	2.1	1.9
Ph_2SO		(1.0)	(1.0)	(1.0)	(1.0)
n-Bu_2S	61	53	51		*d*
$PhSCH_3$	5.7	7.7	6.2		*d*
Ph_2S	(1.0)	(1.0)	(1.0)		*d*

[a] Data from ref 9. [b] Under the standard conditions described in the text. [c] In ethanol–dioxane (70:30 v/v) at −20 °C; [sulfide] = [sulfoxide] = 0.025 M, [MCPBA] = 0.01 M; $[CH_3SO_3H]$ = $[EtO^-]$ = 0.1 M. [d] No reaction. No appreciable variation of iodometric titer after the 24 h under the conditions described in footnote *c*.

plexes[8] and is confirmed by the less than stoichiometric (see Experimental Section) production of sulfone. In fact, by running the experiments under otherwise identical conditions but in the absence of **2**, disappearance of H_2O_2 and formation of the diethyl acetal of acetaldehyde is observed. The measured rate of this oxidation, again zero-order in H_2O_2, is in very good agreement with the value of the intercept of the plot of R_o vs [substrate]. Therefore, the rate law in basic media is as in eq 3, where

$$-d[H_2O_2]/dt = R_S + R_o = R_S + k_2[\text{substrate}][\text{Mo(VI)}] \quad (3)$$

R_S is the rate of hydrogen peroxide disappearance in the absence of substrate, which has been measured in all the experiments and subtracted from the overall rate.

Under the standard acid and alkaline conditions adopted in the oxidation of **2**, the rates of oxidation of **1** and **3** with the H_2O_2–Mo(VI) system, the rate constants of the oxidation of the three sulfoxides with MCPBA, either in acid or basic media, and the oxidation rates of the parent sulfides with the H_2O_2–Mo(VI) system have been measured. All the pertinent results are reported in Table II together with the literature results[9] referring to the acid-catalyzed ($HClO_4$) oxidation of sulfides with H_2O_2.

For all the oxidizing systems considered, with the exception of anionic MCPBA, the reactivity order parallels the nucleophilicity of the substrates, i.e., **1** > **2** > **3**. In particular, the results concerning the $HClO_4$-catalyzed oxidation of sulfides with H_2O_2, a most typical electrophilic oxidation, show a very nice correlation (see Figure 1) with the behavior of the H_2O_2–Mo(VI) system in the oxidation of sulfides and of sulfoxides either in acid or basic media and with the oxidation of sulfoxides with MCPBA thus suggesting that the transition states of the various oxidations have similar character. Significantly, *m*-chloroperbenzoate anion *does not oxidize the sulfides*, under the same experimental conditions adopted for sulfoxides (see footnote *d*, Table II). This is not surprising as this process would require the reaction of the powerful nucleophilic peroxo anion with the electron-rich sulfur atom. By contrast, the perbenzoate anion does oxidize the sulfoxides. However, the reactivity order, i.e., **1** < **2** > **3**, is different from all the other systems. Therefore, it is likely that this

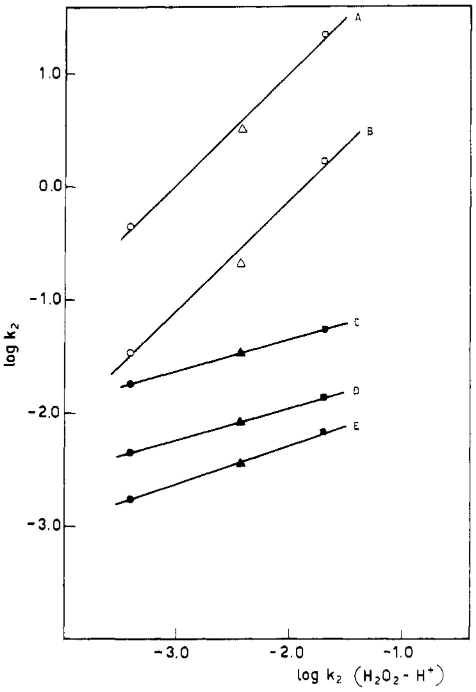

Figure 1. Logarithmic plots of rate constants for the oxidation of (○) Ph_2S, (△) PhSMe, (□) n-Bu_2S with (A) $MoO_2(acac)_2$–H_2O_2 (acid) in EtOH at 40 °C and (B) $MoO_2(acac)_2$–H_2O_2 (alkaline) in EtOH at 40 °C and of the corresponding sulfoxides (●) Ph_2SO, (▲) PhS(O)Me, (■) n-Bu_2SO with (C) $MoO_2(acac)_2$–H_2O_2 (acid) in EtOH at 40 °C, (D) $MoO_2(acac)_2$–H_2O_2 (alkaline) in EtOH at 40 °C, and (E) MCPBA (acid) in EtOH–dioxane (70:30) at −20 °C vs rate constants for the $HClO_4$-catalyzed oxidation of the same substrates with H_2O_2.[9]

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[8] (a) Jacobson, S. E.; Mucigrosso, D. A.; Mares, F. *J. Org. Chem.* **1979**, *44*, 921. (b) Trost, B. M.; Masuyama, Y. *Tetrahedron Lett.* **1984**, *25*, 173. (c) Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1986**, *51*, 2661. (d) Bortolini, O.; Bragante, L.; Di Furia, F.; Modena, G.; Cardellini, L. *Chim. Oggi* **1986**, 69.

[9] Modena, G.; Maioli, L. *Gazz. Chim. Ital.* **1957**, *87*, 1306.

process occurs via a nucleophilic mechanism, most likely a two-step process where the overall rate constant may result from the balance of the equilibrium constant of the formation of the intermediate and the rate constant of its cleavage to products, the electronic features of the substrates playing an opposite role.

Conclusions

It appears that the only nucleophilic oxidation observed in this study is the oxidation of sulfoxides with *m*-chloroperbenzoate anion. Therefore, even the Mo(VI)-peroxo anions formed in basic media oxidize the model sulfoxides via an electrophilic oxygen transfer, though less efficiently than the corresponding neutral species. This behavior has been previously observed in similar systems.[4] In the light of these results it appears rather unlikely that the structure of the peroxomolybdenum anion could be similar to that of *m*-chloroperbenzoate anion, i.e., involving the Mo–O–O^- moiety, as a result of the opening of the peroxo bridge. A possible alternative is the formation of an oxo anion where the negative charge on the oxo oxygen or on the peroxometal complex as a whole reduces, but not eliminates, the electrophilic character of the peroxo oxygens.

Experimental Section

Materials. Di-*n*-butyl sulfoxide, phenyl methyl sulfoxide, and diphenyl sulfoxide and the corresponding sulfones were prepared by oxidation of the commercially available sulfides with hydrogen peroxide in the presence of catalytic amounts of $MoO_2(acac)_2$ in ethanol, by using 1 or 2 equiv, respectively, of H_2O_2. The products were purified by column chromatography. Commercial bis(acetylacetonato)dioxomolybdenum(VI), $MoO_2(acac)_2$, was purified by crystallization from acetone–acetylacetone (1:4).

Sodium ethoxide was prepared by dissolving metallic sodium in ethanol and standardized by acid–base titration.

m-Chloroperbenzoic acid (MCPBA) free of *m*-chlorobenzoic acid was obtained from the commercially available material according to the following procedure: 50 g of the product was dissolved in benzene (1 L) and washed with an aqueous solution buffered at pH 7.4 (NaH_2PO_3–NaOH) (5 × 100 mL). The organic layer was dried over $MgSO_4$ and carefully evaporated, under vacuum. The remaining solid was then purified by two subsequent cyrstallizations (CH_2Cl_2, Et_2O): active oxygen, 98% (iodometric titer).

Anhydrous ethanol was obtained by standard procedures from highly pure commercial samples.

All other chemicals were used as received.

Procedures. The stoichiometry of the oxidation was determined by mixing a solution of H_2O_2 (0.55 mmol) in EtOH–0.5 M H_2O with a solution of the PhS(O)CH_3 (1.1 mmol) and the catalyst (0.028 mmol) in the same solvent (final volume 55 mL) in the presence of CH_3SO_3H (5.5×10^{-3} mmol) or EtONa (5.5×10^{-2} mmol). After completion of the reaction (absence of iodometric titer) an appropriate internal standard was added and the reaction mixture analyzed by GLC on a FFAP 3% (2.5 m) on Chromosorb WAW DMCS using a Varian 3700 equipped with a Varian CDS 401 integrator: $PhSO_2CH_3$, 0.54 mmol (98% yield) acidic conditions, 0.45 mmol (82% yield) alkaline conditions.

All kinetic runs were carried out in a thermostatic bath with temperature control to better than ±0.05 °C. Aliquots of the reaction mixture were withdrawn at various times and analyzed for H_2O_2 content by iodometry, as reported in previous papers of this series.

Caution. Care should be exercized in handling peroxides, particularly in the purification of commercial MCPBA.[10]

Registry No. MCPBA, 937-14-4; *n*-Bu_2SO, 2168-93-6; PhS(O)CH_3, 1193-82-4; Ph_2SO, 945-51-7; *n*-Bu_2S, 544-40-1; $PhSCH_3$, 100-68-5; Ph_2S, 139-66-2; H_2O_2, 7722-84-1; MoO_2 $(acac)_2$, 17524-05-9.

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(10) *Organic Peroxides*; Swern, D., Ed.; Wiley-Interscience: New York, 1971; Vol. 2, Chapter 6.

Search for Ethynylogues of Allenylidene. Zwitterionic Nature of Dimethylpentatetraenylidene[1]

Sanjay Basak, Sushil Srivastava, and W. J. le Noble*

Department of Chemistry, State University of New York, Stony Brook, New York 11794

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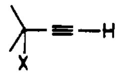
5-Chloro-5-methylhexa-1,3-diyne (**7**-Cl) reacts with alkoxide bases to give transient dimethylpentatetraenylidene (**8**). In methanol, this reaction is strongly accelerated by pressure, permitting the conclusion that this intermediate has a much larger dipole moment than the corresponding allenylidene **2**. The products are the unrearranged methyl ether **7**-OMe and the rearranged chloroallene **9**; the latter compound is the result of return, presumably internal. This return is also manifested by a sharp break in the rate plot of chloride ion formation. In *tert*-butyl alcohol–tetramethylethylene, **8** is trapped to give an adduct that dimerizes to **14**, or possibly **15**; oxygen sensitivity of this material prevented its complete characterization. The adamantane analogue **16**-Cl permitted the isolation of monomeric trapping product **17**. Attempts at extension to the next higher ethynylogue were not successful.

Introduction

The work reported herein was inspired by our observation[2] that the well-known[3-5] generation of allenylidenes from propargyl halides and base responds to the application of hydrostatic pressure in an unusual way; whereas haloform solvolyses are strongly retarded in their formation of dihalocarbenes under these conditions,[6] the reaction of 3-chloro-3-methylbut-1-yne (1-Cl) is essentially unaffected.



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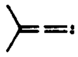
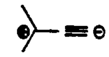


2a



2b

The volume expansion characterizing these reactions evidently does not occur in this case, although dimethyl-

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(1) (a) Preliminary communication: le Noble, W. J.; Basak, S.; Srivastava, S. *J. Am. Chem. Soc.* **1981**, *103*, 4638. (b) Full details may be found in: Basak, S. Ph.D. Thesis, SUNY at Stony Brook, NY, 1984.

(2) le Noble, W. J. *J. Am. Chem. Soc.* **1965**, *87*, 2434.

(3) Hennion, G. F.; Nelson, K. W. *J. Am. Chem. Soc.* **1957**, *79*, 2142.

(4) Hartzler, H. D. *J. Am. Chem. Soc.* **1961**, *83*, 4990, 4997.

(5) Shiner, V. J.; Wilson, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 2402.

(6) le Noble, W. J.; Duffy, M. *J. Am. Chem. Soc.* **1964**, *86*, 4512.

0022-3263/87/1952-5095$01.50/0