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The Relative Reactivity of Thioethers and Sulfoxides toward Oxygen Transfer Reagents: The Oxidation of Thianthrene 5-Oxide and Related Compounds by MoO_5HMPT

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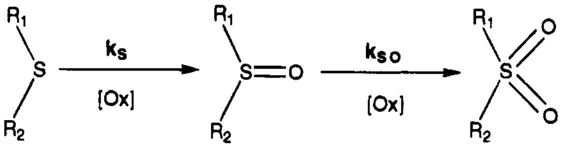
The oxidation of thianthrene 5-oxide (**SSO**) by MoO_5HMPT has been studied in 1,2-dichloroethane at 40 °C. Under conditions of excess substrate over the oxidant, three products are formed, i.e., two isomeric *cis* and *trans* bissulfoxides (**SOSO**) and sulfide−sulfone (**SSO_2**) which quantitatively account for the active oxygen of MoO_5HMPT consumed. The rates of appearance of the products at different reactant concentrations have been measured. A second-order rate law has been established. The ratios of the rate constants and of the final concentrations of the three products, i.e., k_2(*cis*-**SOSO**):k_2(*trans*-**SOSO**):k_2(**SSO_2**) = 1.0:4.0:1.0; $[cis\text{-}\mathbf{SOSO}]_\infty:[trans\text{-}\mathbf{SOSO}]_\infty:[\mathbf{SSO_2}]_\infty$ = 1.0:4.5:1.2, are in good agreement. The *trans*-**SOSO**-forming reaction is only 4-fold faster than that leading to **SSO_2**. *cis*-**SOSO** and **SSO_2** are produced at almost the same rate. Evidence is presented that all the oxidation reactions are electrophilic processes taking place via a simple bimolecular mechanism not involving the coordination of the substrate to the metal. The low selectivity is due to the scarce reactivity of the thioether center in thianthrene 5-oxide. The investigation of the oxidative behavior of structurally related compounds reveals that such a low reactivity results from a combination of stereoelectronic effects. These findings provide a rationale to some ambiguous results obtained when thianthrene 5-oxide is employed as a mechanistic probe of the electronic character of the oxidants.

Introduction

The factors controlling the selectivity (k_S/k_{SO}) of the oxidation of thioethers and of sulfoxides are receiving renewed interest in connection with the use of such reactions as mechanistic probes of the electronic character of the oxidants,[1] based on the assumption that electrophilic oxidants preferentially oxidize thioethers while nucleophilic ones oxidize sulfoxides.[1c]

Recently we called for caution in using such probes particularly if they are aimed at providing quantitative information.[2] Thus, we showed that the formation of sulfone in experiments in which a thioether and a sulfoxide are pitted together to compete against each other for an oxidant does not necessarily imply that such an oxidant has some nucleophilic character[2] (see eq 1).



(1)

In fact, sulfone may result from the electrophilic oxidation of the sulfoxide, which is a biphilic substrate,[3] if strong and rather unselective oxidants are used. As an example, a k_S/k_{SO} value of 3 has been determined for the competitive oxidation of p-$Cl-C_6H_4-S-CH_3/C_6H_5-SO-CH_3$ in CH_3Cl at 0 °C by (trifluoromethyl)methyldioxirane which may be considered one of the most powerful electrophilic oxidants.[2,4]

Small selectivity values may also be observed if the competing substrates are not properly selected. This appears to be the case of the probe based on thianthrene 5-oxide (**SSO**) in which the two oxidizable competing centers are found within the same molecule.[1]

With the exception of $H_3O_2^+$, which gives almost exclusively **SOSO**,[5,6] all other electrophilic oxidants tested with **SSO**, together with **SOSO**, also provide **SSO_2** in variable amounts (eq 2). This feature might be taken as evidence of a biphilic character of the oxidants. Alternatively, we proposed[2] that the reactivity of the

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(6) In the case of $H_3O_2^+$ oxidation, the *cis* and *trans* **SOSO** isomers are obtained in different amounts depending on the reaction conditions.[5] As an example, no **SSO_2** is detected when $[H_3O_2^+]$ = [**SSO**].

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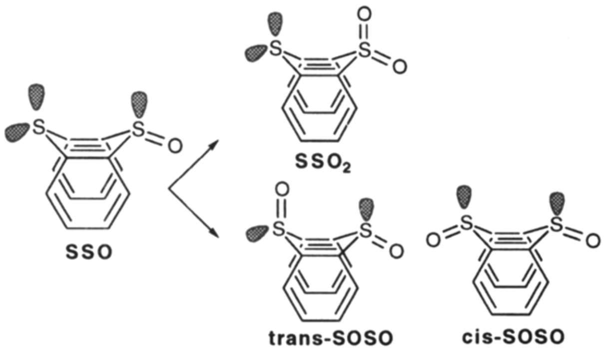

(2)

thioether sulfur in thianthrene 5-oxide is low, so that it is comparable with that of the sulfoxide sulfur. This accounts for the small selectivity observed.

A necessary corollary of such an alternative is that the reactivity of the sulfoxide sulfur toward electrophilic oxidants is less affected by the nature of the substituents than that of the thioether sulfur.[7] This is well documented. As an example, ϱ values of *ca* -1.0 are found for the oxidation of aromatic thioethers[3,8] while, under analogous reaction conditions, the ϱ values range in the interval $-0.6/-0.1$ for structurally similar sulfoxides.[3,8]

A small selectivity in the oxidation of thianthrene 5-oxide, simply due to comparable reactivity of the two oxidizable centers, should, in principle, be found for all the electrophilic oxidants, including transition metal peroxo complexes.[1b,e] However, for this class of oxidants, more complicated oxidation mechanisms[1b] involving the complexation of thianthrene 5-oxide to the metal have been suggested.[1e] Thus, we have investigated the oxidation of thianthrene 5-oxide and structurally related substrates by the oxo–diperoxomolybdenum complex MoO_5HMPT. The results presented in this paper rule out the occurrence of the complexation of molybdenum by thianthrene 5-oxide. They also provide more information on the behavior of this substrate in oxidative processes and, in particular, on its drawbacks as a mechanistic probe.

Results and Discussion

Figure 1 shows a typical oxidation of thianthrene 5-oxide by MoO_5HMPT, in 1,2-dichloroethane at 40 °C carried out by using a 10-fold excess of the substrate over the oxidant to avoid overoxidation of the products. At the end of the reaction the oxidized products, i.e., the two isomeric **SOSO** and **SO₂** quantitatively (>97%) account for the active oxygen consumed. The rates of formation of the three products have been measured. Such rates conform to a first-order rate law. In fact, plots of log([Prod]$_\infty$−[Prod]$_t$) vs time are linear up to 90%. The slopes of such plots directly provide the pseudo-first-order rate constants k_1. Table 1 collects k_1 values obtained under various experimental conditions. A kinetic order of one of the substrates has been experimentally determined for the *trans*-**SOSO**- and the **SSO₂**-forming reactions (entries 1–4 of Table 1). Thus the second-order rate constants k_2 are simply obtained as k_1/[substrate]. Only some selected data have been collected for the *cis*-**SOSO** forming reaction. In the entire range of substrate concentrations explored, (see Table 1) the ratios of the products, measured at 90% consumption of the active oxygen, correspond to the ratios of the second-order rate constants. As an example, under the experimental conditions of Figure 1, in which all three k_2 values are available, the following is found: [*cis*-**SOSO**]:[*trans*-**SOSO**]:[**SSO₂**] = 1.0:4.5:1.2; k_2(*cis*-**SOSO**):k_2(*trans*-**SOSO**):k_2(**SSO₂**) = 1.0:4.0:1.0.

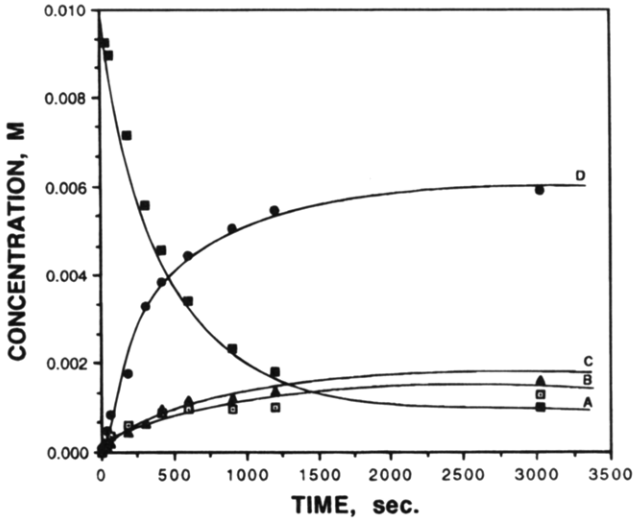

Figure 1. Oxidation of **SSO** (0.1 M) by MoO_5HMPT (0.005 M) in DCE at 40 °C, monitored by following: (A) the disappearence of the active oxygen and the formation of (B) *cis*-**SOSO**, (C) **SSO₂**, and (D) *trans*-**SOSO**.

These results suggest that three parallel and independent oxidation reactions are occurring. The selectivity k_S/k_{SO} is rather low. In fact it is *ca.* 4 if one takes into account the rates of formation of *trans*-**SOSO** and of **SSO₂** while it drops to *ca.* 1 if the rate of formation of *cis*-sulfoxide is considered.

Incidentally, it may be noted that examples of thioethers reacting with an oxidant at almost the same rate than that of the structurally similar sulfoxides are rather unprecedented.[2,7,9] The rate of formation of the *cis* isomer is slow in comparison with that of the *trans* isomer, likely because of steric factors.[10] This is confirmed by inspection of the plausible approaches of the oxidant in the two processes considering the simple hypothesis of an external attack (Figure 2).

In particular, it may be observed that the *peri*-aromatic hydrogens of the substrate hinder the attack which leads to the *cis*-sulfoxide, while their interference with the process forming the *trans* isomer is much less severe. However even in the absence of steric factors, the *trans*-**SOSO**-forming reaction is considerably slow compared with the **SSO₂**-forming one. This suggests that the reactivity of the thioether sulfur in thianthrene 5-oxide is smaller than that of simple thioethers. We shall return to this point later in this paper.

The general mechanistic scheme, suggested at this stage, is that the oxidation of the thioether and of the sulfoxide sulfur of thianthrene 5-oxide by MoO_5HMPT

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Table 1. Oxidation of Thianthrene 5-Oxide by MoO_5HMPT[a]

	SSO	HMPT	10^3k, s^{-1}			ratios of products[b]
no.	M	M	*cis*-**SOSO**	*trans*-**SOSO**	**SO_2**	*cis*-**SOSO**:*trans*-**SOSO**:**SSO_2**
1	0.05	0		0.52	0.13	[c]:3.9:1.0
2	0.10	0	0.23	0.93	0.22	1.0:4.5:1.3
3	0.20	0		1.74	0.40	[c]:4.3:1.0
4	0.40	0		3.56	0.85	[c]:3.8:1.0
5	0.10	0.030		0.78	0.20	[c]:3.6:1.0
6	0.10	0.060		0.51	0.11	[c]:4.6:1.0
7	0.10	0.10		0.41	0.09	[c]:4.0:1.0
8	0.10	0.20	0.05	0.26	0.06	1.0:5.4:1.2
9[d]	0.10	0	>3.0	>14.0	>2.0	2.0:6.8:1.0

[a] All reactions were carried out in dichloroethane at 40 °C. [b] Product distributions determined at 90% consumption of active oxygen. [c] Not determined. [d] Reaction carried out in the presence of methanesulfonic acid (0.01 M). The reaction is too fast to allow accurate determination of the k_1 values.

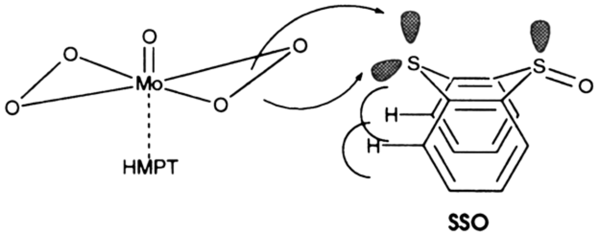


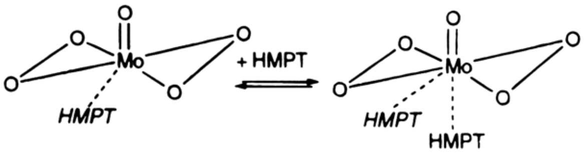
Figure 2. Plausible approaches of MoO_5HMPT to the thioether sulfur in **SSO**.

are both electrophilic reactions[8d,10a] which, from a kinetic point of view, are simple bimolecular processes.[8d,10a] The electrophilic character of the oxidation is demonstrated by the last entry of Table 1 which shows the accelerating effect of added acid on the rates of product formation.[11] Note, in particular, that the oxidation of the sulfoxide in the presence of acid is 10-fold faster than in its absence. The product distribution is modified by the presence of acid as the result of the fact that the rate enhancement is larger for the reaction producing *trans*-**SOSO** than for that forming **SSO_2**. The final yield and the rate of formation of *cis*-**SOSO** are also moderately enhanced.

The observation that an increase of the acidity of the medium favors the *trans*-**SOSO**-forming reaction over the other two oxidative processes is confirmed by the behavior of the rate constants measured in three different chlorinated solvents: [*cis*-**SOSO**]:[*trans*-**SOSO**]:[**SSO_2**] = 1.0:4.5:1.2 (DCE); 1.1:5.1:1.0 (CH_2Cl_2); 2.5:13:1.0 ($CHCl_3$). Thus the enhancement of the electrophilic character of the solvent[12] leads to larger production of *trans*-**SOSO** over **SSO_2**. The information provided by these data may be summarized as follows: (1) The oxidations of the thioether and of the sulfoxide centers in thianthrene 5-oxide are both acid-catalyzed processes as expected for electrophilic oxidative processes. (2) Thioether oxidation is more sensitive to acid catalysis than that of sulfoxide. Therefore one may expect better selectivities in acidic media.

Additional data have been collected in order to demonstrate that the oxidation mechanism is a simple bimolecular process not involving coordination of the substrate to the metal. It should be mentioned that such a coordination has been suggested by other authors.[1e] In particular, it has been proposed that thianthrene 5-oxide coordinates via the S group to molybdenum thus favoring a transannular oxygen transfer to the SO group.[1e] The kinetic order one of the substrates is already an indication that, if a substrate–oxidant association occurs, the equilibrium constant of such a process should be rather small. The data collected in Table 1 (entries 5–8) appear to rule out such a possibility. The oxidation of thianthrene 5-oxide has been carried out in the presence of HMPT, which competes with the substrate for the complexation to molybdenum without being oxidized.[13,14] Although the rates of oxidation do decrease by increasing the HMPT concentration, at large excesses of HMPT over the oxidant, they tend to a plateau. The rate decrease is rather modest. Furthermore, the reciprocal plots of Figure 3 reveal that at formally infinite HMPT concentration the selectivity is almost the same than that measured without added HMPT (entries 2 and 8 in Table 1).

In the framework of a bimolecular reaction, the inhibitory effect of added HMPT may be simply rationalized on the basis of the formation of $MoO_5(HMPT)_2$ which is a weaker electrophilic oxidant than the corresponding monocoordinated complex (eq 3).[14]



(3)

An attempt to obtain a direct evidence of this rationale has been made by preparing $MoO_5(HMPT)_2$, which can be isolated by crystallization from a solution of the monocoordinated complex in neat HMPT. However, ^1H-NMR analysis of a 0.005 M solution of such a complex in $CHCl_3$ reveals that the apical molecule of HMPT is immediately released (see Experimental Section). A similar experiment has been previously described, the only difference being that in solution, together with $MoO_5(HMPT)_2$, thianthrene 5-oxide was also present.[1e] In that case the observation of free HMPT was taken as evidence that the substrate had displaced the ligand. In the light of our result such evidence of substrate complexation is at least questionable.

In order to gain some more information on the origin of the low selectivity observed in the electrophilic oxidation of thianthrene 5-oxide and, in particular, of the weak reactivity of the thioether sulfur, the oxidative behavior of a series of related substrates was examined by measuring the rate constants of their oxidation by MoO_5-

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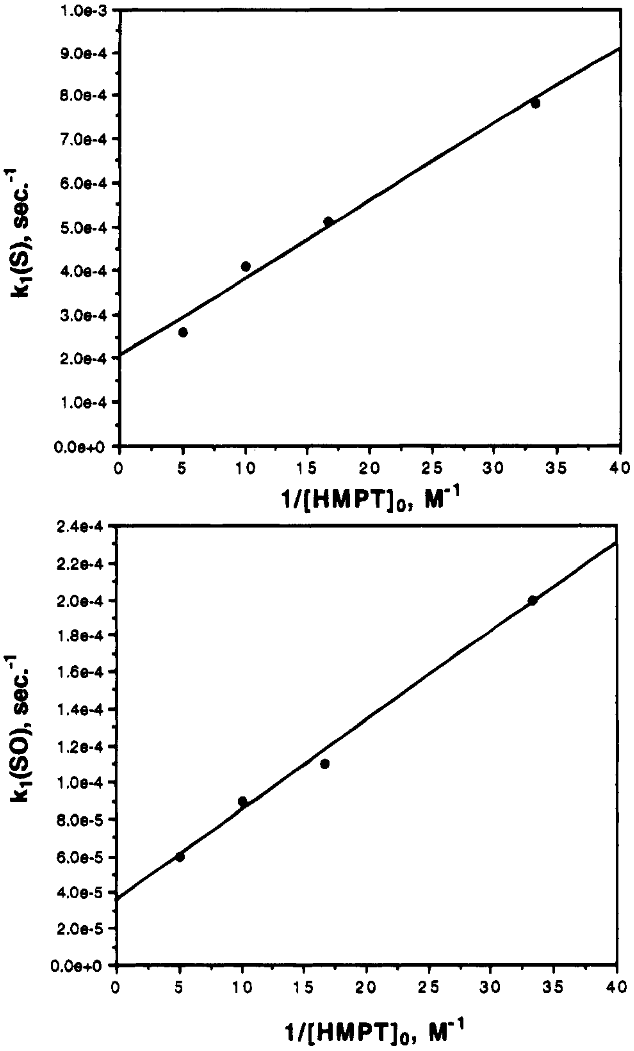


Figure 3. Plot of the first-order rate constants of the formation of *trans*-**SOSO** (k_1(S)) and of **SSO$_2$** (k_1(SO)) vs 1/[HMPT]$_0$ in the oxidation of **SSO** by MoO$_5$HMPT in the presence of added HMPT.

HMPT. These are shown in Tables 2 and 3. The data of Table 2 confirm the previous observations that the oxidation of the sulfoxide group is less sensitive to stereoelectronic effects than that of the thioether sulfur.[9] As an example, diphenylsulfide is ca. 800-fold more reactive than dibenzothiophene (entries 1 and 2 in Table 2) whereas the oxidation of diphenyl sulfoxide is only ca. 130 times faster than that of dibenzothiophene sulfoxide (entries 4 and 5 in Table 2). Accordingly, the selectivity k_S/k_{SO} for the substrates examined decreases rather sharply from ca. 30 for the diphenyl sulfide–diphenyl sulfoxide couple to ca. 4 for thianthrene 5-oxide (entries 3 and 6, Table 2).

An interesting feature revealed by the data of Table 2 is the remarkable decrease of the reactivity of both thioether and sulfoxide sulfur caused by their insertion into a cyclic structure. As a result, the oxidation of the thioether sulfur in thianthrene 5-oxide is indeed very slow compared with that of simple diaryl sulfides. Moreover, comparison of the rates of oxidation of dibenzothiophene and of thianthrene 5-oxide to the corresponding sulfoxides (entries 2 and 3 in Table 2) suggests that the lower reactivity of the latter might originate from additional effects. These are likely related to the presence of the sulfoxide group within the same molecule. The data of Table 3 support this hypothesis. In fact, by allowing for the statistical factor of 2 favoring thianthrene, it may be observed that its oxidation to the corresponding monosulfoxide is at least 8-fold faster than that of thianthrene 5-oxide to the bissulfoxide (entries 1 and 2 in Table 3).

The results of Table 3 establish the relevance of the "facing" group in determining the reactivity of the center that undergoes oxidation. While it seems rather clear that such a facing effect plays an important role, the data so far available provide contradictory information, thus suggesting the occurrence of complex interactions. In fact, taking the thioether facing group as reference, it may be seen that its substitution with a sulfoxide group strongly decreases the reactivity of the thioether sulfur (entries 1 and 2 in Table 3) while it slightly enhances the reactivity of the sulfoxide one (entries 4–6 in Table 3). By contrast the sulfone facing group decreases in both cases (entries 1–3 and 1–7 in Table 3) the reactivity of the center which is oxidized as it might have been expected on the basis of its electron-withdrawing ability.

Conclusions

The data presented in this paper allow some conclusions to be drawn. These may be summarized as fol-

Table 2. Oxidation of Aromatic Thioethers and Sulfoxides [0.1 M] by MoO$_5$HMPT [0.005 M] in DCE [20 mL] at 40 °C

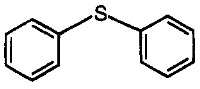
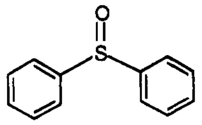
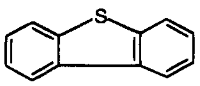
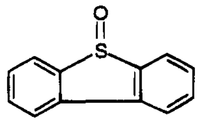
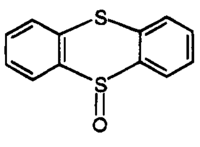
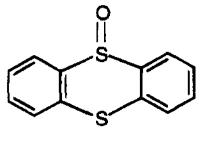
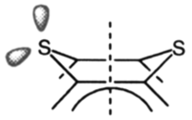
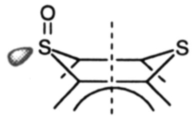
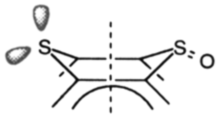
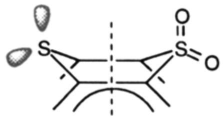
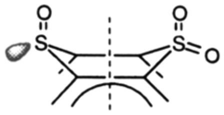
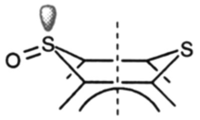
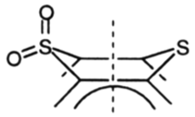
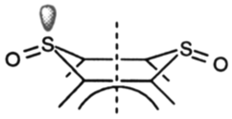
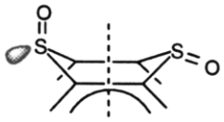
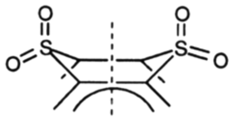
no.	thioethers	k(S), M^{-1} s^{-1}	no.	sulfoxides	k(SO), M^{-1} s^{-1}
1		**34**	4		**1.2**
2		**0.042**	5		**0.0089**
3		**0.0093**	6		**0.0022**

Table 3. Oxidation of the Thioether and Sulfoxide Functions in Thianthrene-like Molecules ([substrate] = 0.1 M) by MoO_5HMPT [0.005 M] in DCE (20 mL) at 40 °C. Effect of the "Facing" Group

no.	substrate	$10^3k\cdot M^{-1}\,s^{-1}$	product
1	 thianthrene	**150**	 thianthrene 5-oxide
2	 thianthrene 5-oxide	**9.3**	 *trans*-thianthrene 5,10-dioxide
3	 thianthrene 5,5-dioxide	**2.1**	 thianthrene 5,5,10-trioxide
4	 thianthrene 5-oxide	**2.2**	 thianthrene 5,5-dioxide
5	 *cis*-thianthrene 5,10-dioxide	**19.0**	 thianthrene 5,5,10-trioxide
6	 *trans*-thianthrene 5,10-dioxide	**3.4**	 thianthrene 5,5,10-trioxide
7	 thianthrene 5,5,10-trioxide	**0.23**	 thianthrene 5,5,10,10-tetraoxide

lows: (1) Thianthrene 5-oxide is oxidized by MoO_5HMPT to the bissulfoxides and to the sulfide-sulfone via parallel reactions. (2) Such reactions are simple bimolecular oxygen transfers from the oxidant to the substrate involving no complexation equilibrium between the two reactants. (3) Accordingly, the formation of **SSO_2** cannot be interpreted as an indication that MoO_5HMPT, in spite of its definite nature as an electrophilic oxidant, may display some nucleophilic character. **SSO_2** is formed because of the small difference of reactivity of the two centers in thianthrene 5-oxide toward electrophilic oxidants. (4) The similar reactivity of the two centers is due, in turn, to the very low reactivity of the thioether sulfur. (5) Thianthrene 5-oxide is rather peculiar since the reactivity of its thioether sulfur toward electrophiles is strongly reduced by a combination of effects. (6) Together with inductive effects, the cyclic structure and the "facing" group appear to play important roles.

It may be anticipated that the information provided by this investigation may help in developing a more reliable mechanistic probe capable of providing quantitative information on the electronic character of oxidants.

Experimental Section

Materials. 1,2-Dichloroethane (99%, Aldrich) was washed with concentrated sulfuric acid, dried over $CaCl_2$, and distilled over P_2O_5. HMPT (Aldrich) and CH_3SO_3H (Fluka), commercially available products, were used as received. Phenyl sulfide (Fluka) was purified by distillation under reduced pressure. Phenyl sulfoxide (Aldrich), and dibenzothiophene (Aldrich) were purified by crystallization. Thianthrene 5-oxide (**SSO**) was prepared as previously reported,[1b] and dibenzothiophene sulfoxide was prepared by following an analogous procedure.

Thianthrene 5,5-Dioxide (SSO_2). A solution of **SSO** (1g, 4.3 mmol) in acetone (30 mL) in the presence of anhydrous $MgSO_4$ (5 g) was cooled to 0 °C, and a solution of $KMnO_4$ (0.45g, 2.9 mmol) was added, dropwise over 3 h. The mixture returned to room temperature while stirring for an additional hour and was then filtered through Celite. The solvent was removed under vacuum. Flash chromatography of the crude product, on silica gel (CH_2Cl_2/hexane, 70:30), afforded 1.0 g of **SSO_2** (94% yield), mp 266–267 °C. ^1H NMR (CD_2Cl_2): δ 8.21–8.13 (2H, m), 7.73–7.64 (2H, m), 7.63–7.50 (4H, m). MS (from GC–MS): 248 (100, M^+), 216 (5), 200 (47), 184 (19), 168 (10), 139 (12), 108 (5), 96 (5), 69 (12), 50 (6).

***cis*-Thianthrene 5,10-Dioxide (*cis*-SOSO) and *trans*-Thianthrene 5,10-Dioxide (*trans*-SOSO).** To a solution of **SSO** (0.5 g, 2.1 mmol) and 0.2 mL of H_2O_2 (10 M, 2.0 mmol) in CH_3OH (15 mL) was added concentrated HCl (1 mL). The mixture was stirred at room temperature overnight. After addition of 10% aqueous $NaHCO_3$ (5 mL) the reaction solution was extracted (3 × 5 mL) with $CHCl_3$. The combined organic extracts were washed with a saturated solution of $Na_2S_2O_5$ (1 × 5 mL) and subsequently with water (2 × 5 mL), dried over $MgSO_4$, and concentrated under vacuum. Flash chromatography of the crude product, on silica gel (toluene/ethyl acetate, 95:5), afforded almost equal amounts of the two isomeric dioxides (90% overall yield). For *cis*-**SOSO**, 282–283 °C. ^1H NMR (CD_2Cl_2): δ 8.08–7.99 (4H, m), 7.77–7.68 (4H, m). MS (from GC–MS): 248 (100, M^+), 216 (53), 200 (47), 184 (49), 168 (8), 139 (17), 108 (8), 69(18), 44(12). For *trans*-**SOSO**, mp 248–249 °C. ^1H NMR (CD_2Cl_2): δ 8.13–8.04 (4H, m), 7.71–7.62 (4H, m). MS (from GC–MS): 248 (100, M^+), 216 (34), 200 (55), 184 (50), 171(40), 139 (15), 108 (8), 69(20), 50(12).

Thianthrene 5,5,10-Trioxide ($SOSO_2$). The oxidation of thianthrene was carried out as previously reported[1b] by using an excess of *m*-CPBA. The product was purified by flash chromatography on silica gel (CH_2Cl_2/hexane, 70:30), mp 220–221 °C. ^1H NMR (CD_2Cl_2): δ 8.16–8.08 (4H, m), 7.83–7.67 (4H, m). MS (from GC–MS): 264 (21, M^+), 248 (100), 216 (41), 200 (50), 184 (24), 171(46), 139 (26), 108 (15), 69(27), 50(12).

$MoO_5(HMPT)_2$. To a solution of MoO_5HMPT (0.5 g, 14.1 mmol) in 5 mL of neat HMPT were added a few drops of anhydrous hexane. The mixture was kept overnight at 4 °C. Bright yellow crystals were obtained whose purity (>98%), measured as active oxygen content, was determined by iodometric titration. Anal. Calcd for $C_{12}H_{36}N_6O_7P_2Mo$: C, 26.97; H, 6.79; N, 15.73. Found: C, 27.54; H, 6.88; N, 15.67. ^1H NMR analyses of a solution of $MoO_5(HMPT)_2$ (0.005 M) in $CDCl_3$ gave δ 2.79 (d, J_{PH} = 10.2 Hz, 18H), and 2.65 (d, J_{PH} = 9.1 Hz, 18H), assigned to bound and free methyl HMPT hydrogens, respectively.[15]

Oxidation Procedures and Product Analyses. All the oxidation reactions were carried out in a jacketed glass reactor with a temperature control better than ±0.05 °C. In a typical run a DCE solution (10 mL) of the substrate was added to a DCE solution (10 mL) of the oxidant at 40 °C. Aliquots of 1 mL of the reaction mixture were taken at appropriate time intervals and quenched in a test tube with an excess of $(n\text{-}Bu)_2S$. In order to monitor at the same time both the decrease of the active oxygen (calculated from the $(n\text{-}Bu)_2SO$ formation)[16] and the increase of the oxidation products, different quenched aliquots, after addition of an appropriate standard solution, were filtered through a small Celite column to eliminate the metal derivative and analyzed by GC and HPLC. The oxidation products were identified by GC–MS comparison with authentic samples. Quantitative GC analysis (error ±3%) of the $(n\text{-}Bu)_2SO$ formation was carried out on a FFAP 3% on Chromosorb WAW DMCS, 50 cm length glass column using benzophenone as internal standard. Quantitative HPLC analyses (error ±3%) were carried out isocratically on a Econosil silica gel column (10 mesh, 250 × 4.6 mm) with the variable wavelength detector set at 254 nm. Different compositions of the mobile phase and flow rates were used for the various products in order to have in all cases retention times in the range 3–5 min and similar peak widths. The following conditions were adopted: **SSO_2** and dibenzothiophene sulfone, chloroform, flow rate =1.0 mL/min, standard = naphthalene; *trans*-**SOSO** and dibenzothiophene sulfoxide, hexane/ethyl acetate 40:60, flow rate = 2.5 mL/min, standard = *p*-nitrophenyl sulfoxide; *cis*-**SOSO** hexane/ethyl acetate 75:25, flow rate = 1.7 mL/min, standard = *p*-bromophenyl sulfone. The rate constants were obtained by using a nonlinear regression data analysis computer program. The fit error on the rate constants was less than 1%. Duplicate runs agreed within 3%–5%.

Instrumentation. Melting points were determined on a Leitz Watzler-Laborlux 12 instrument and are uncorrected. ^1H NMR spectra were recorded on a Bruker WP-200 spectrometer. The GC and HPLC analyses were performed, respectively, on a Varian 3700 gas chromatograph, equipped with a Varian CDS 401 integrator, and on a Waters instrument equipped with a UV–vis detector (Waters 480) and a Hewlett-Packard 3390A integrator. GC–MS analyses were carried out with a Hewlett-Packard 5890 gas chromatograph, connected to a 5970 mass-selective detector, using a 15 m OV-17 capillary column 0.25 mm i.d.

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