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Metal Catalysis in Oxidation by Peroxides. 30.[1] Electrophilic Oxygen Transfer from Anionic, Coordinatively Saturated Molybdenum Peroxo Complexes

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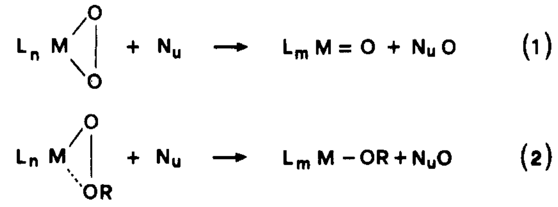
Two anionic and coordinatively saturated oxodiperoxomolybdenum complexes, $[MoO(O_2)_2L]^-Bu_4N^+$ (L = $C_5H_4NCO_2^-$ or $C_5H_4N(O)CO_2^-$), have been used as oxidants for a series of organic sulfides and sulfoxides in DCE. Quantitative yields of sulfoxides and sulfones, respectively, have been obtained. Spectroscopic (^1H and ^{13}C NMR) and kinetic evidence rule out any coordination process between the substrate and the oxidant requiring the formation of an unsaturated site on the metal. The data collected point to an oxidation mechanism involving a bimolecular reaction. This, at least for sulfide oxidations, appears to proceed through an electrophilic oxygen transfer from the peroxo complex to the substrate.

The mechanism of oxygen transfer from peroxometal complexes to nucleophilic substrates, Scheme I, is still a matter of controversy.[2] Basically, two alternatives have been proposed. According to some authors,[2b,g,h] the reactions of eq 1 and 2 proceed through a simple, bimolecular mechanism similar to that established for the oxidations by hydrogen peroxide or by organic peracids.[3] Others[2a,k,p] favor a mechanism that involves formation of an intermediate resulting from the coordination of the substrate to the metal. An explicit corollary of the latter mechanism is that there must be a free coordination site on the metal center or a labile ligand.[2m]

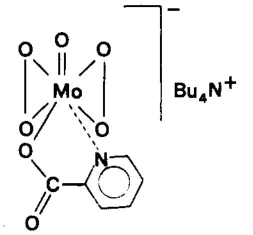
Recently we became involved in the chemistry of anionic peroxomolybdenum complexes.[4] Among these, complexes 1 and 2, containing the picolinato and the picolinate *N*-oxido ligands respectively, revealed particularly interesting properties. Owing to the presence of the lipophilic cation Bu_4N^+, both 1 and 2 are fairly soluble in nonpolar solvents, such as dichloroethane (DCE), where they very selectively oxidize primary and secondary alcohols[4] to aldehydes and ketones, respectively. In the course of our investigation on the chemistry of 1 and 2 we observed that they regiospecifically epoxidize geraniol at the 2,3-double bond and also oxidize organic sulfides to sulfoxides though less efficiently than neutral molybdenum peroxo complexes.[4,5]

Scheme I



M = Ti(IV), V(V), Mo(VI), W(VI);

Nu = phosphines, organic sulfides, alkenes, etc



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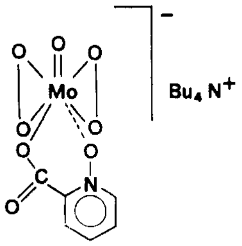

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In the light of the mechanistic controversy mentioned above, we have studied in some detail the sulfide oxidations by 1 and 2. In fact, such a process formally amounts to an oxygen transfer reaction from anionic and coordinatively saturated peroxo complexes. Here we present and discuss evidence strongly suggesting that coordination of the sulfides to molybdenum does not occur. For comparison purposes we have also studied the oxidation of sulfoxides to sulfones by 1 and 2. Such a reaction, owing to the peculiar character of sulfoxides which may be oxidized either by electrophilic or nucleophilic reagents, is in some instances a useful mechanistic probe.[2a,6] The evi-

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Table I. Second-Order Rate Constant[a] Data for Oxidation of PhSMe by Complex 1 in Dichloroethane

[PhSMe], M	[1], M	*t*, °C	10^3k_2, M^{-1} s^{-1}
0.2	0.01	40	2.9
0.4	0.01	40	3.1
0.8	0.01	40	3.0
0.8	0.02	40	2.7
0.8	0.04	40	2.6
0.2	0.01	30	1.4
0.2	0.01	50	5.3
0.2	0.01	60	10.8

[a] Calculated as $k_1/[\text{substrate}]_0$; k_1 obtained as slope of plots of ln ($[\text{product}]_\infty - [\text{product}]_t$) vs time, linear for at least 2 half-lives; the estimated error in k_2 is ±3%.

Table II. Second-Order Rate Constant[a] Data for Oxidation of Various Sulfides by Complex 2[b] in Dichloroethane

compound (M)	*t*, °C	10^3k_2, M^{-1} s^{-1}
PhSMe (0.2)	40	2.5
PhSMe (0.4)	40	2.4
PhSMe (0.8)	40	2.4
PhSMe (0.2)	30	1.2
PhSMe (0.2)	50	5.5
PhSMe (0.2)	60	9.5
PhSMe (0.4)	40	2.4[c]
PhSMe (0.4)	60	9.3[d]
p-$CH_3C_6H_4SMe$ (0.4)	40	3.3
p-ClC_6H_4SMe (0.4)	40	1.8
m-ClC_6H_4SMe (0.4)	40	1.5
p-$NO_2C_6H_4SMe$ (0.4)	40	0.76
n-BuS-*n*-Bu (0.4)	40	11.8
PhSPh (0.4)	40	0.26

[a] See note *a*, Table I. [b] $[2]_0$ = 0.01 M. [c] In the presence of HMPT, 0.2 M. [d] In the presence of AIBN, 5×10^{-3} M.

Table III. Second-Order Rate Constant[a] Data for Oxidation of Various Sulfoxides by Complexes 1 or 2[b] in Dichloroethane

compound (M)	oxidant	*t*, °C	10^3k_2, M^{-1} s^{-1}
PhS(O)Me (0.2)	1	40	0.76
PhS(O)Me (0.4)	1	40	0.78
PhS(O)Me (0.8)	1	40	0.78
PhS(O)Me (0.2)	1	50	1.5
PhS(O)Me (0.2)	1	60	2.8
PhS(O)Me (0.2)	2	40	0.74
PhS(O)Me (0.4)	2	40	0.75
PhS(O)Me (0.4)	2	40	0.74
PhS(O)Me (0.8)	2	50	1.6
PhS(O)Me (0.2)	2	60	3.5
PhS(O)Me (0.2)	2	40	0.68[c]
p-$CH_3C_6H_4S(O)Me$ (0.2)	2	40	0.80
p-$ClC_6H_4S(O)Me$ (0.2)	2	40	0.90
m-$ClC_6H_4S(O)Me$ (0.2)	2	40	0.83
p-$NO_2C_6H_4S(O)Me$ (0.2)	2	40	0.83
n-BuS(O)-*n*-Bu (0.4)	2	40	1.1
PhS(O)Ph (0.4)	2	40	0.22

[a] See note *a*, Table I. [b] $[1]_0 = [2]_0$ = 0.01 M. [c] In the presence of HMPT, 0.2 M.

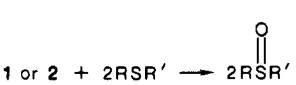
dence collected for sulfoxides is also against any coordination to the metal. Some of this work has appeared in a preliminary form.[5]

Results

Nature of the Oxidants in Solution. The preparation and characterization of complexes 1 and 2, including the determination of their molecular geometry by X-ray diffraction, have been described elsewhere.[4,7] In summary, in the solid state a slightly distorted pentagonal bipyramid arrangement is observed where the four peroxo oxygens and the carboxylato oxygen lay in the equatorial plane and the oxo oxygen occupies one of the two apical positions. The last coordination site, i.e. the second apical position, is occupied by the pyridine nitrogen in 1 and by the *N*-oxido oxygen in 2.

In DCE, solvolytic processes involving the ligands are hardly conceivable. Therefore, in such a noncoordinating solvent, the coordination sphere of 1 and 2 determined in the solid state should be maintained. Indeed, based on conductometric measurements, it has been reported that, even in methanol, dissociation of the picolinato ligand of 1 does not take place.[7] Nevertheless, we have looked for some evidence on the occurrence of ligand dissociation in DCE solutions of 1 and 2. This has been made by ^1H and ^{13}C NMR spectroscopy by comparing the resonances of the peroxo complexes with those of the ligands, dissolved either as tetrabutylammonium salts or as acids. The variations observed upon complexation (see the Experimental Section), largely beyond the experimental errors, allow us to rule out the occurrence of free ligand in solutions of 1 and 2.

Kinetics. All the sulfides investigated are oxidized by 1 and 2 to the corresponding sulfoxides in quantitative yield according to the stoichiometry:



$$1 \text{ or } 2 + 2RSR' \longrightarrow 2R\overset{O}{\overset{\|}{S}}R'$$

Thus, both peroxo groups of 1 and 2 are active in the oxidation of sulfides as previously observed for neutral species.[2a]

This has no consequences as far as the kinetics are concerned, likely because a fast disproportionation of the monoperoxo species resulting from the transfer of the first peroxo oxygen occurs, as discussed in previous papers of this series.

Kinetic measurements were carried out under pseudo-first-order conditions (excess of the substrate over the oxidant) by monitoring the appearance of the sulfoxide by GC. The rate law was determined by using $PhSCH_3$ as model substrate. The oxidation was found to be first-order in sulfide and first-order in oxidant. Pseudo-first-order plots of ln ($[\text{sulfoxide}]_\infty - [\text{sulfoxide}]_t$) vs time are linear over 2 or more half-lives. The second-order rate constants of the oxidation of $PhSCH_3$ and other representative sulfides by 1 and 2 are presented in Tables I and II. The temperature dependence of the oxidation of $PhSCH_3$ was measured. By using the data of Tables I and II, linear Arrhenius plots, in the temperature interval 30–60 °C, were obtained (r = 0.999 for 1 and r = 0.998 for 2), which provided the activation parameters ($\Delta H^{\ddagger}$ = 53 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −125 J K^{-1} mol^{-1} for 1 and $\Delta H^{\ddagger}$ = 56 kJ mol^{-1}, $\Delta S^{\ddagger}$ = −116 J K^{-1} mol^{-1} for 2). The effect of some additives on the rates was also briefly examined (Table I). Addition of AIBN, a radical initiator, or of HMPT, a well-known inhibitor of oxidations by neutral molybdenum peroxo complexes,[2a] has almost no effect on oxidation rates. Rates are also unaffected either by the presence or the absence of dioxygen.

A parallel investigation on the oxidation of sulfoxides to sulfones was carried out. Also in this transformation, quantitative yields of the products are obtained. An overall second-order rate law, first-order in substrate and first-order in oxidant is obeyed. The second-order rate constants of the oxidation of $PhS(O)CH_3$ and of a series of sulfoxides are collected in Table III. Linear (r = 0.999 for 1 and 2) Arrhenius plots are obtained for $PhS(O)CH_3$ oxidation in the temperature range 40–60 °C. The measured activation parameters are $\Delta H^{\ddagger}$ = 53 kJ mol^{-1}, $\Delta S^{\ddagger}$

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[7] Jacobson, S. E.; Tang, R.; Mares, F. *Inorg. Chem.* **1978**, *17*, 3055.

Table IV. Second-Order Rate Constant Data[a] for Oxidation of Ph-S-Me and Ph-S(O)-Me by Complex 2[b] in Various Solvents, at 40 °C

compound	solvent	10^3k_2, M^{-1} s^{-1}
PhSMe	$CHCl_3$	7.1
PhSMe	$PhNO_2$	2.6
PhSMe	DCE	2.4
PhSMe	CH_3CN	1.8
PhSMe	DMF	1.1
PhS(O)Me	$CHCl_3$	0.81
PhS(O)Me	$PhNO_2$	0.76
PhS(O)Me	DCE	0.74
PhS(O)Me	CH_3CN	0.50
PhS(O)Me	DMF	0.20

[a] See note *a*, Table I. [b] $[\text{Substrate}]_0 = 0.4$ M, $[2]_0 = 0.01$ M.

$= -137$ J K^{-1} mol^{-1} for 1 and $\Delta H^{\ddagger} = 65$ kJ mol^{-1}, $\Delta S^{\ddagger} = -96$ J K^{-1} mol^{-1} for 2. Also in sulfoxide oxidations added HMPT (Table III) has very little effect on the rate constants.

The solvent dependence of sulfide and sulfoxide oxidation rates has been examined by obtaining the second-order rate constants of the oxidation of $PhSCH_3$ and $PhS(O)CH_3$ by 2 in five solvents ranging from nonpolar to dipolar aprotic ones. The results of this study are collected in Table IV. Control experiments, carried out by ^1H and ^{13}C NMR spectroscopy, have confirmed that in all the solvents employed, dissociation of the ligands does not occur. Although the variations of the rates with the nature of the solvent are relatively modest (a 7-fold increase in passing from DMF to $CHCl_3$ for $PhSCH_3$ and a 4-fold increase for $PhS(O)CH_3$), the trend appears to be that in basic solvents the rates of oxidation are depressed in comparison with those observed in more acidic media.

Discussion

In interpreting the results presented in the preceding section, we focus our attention on the finding that 1 and 2 display a very similar oxidizing ability toward both sulfides and sulfoxides. As an example, 2 is only ca. 20% more reactive than 1 in the oxidation of $PhSCH_3$ whereas in the oxidation of $PhS(O)CH_3$ the second-order rate constants for 1 and 2 are identical within the experimental error. Therefore, in such oxygen transfer reactions, the nature of the coordination sphere of the molybdenum peroxo complexes plays a very modest role. By contrast, it has been observed that in the oxidation of alcohols, in DCE, 2 is at least 30-fold more reactive than 1.[5] Evidence suggesting that alcohol oxidations proceed through coordination of the substrate to the metal has been provided.[5] Therefore, it seems reasonable to conclude that the absence of ligand effects on oxidation rates is good evidence for a process not involving association of the substrate to the metal, particularly in systems, like the ones under consideration, where such a coordination should necessarily occur via substitution at an occupied coordination site.[2k,m]

In agreement with this conclusion, we observed that added HMPT has no effect on oxidation rates. Thus, even a very good ligand for molybdenum(VI),[8] possibly more nucleophilic than the organic sulfides and sulfoxides examined here, is not able to displace the bidentate picolinato and picolinate *N*-oxido ligands.

The other kinetic results are also in accord with the absence of substrate coordination. In the fairly large concentration intervals examined and for all the substrates, a first-order dependence of oxidation rates is observed. Some deviation from first-order toward saturation kinetics should be expected, under our experimental conditions, i.e. excess of substrate over the peroxo complex, if an association between the nucleophile and the metal were operative. Furthermore, the activation parameters determined and in particular the large and negative entropy of activation, though determined in a limited temperature interval, are those expected for a bimolecular process.

Again, the comparison with the oxidation of alcohols by 1 or 2 gives useful information. In alcohol oxidations, still negative but very small, 12–16 J K^{-1} mol^{-1}, entropies of activation have been measured,[5] in line with the formation of an intermediate preceding the transition state of the rate-limiting step.

Therefore, both sulfides and sulfoxides are oxidized by 1 or 2 in a bimolecular reaction, which presumably involves an attack of the substrate on the peroxidic oxygen. Although the occurrence of a radical mechanism, possibly triggered by an electron transfer from the sulfide to the peroxo complex, cannot be ruled out on the basis of the data available, it appears, however, rather unlikely that we are dealing with *free* radicals in solution. In fact, the radical initiator AIBN, at 60 °C, under conditions that allow the formation of radical species, does not affect the rates of sulfide oxidation. Moreover, by changing the solvent from DCE to $PhNO_2$, almost no effect on the oxidation of both $PhSCH_3$ and $PhS(O)CH_3$ is observed. $PhNO_2$, particulary when used as solvent, may act as an effective radical trap. Therefore, at least for sulfide oxidations, the more reasonable mechanism is the one involving a nucleophilic attack of the substrate to the peroxidic oxygen of 1 or 2. The anionic nature of the peroxo complexes accounts for their reduced ability as electrophilic oxidants, as compared with neutral peroxo species. In fact 1 and 2 may be estimated to be ca. 1000-fold less reactive than MoO_5HMPT under similar conditions.[9] As an example, the second-order rate constant of the oxidation of $PhSCH_3$ by MoO_5HMPT in DCE at −15 °C is 4.4×10^{-2} M^{-1} s^{-1}.[9]

On the other hand, a recent ^{17}O NMR spectroscopic investigation of a series of molybdenum peroxo complexes,[1] either neutral or anionic, has provided evidence that in complexes 1 and 2 the negative charge is located mainly on the ligand, which rules out the occurrence of structures such as $MoOO^-$ or MoO^-. The solvent dependence of oxidation rates is in accord with the electrophilic nature of the oxidant, which is increased when the net negative charge of the peroxo complexes is reduced by specific solvation. As observed in previous investigations,[10] specific solvation involving the substrates should also operate. In particular, the data concerning $CHCl_3$ may be interpreted on the basis of a specific interaction with the SO group. In sulfide oxidation such an effect manifests itself as a stabilization of the transition state, which contributes to the rate acceleration, whereas in sulfoxide oxidation the retarding effect due to ground-state stabilization competes with the acceleration caused by solvation of the oxidant.

The effect of the structure of the sulfides on oxidation rates confirms that the substrates are the nucleophilic partners of the oxidation process. The rates increase with increasing nucleophilicity of the substrates, i.e. *n*-BuS-*n*-Bu > PhSMe > PhSPh. Indeed, as shown in Figure 1, the second-order rate constants of the oxidation of the three sulfides by 2 plotted, in a log–log plot, against those of the oxidation of the same substrates by H_2O_2 under mineral

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(9) Tomaselli, G. A., personal communication.

(10) Modena, G.; Todesco, P. E. *Boll. Sci. Fac. Chim. Ind. Bologna* **1965**, *23*, 31; *Chem. Abstr.* **1965**, *63*, 8168*e*.

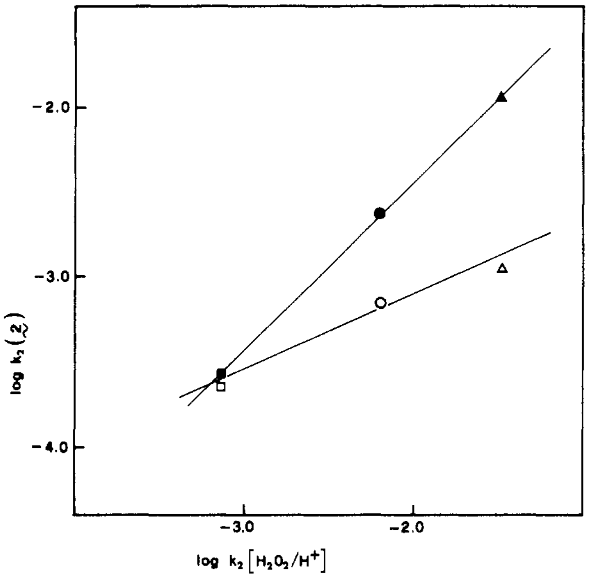

Figure 1. Logarithmic plots of rate constants for the oxidation of (■) PhSPh, (●) PhSMe, (▲) *n*-BuS-*n*-Bu by complex **2** in DCE at 40 °C and of the corresponding sulfoxides (□) PhS(O)Ph, (○) PhS(O)Me, (△) *n*-BuS(O)-*n*-Bu with complex **2** in DCE at 40 °C vs rate constants for the $HClO_4$-catalyzed oxidation of the same substrates with H_2O_2.[11]

acid catalysis,[11] a most typical electrophilic oxidant, gives a straight line ($r = 0.999$) whose slope is almost one (0.99).

This is taken as evidence that the transition states of the oxidations by H_2O_2 and by **2** have strictly similar requirements, both likely involving a nucleophilic displacement on the peroxide oxygen.[3] Furthermore, within the series of arylalkyl sulfides a Hammett σ -0.49 is derived as expected for the sulfides acting as nucleophiles.

The overall picture, as far as sulfoxides are concerned, is less conclusive. Within the frame of a mechanism not involving coordination to the metal and, likely, heterolytic in nature, somehow conflicting evidence on the nature of the oxygen transfer, either electrophilic, as in sulfide oxidations, or nucleophilic, is obtained. The activation parameters and the reactivity order *n*-BuS(O)-*n*-Bu > PhS(O)Me > PhS(O)Ph would support an electrophilic oxygen transfer. However, as shown in Figure 1, a poorer ($r = 0.983$, slope 0.42) correlation with the oxidation of sulfides by hydrogen peroxide is observed. Much more interesting is the finding that, within the series of arylalkyl sulfoxides, the rates are almost unaffected by the nature of the substituent in the aromatic ring in passing from *p*-CH_3 to *p*-NO_2. Control experiments have shown that an identical behavior is observed at higher temperature (*t* 60 °C), thus making it unlikely that we are near the isokinetic temperature. As an additional observation, it may be noticed that the reactivity ratio sulfide–sulfoxide, under identical experimental conditions, is considerably lower than that usually observed with classical electrophilic reagents such as organic peracids in their undissociated form. As a general rule, sulfoxides are less reactive than sulfides toward electrophilic oxidants, whereas the opposite is true with nucleophilic oxidants.[2e,3] As an example, the *m*-chloroperbenzoato anion does not oxidize organic sulfides under experimental conditions, which allow a very fast oxidation of sulfoxides.[2q] As a conclusion, it appears that more experimental evidence is required before a detailed mechanism of sulfoxide oxidations by **1** or **2** may be proposed.

Conclusions

It has been shown that coordination of a nucleophilic substrate to the metal center of a peroxometal complex is not a necessary requisite for the occurrence of an oxygen-transfer reaction.

The data discussed here refer to the specific reaction of anionic molybdenum peroxo complexes with organic sulfides and sulfoxides. Therefore, care should be exercised in drawing general mechanistic conclusions. Nevertheless, we believe that our study has presented a clearcut evidence for the availability of an oxidative pathway involving an "external" nucleophilic attack of substrates to the peroxide oxygen of peroxometal complexes.

Experimental Section

Materials. 4-Chloro-, 3-chloro-, 4-methyl-, and 4-nitrophenyl methyl sulfides were prepared by literature methods. The other sulfides were commercially available products. Sulfoxides and sulfones were prepared by oxidation of the corresponding sulfides with hydrogen peroxide in the presence of catalytic amounts of $MoO_2(acac)_2$ in ethanol, with 1 or 2 equiv, respectively, of H_2O_2. All the sulfides, sulfoxides, and sulfones were purified by column chromatography and identified by their spectroscopic and MS properties.

The solvents used were purified by standard procedures. All other chemicals were commercially available and used as received.

The synthesis and the characterization of complexes **1** and **2** have been reported elsewhere.[4]

Spectroscopic Experiments. ^1H (in $CDCl_3$) and ^{13}C NMR (in DCE) spectra of complexes **1** and **2**, together with those of picolinic acid and picolinic acid *N*-oxido and of their corresponding tetrabutylammonium salts, were recorded on a Bruker WP-200-SY spectrometer. All the ^1H and ^{13}C NMR chemical shifts (ppm, TMS internal reference) vary in passing from the acids to the salts and to the complexes. As an example, the resonances of the protons in position 6 of the picolinic acid ring are found at 8.82 (d) ppm in the acid, at 8.54 (dm) ppm in the salt, and at 8.14 (d) ppm in complex **1**. For picolinic acid *N*-oxido, the sequence is 8.39 (dm), 7.89 (d) and 7.92 (d) ppm. The carboxylic carbon of picolinic acid is shifted from 160.9 ppm in the free acid to 170 ppm in the salt and 169 ppm in complex **1**, whereas for picolinic acid *N*-oxido the corresponding values are 160.9, 165.3, and 162.9 ppm, respectively.

Procedures. In a typical run, 1 mL of DCE containing 2.4 mmol of substrate was added to a DCE solution (5 mL) containing 0.06 mmol of complex and an internal GC standard, in a glass reactor maintained at the appropriate temperature.

Aliquots of the reaction mixture were withdrawn at various time intervals, the residual active oxygen was quenched with $(Ph)_3P$ in excess, and the products were determined by GLC on FFAP 3% on Chromosorb W AW DMCS column (2.5 m). In all cases, the final yields calculated after complete consumption of the oxidant, were ≥90%. The response factor of each product versus the internal standard used was separately calculated.

All kinetic runs were carried out in a thermostatic bath with temperature control better than ±0.05 °C.

Registry No. **1**, 105177-38-6; **2**, 105194-63-6; PhSMe, 100-68-5; *p*-$CH_3C_6H_4SMe$, 623-13-2; *p*-ClC_6H_4SMe, 123-09-1; *m*-ClC_6H_4SMe, 4867-37-2; *p*-$NO_2C_6H_4SMe$, 701-57-5; *n*-BuS-*n*-Bu, 544-40-1; PhSPh, 139-66-2; PhS(O)Me, 1193-82-4; *p*-$CH_3C_6H_4S(O)Me$, 934-72-5; *p*-$ClC_6H_4S(O)Me$, 934-73-6; *m*-$ClC_6H_4S(O)Me$, 13150-73-7; *p*-$NO_2C_6H_4S(O)Me$, 940-12-5; *n*-BuS(O)-*n*-Bu, 2168-93-6; PhS(O)Ph, 945-51-7.

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(11) Modena, G.; Maioli, L. *Gazz. Chim. Ital.* **1957**, *87*, 1306.