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# Application of the Thianthrene 5-Oxide Mechanistic Probe to Peroxometal Complexes

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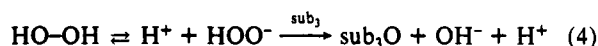
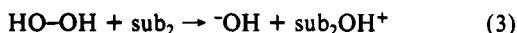
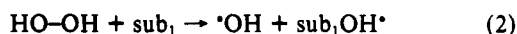
**Abstract:** The applicability of thianthrene 5-oxide as a mechanistic probe for distinguishing between the electrophilic and the nucleophilic character in oxygen-transfer processes from a series of Mo(VI) and W(VI) peroxo complexes has been investigated. In almost all the cases examined, the predominant formation of the corresponding sulfone has been observed. This would indicate a nucleophilic nature of the oxidants, which is, however, at odd with known chemistry of such species. In fact, competitive experiments performed by employing *p*-chlorophenyl methyl sulfide and phenyl methyl sulfoxide together in equivalent amounts as substrates revealed the preferred oxidation of the former over the latter as expected for an electrophilic oxygen transfer. These apparently contrasting findings are interpreted in terms of an incursion of radical pathways in the oxidation reactions of thianthrene 5-oxide by these peroxo complexes.

## Introduction

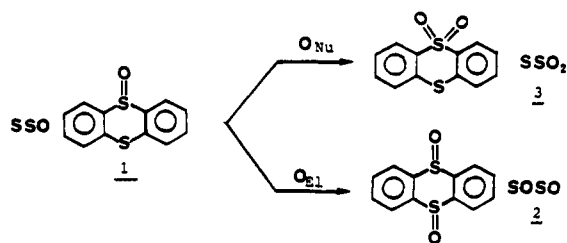
Organic and inorganic peroxides, such as alkyl hydroperoxides, peracids, and hydrogen peroxide, are able to oxidize sulfides to



sulfoxides and these to sulfones.<sup>1</sup> The reaction, formally amounting to an oxygen transfer from the peroxide to the substrate, may proceed through either the homolytic (eq 2) or heterolytic (eqs 3 and 4) cleavage of the peroxidic oxygen–oxygen bond<sup>2</sup> as schematically shown below taking hydrogen peroxide as the model oxidant.



Within the domain of heterolytic reactions, two mechanistic pathways may operate.<sup>2b</sup> Thus, the transferred oxygen may have either an electrophilic (eq 3) or a nucleophilic character (eq 4). However, a distinction between the two alternatives is not always straightforward. To this aim, an elegant probe has been devised some years ago by Adam et al. based on the use of thianthrene 5-oxide (1).<sup>3</sup>



The rationale behind such a probe is that the sulfide sulfur is usually more nucleophilic than the sulfoxide sulfur.<sup>2b,3</sup> Therefore, it is expected that an electrophilic oxidant would react with 1 to provide the bis(sulfoxide) 2, whereas a nucleophilic one would lead to the formation of the sulfone 3. The validity of Adam's probe has been unequivocally established by the observation that the reaction of the anion of hydrogen peroxide,  $HOO^-$ , with 1 provides only 3 whereas protonated hydrogen peroxide,  $H_3O_2^+$ , gives almost quantitatively 2.<sup>3</sup>

The oxidation chemistry of peroxometal complexes, namely, Ti(IV), V(V), Mo(VI), and W(VI) derivatives, closely resembles,

as already pointed out, that of simple peroxides.<sup>2,4</sup> However, an inspection of the literature reveals that clear-cut examples of nucleophilic oxidations by peroxometal complexes are not available. This is true even for species, such as the anionic peroxo complexes, where such a reactivity could be expected.<sup>5</sup> In order to gain more information on this aspect, we decided to apply the Adam's probe to a series of either neutral or anionic peroxo complexes.

## Results and Discussion

**Oxidation of Thianthrene 5-Oxide.** Oxidation of thianthrene 5-oxide by nine both neutral and anionic peroxometal complexes was performed in chloroform at 40 °C, by employing a molar ratio substrate/oxidant in the range 15–80 in order to minimize secondary oxidation products.

The results of such an investigation are collected in Table I.<sup>6</sup> At first glance, it appears that the data of Table I are hardly accommodated within the mechanistic framework presented above. In fact, it is found that  $MoO_3 \cdot HMPT$ , 5, and  $WO_3 \cdot HMPT$ , 6, classical electrophilic oxidants,<sup>2b,7</sup> typically employed for the stereoselective epoxidation of alkenes,<sup>7</sup> provide the sulfone 3 as the major product of oxidation (entries I and II). By contrast, for the anionic picolinate *N*-oxide molybdenum, 7, and tungsten, 8, oxodiperoxo complexes, an opposite product distribution is observed, being the bis(sulfoxide) 2 predominant over the sulfone 3 (entries III and IV). It should be mentioned that previous investigations<sup>5</sup> have indicated a poor electrophilic character of both 7 and 8, which inter alia, are not able to epoxidize even highly nucleophilic olefins.<sup>5</sup>

(1) Madesclaire, M. *Tetrahedron* **1986**, *42*, 5459 and references therein.  
(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. In *Organic Peroxides*; Swern, D., Ed.; Wiley: New York, 1970; Vol. 1, pp 199–264 and references therein.

(3) Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020.  
(4) Di Furia, F.; Modena, G. *Rev. Chem. Intermed.* **1985**, *6*, 51.  
(5) Campestri, S.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1988**, *53*, 5721.

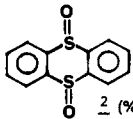
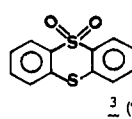
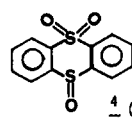
(6) It should be mentioned that a discrepancy between our data concerning the reactivity of SSO with  $MoO_3 \cdot HMPT$  and  $WO_3 \cdot HMPT$  and those reported by Adam (Adam, W.; Lohray, B. B. *Angew. Chem.* **1986**, *25*, 188) is observed. In particular, in Adam's work, a ratio  $SSO_2:SOSO = 1$  is found. We observed that such a ratio is obtained when aged stock of the peroxo complexes is used. At this stage, it is difficult to provide a rationale for the process involving the peroxo complexes presumably on standing.

(7) (a) Bortolini, O.; Di Furia, F.; Modena, G.; Scardellato, C.; Scrimin, P. *J. Mol. Catal.* **1981**, *11*, 107. (b) Bortolini, O.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1983**, *19*, 331. (c) Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1983**, *18*, 177. (d) Arcoria, A.; Ballistreri, F. P.; Tomaselli, G. A.; Di Furia, F.; Modena, G. *J. Mol. Catal.* **1984**, *24*, 189. (e) Ballistreri, F. P.; Failla, S.; Spina, E.; Tomaselli, G. A. *J. Mol. Catal.* **1988**, *50*, 39. (f) Arcoria, A.; Ballistreri, F. P.; Spina, E.; Tomaselli, G. A.; Toscano, R. M. *Gazz. Chim. Ital.* **1990**, *120*, 309.

<sup>†</sup> Università di Catania Viale A. Doria 6.

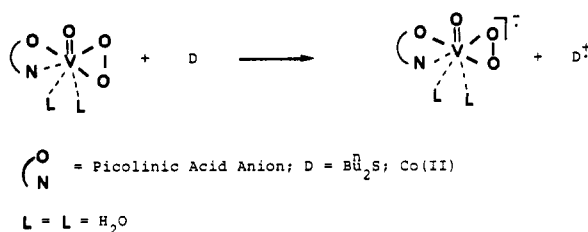
<sup>‡</sup> Università di Padova Via Marzolo 1.

**Table I.** Oxygen-Transfer Processes to Thianthrene 5-Oxide by Peroxometal Complexes<sup>a,b</sup>

peroxometal		 2 (%) <sup>c</sup>	 3 (%) <sup>c</sup>	 4 (%) <sup>c</sup>
I	MoO(O <sub>2</sub> ) <sub>2</sub> OP[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (5)	26	74	
II	WO(O <sub>2</sub> ) <sub>2</sub> OP[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub> (6)	32	68	
III	[MoO(O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> C(O)NC <sub>5</sub> H <sub>4</sub> ] <sup>-</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> (7)	59	25	16
IV	[WO(O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> C(O)NC <sub>5</sub> H <sub>4</sub> ] <sup>-</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup> (8)	45	39	16
V	VO(O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> CNC <sub>5</sub> H <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> <sup>d</sup> (9)	50	46	4
VI	[PMo <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [C <sub>5</sub> H <sub>5</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ] <sub>3</sub> (10)	14	76	10
VII	[PW <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [C <sub>5</sub> H <sub>5</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ] <sub>3</sub> (11)	20	55	25
VIII	[PMo <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [(C <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> N <sup>+</sup> ] <sub>3</sub> (12)	6	86	8
IX	[PW <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [(C <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> N <sup>+</sup> ] <sub>3</sub> (13)	3	88	9

<sup>a</sup>All the reactions were performed in CHCl<sub>3</sub> at 40 °C by employing a molar ratio thianthrene 5-oxide/oxidant in the range 15–80. <sup>b</sup>Oxidation products were determined by GLC on a DB-1 20 m capillary column using anthracene as internal standard. <sup>c</sup>Percent distribution of products determined at 70% consumption of the oxidant. <sup>d</sup>CH<sub>3</sub>CN as solvent.

A way of escape from such puzzling results is however provided by the data concerning the reactivity of the picolinate vanadium oxodiperoxo complex, **9**. This neutral species provides, upon reaction with **1**, almost equal amounts of **2** and **3** (entry V). In fact, **9** is a typical radical oxidant<sup>8,9</sup> that is capable of hydroxylating benzene to phenol,<sup>10</sup> whereas it reacts with alkenes<sup>10</sup> and sulfides<sup>9</sup> in a rather unselective manner, providing several kinds of products. As a further piece of information, it has been recently reported that the radical reactivity of **9** is considerably enhanced by the addition of one-electron donors, e.g., Co(II) and also organic sulfides.<sup>9</sup> Such an enhancement is believed to arise from a faster formation of the radical anion of **9**, which is the real oxidant in solution.<sup>11</sup>



If the assumption is made that also the oxidation of **1** by **9** has a substantial radical character proceeding through a preliminary electron transfer from **1** to the oxidant, the low selectivity exhibited by **9** may be rationalized. This would result from the coexistence of the neutral species and of the radical anion of **9**, the latter being quite reactive toward the sulfoxide sulfur. A low selectivity of **9** in the oxidation of sulfides leading to both sulfoxides and sulfone has been documented.<sup>9</sup> The next step toward an interpretation of the results so far presented requires that the possibility of occurrence of an electron-transfer step leading to the radical anion of the peroxide and to the radical cation of SSO is taken into account also for **5**, **6**, **7**, and **8**. This would imply the presence of different oxidizing species in solution, both radical anions and neutral, which may react with SSO and SSO<sup>•+</sup> to yield the observed oxidation products.<sup>12</sup> If this is the case, the main difference between neutral (**5**, **6**) and anionic complexes (**7**, **8**) should be in their abilities to accept an electron from the substrate, the anionic oxidants being less prone to accommodate a second

negative charge. Consequently, the extent of radical process should be larger for neutral complexes, as the experimental results observed for **5** and **6** seem to indicate. By contrast, both complexes **7** and **8** react mainly with SSO as electrophiles, thus preferring the sulfide sulfur.

In the light of such a mechanistic hypothesis, the data referring to the oxidation of **1** by peroxopolyoxo complexes (entries VI–IX) appear of particular interest because they would indicate that, for such species, though at a different extent, the radical pathway is more accessible than for the corresponding monomeric anionic peroxo complexes **7** and **8** where the negative charge is, very likely, much less delocalized.<sup>7f</sup> This feature would explain the broad reactivity of peroxopolyoxo complexes, which oxidize a large variety of organic substrates<sup>13</sup> presumably through different mechanistic pathways.

**Competitive Experiments.** An alternative, more classical, approach to the use of thianthrene 5-oxide as a probe of the nucleophilic or the electrophilic character of the oxygen transfer is to run kinetic experiments in which a suitable pair of a sulfide and a sulfoxide are in competition for the oxidant. The procedure involves the reaction of the sulfide and the sulfoxide in excess with respect to the oxidant and the determination of the products before the complete consumption of the oxidant.

A large formation of sulfoxide would indicate an electrophilic character of the oxidant, whereas high yields of sulfone would be indicative of a nucleophilic character.

The comparison of the results obtained by this procedure with those found by using SSO might provide further evidence of the possibility of incursion of electron-transfer processes in the oxidation of SSO by the peroxometal complexes **5**–**13**, pointing also to a peculiarity of SSO as substrate in such reactions.

In fact, such competitive experiments were run by pitting together *p*-chlorophenyl methyl sulfide and methyl phenyl sulfoxide one against the other to compete for peroxometal complexes **5**–**13**.

These substrates have been selected in the light of several pieces of evidence that their oxidation by electrophilic reagents is mostly a heterolytic process. Likely a value of Hammett  $\rho$  –1.6 observed in the oxidation reactions of *p*-XC<sub>6</sub>H<sub>4</sub>SC<sub>2</sub>H<sub>5</sub> with **10** would point out to an electrophilic oxygen transfer.<sup>7f</sup>

The data concerning the product distribution are reported in Table II. Preliminarily, the competitive procedure was tested against acidic and alkaline hydrogen peroxide (entries X–XI), and the exclusive formation of the oxidation product deriving in one case from the electrophilic attack (sulfoxide) and in the other case from the nucleophilic attack (sulfone) of the oxidant confirms the reliability of such a procedure.

Inspection of the remaining data reported in Table II is quite revealing.

The almost exclusive formation of sulfoxide, as shown in entries XII and XIII, clearly indicates that MoO<sub>3</sub>HMPT and

(8) Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1989**, *54*, 4368.

(9) Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G.; Padovani, C.; Sivak, M. *Res. Chem. Intermed.* **1989**, *12*, 111.

(10) Mimoun, H.; Saussine, L.; Daire, E.; Postel, M.; Fisher, J.; Weiss, R. *J. Am. Chem. Soc.* **1983**, *105*, 3101.

(11) It should be noted that the oxidation of simple sulfides by **5** and **6** is, on the basis of several pieces of evidence,<sup>7</sup> a clean heterolytic process, which does not involve electron-transfer steps. However, the sulfide moiety in **1** is a rather peculiar one. Indeed the particularly folded conformation might render **1** much more prone than typical sulfides to act as a one-electron donor.

(12) Unfortunately no information is available on the reactivity of SSO<sup>•+</sup> with peroxometal complexes, so that any prediction on products distribution would be hazardous at this stage.

(13) (a) Ishii, Y.; Yamaki, K.; Ura, T.; Yamada, H.; Yoshida, T.; Ogawa, M. *J. Org. Chem.* **1988**, *53*, 3587. (b) Ballistreri, F. P.; Failla, S.; Spina, E.; Tomaselli, G. A. *J. Org. Chem.* **1989**, *54*, 947.

Table II. Oxygen-Transfer Processes to *p*-ClC<sub>6</sub>H<sub>4</sub>SOCH<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>SOCH<sub>3</sub> by Peroxometal Complexes<sup>a,b</sup> (Competitive Experiments)

	oxidant	<i>p</i> -ClC <sub>6</sub> H <sub>4</sub> SOCH <sub>3</sub> (%) <sup>c</sup>	C <sub>6</sub> H <sub>5</sub> SO <sub>2</sub> CH <sub>3</sub> (%) <sup>c</sup>
X	H <sub>2</sub> O <sub>2</sub> /H <sup>+</sup> <sup>d</sup>	100	
XI	H <sub>2</sub> O <sub>2</sub> /OH <sup>d</sup>		100
XII	MoO(O <sub>2</sub> ) <sub>2</sub> OP[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	96	4
XIII	WO(O <sub>2</sub> ) <sub>2</sub> OP[N(CH <sub>3</sub> ) <sub>2</sub> ] <sub>3</sub>	86	14
XIV	[MoO(O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> C(O)NC <sub>5</sub> H <sub>4</sub> ] <sup>-</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup>	95	5
XV	[WO(O <sub>2</sub> ) <sub>2</sub> O <sub>2</sub> C(O)NC <sub>5</sub> H <sub>4</sub> ] <sup>-</sup> (C <sub>4</sub> H <sub>9</sub> ) <sub>4</sub> N <sup>+</sup>	90	10
XVI	[PMo <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [C <sub>5</sub> H <sub>5</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ] <sub>3</sub>	90	10
XVII	[PW <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [C <sub>5</sub> H <sub>5</sub> N <sup>+</sup> (CH <sub>2</sub> ) <sub>15</sub> CH <sub>3</sub> ] <sub>3</sub>	72	28
XVIII	[PMo <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [(C <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> N <sup>+</sup> ] <sub>3</sub>	96	4
XIX	[PW <sub>4</sub> O <sub>8</sub> (O <sub>2</sub> ) <sub>8</sub> ] <sup>3-</sup> [(C <sub>6</sub> H <sub>13</sub> ) <sub>4</sub> N <sup>+</sup> ] <sub>3</sub>	87	13
XX	VO(O <sub>2</sub> )O <sub>2</sub> CNC <sub>5</sub> H <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub>	60	40

<sup>a</sup> All the reactions were performed in CHCl<sub>3</sub> at 40 °C. <sup>b</sup> In all experiments, [C<sub>6</sub>H<sub>5</sub>SOCH<sub>3</sub>] = [C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CH<sub>3</sub>] = 0.1 M and [oxidant] = 0.002–0.012 M. <sup>c</sup> Percent distribution of products determined at 70% consumption of the oxidant. <sup>d</sup> In ethanol and 1 N HCl or NaOH, respectively.

WO<sub>3</sub>HMPT are electrophilic oxidants, as expected. Indeed also the remaining Mo(VI) and W(VI) peroxo complexes yield sulfoxide rather than sulfone as the main oxidation product (entries XIV–XIX), and therefore, they behave also as electrophilic oxidants. The unique exception to this generally observed behavior is represented by the V(V) peroxometal complex (entry XX) for which similar amounts of sulfoxide and sulfone, within the experimental errors, are observed.

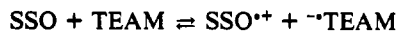
However, such a behavior of the V(V) derivative is expected, in virtue of its ability to carry out electron-transfer processes when reacted with organic sulfides, as already reported.<sup>9,10</sup> It is interesting to notice the close similarity of behavior of the V(V) in the oxidation of SSO (entry V, Table I) as well as in the competitive procedure (entry XX, Table II) as an indication that the oxidation by V(V) occurs also (but not exclusively) through the intermediacy of radical ions regardless of the nature of the substrate.

On the other hand, Mo(VI) and W(VI) peroxo complexes, as a general trend, yield larger amounts of sulfoxide in the competitive procedure, whereas the sulfone derivative **3** represents the predominant product when the SSO probe is used.

These apparently contrasting findings seem to give support to the mechanistic hypothesis, suggested before, that the occurrence of an electron transfer from the thianthrene 5-oxide to the peroxometal complex, leading to the formation of a pair of radical ions, SSO<sup>•+</sup>OX<sup>•-</sup>, is a very probable event along the reaction coordinate in these oxygen-transfer processes from peroxometal complexes.

In fact, the electron transfer to the oxidant is likely to modify the nature of such a reagent, which becoming at least formally a radical anion species, displays an unusual nucleophilic character.

On the other hand, since the reduction potential of **12** (TEAM) is estimated to be  $E_{1/2} = -1.8$  V (DMF)<sup>14</sup> and a value of  $E_{ox} = 1.70$ <sup>14</sup> (1.76)<sup>15</sup> V (CH<sub>3</sub>CN) was measured for the system SSO → SSO<sup>•+</sup>, the application of the Rehm–Weller equation allows one to reckon a value of  $\Delta G^\circ \approx -2.3$  kcal mol<sup>-1</sup> for the SET process



which would be indicative of an exergonic process. Therefore, as Adam himself reports,<sup>15</sup> the use of thianthrene 5-oxide probe might lead to erroneous conclusions as a consequence of electron-transfer processes. However, once one has acquaintance of such complications, Adam's probe still remains a valid diagnostic tool in oxygen-transfer processes.

## Conclusion

The results presented here do not provide evidence of a nucleophilic oxygen transfer from Mo(VI) and W(VI) peroxo complexes.<sup>16</sup> Rather, they indicate that such compounds behave as electrophilic oxidants.

(14) Greci, L. Private communication.

(15) Adam, W. Private communication.

(16) Indeed there is no evidence on the presence in solution of open peroxidic species as MoOO<sup>-</sup> or MoO<sup>-</sup>; recent <sup>17</sup>O NMR measurements (Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* **1988**, *53*, 4581) rule out the existence of such species.

Furthermore, it is pointed out that the incursion of radical pathways is a likely event in the reactions of these oxidants with thianthrene 5-oxide.

It is tempting to suggest that such an indication could be extended to all the oxidative processes where the incursion of electron-transfer steps may be conceived, thus providing a rationale to some discrepancies recently reported in the literature concerning the chemical behavior of dioxirane<sup>17</sup> and bicyclic *gem*-dialkylperoxonium ion.<sup>18</sup>

## Experimental Section

**Materials.** Chloroform (Carlo Erba, RPE) was distilled over P<sub>2</sub>O<sub>10</sub>. Methyl phenyl sulfoxide is a commercially available product (Aldrich), which was distilled before use; 4-chlorophenyl methyl sulfide was prepared by a literature method, as reported previously.<sup>7c</sup>

Thianthrene 5-oxide<sup>19</sup> was prepared by oxidation of the available commercially thianthrene (Aldrich) with 3-chloroperoxybenzoic acid as follows: A solution of 88% 3-chloroperoxybenzoic acid (50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> was added slowly at room temperature to a solution of thianthrene (37 mmol) in CH<sub>2</sub>Cl<sub>2</sub>. The solution was kept at room temperature until disappearance of thianthrene, then washed with 2 L of an aqueous solution of NaHCO<sub>3</sub> (40 g) and with 1 L of H<sub>2</sub>O, dried over MgSO<sub>4</sub>, and reduced to a small volume. Separation of thianthrene 5-oxide from the reaction mixture was performed by column chromatography employing a mixture of cyclohexane/ethyl acetate (9:1) as eluent (mp 143–144).

Molybdenum(VI) and W(VI) peroxo complexes **5**,<sup>20</sup> **6**,<sup>20</sup> **7**,<sup>21</sup> **8**,<sup>22</sup> **10**,<sup>23</sup> **11**,<sup>24</sup> **13**,<sup>25</sup> and **9**<sup>8</sup> were prepared according to already reported original procedures.

Peroxo complex **12** was obtained by a procedure similar to that reported for the W(VI) analogue.<sup>26</sup>

**Procedures and Instrumentation.** All oxidation experiments were carried on under a nitrogen atmosphere. In a typical run, a solution of 5 mL of CHCl<sub>3</sub> containing 1.25 mmol of thianthrene 5-oxide, 0.0154–0.11 mmol of oxidant, and 0.03 mmol of anthracene as internal standard was kept at 40 °C in a thermostatic bath. Two or three aliquots were withdrawn at various time intervals (until 70% consumption of the oxidant) and analyzed quantitatively by GLC on a DB-1 20 m capillary column; the percentages of oxidation products reported in Table I are therefore the average of two or three determinations. Qualitative analysis of the reaction mixture was performed by GC-MS.

Competitive measurements were run by dissolving equal amounts (0.5 mmol) of *p*-chlorophenyl methyl sulfide and phenyl methyl sulfoxide, 0.01–0.06 mmol of oxidant, and 0.08 mmol of *n*-decane as internal

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standard in 5 mL of chloroform and determining the oxidation products by GLC as reported above.

The identity and purity of the peroxidic oxidants were determined by elemental analysis, IR spectra, and iodometric titrations. Gas chromatographic analyses of reaction mixtures were carried out on a Perkin-Elmer 8420 gas chromatograph equipped with a flame ionization detector and program capability. GC-MS analyses were performed by a Hewlett-Packard Model 5890 gas chromatograph (using an HP-1 dimethylpolysiloxane 25 m capillary column), equipped with a Hewlett-Packard MS computerized system, Model 5971A, ionization voltage 70

eV, electron multiplier 1700 V, ion source temperature 280 °C.

<sup>1</sup>H NMR spectra were recorded on a Bruker WP-80 spectrometer with TMS as internal standard.

Oxidation products were identified by comparison of their MS and NMR spectra with those of authentic samples.

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## Diffusion and Percolation of Radical Pairs in Zeolite Media. A Product Analysis Study

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**Abstract:** The photochemistry of dibenzyl-*d*<sub>5</sub> ketone (DBK-*d*<sub>5</sub>) adsorbed in the zeolite NaX was investigated as a function of substrate loading. The cage effect and the relative yields of 1,2-diphenylethane (DPE), *o*-methyl- $\beta$ -phenylacetophenone (*o*-MAP), and *p*-methyl- $\beta$ -phenylacetophenone (*p*-MAP) were found to depend dramatically on the loading of the starting material present. These results and the variations observed in the percent cage effect are described in terms of local and global effects that determine the influence of the zeolite media. Changes in reactivity as a function of reactant loading are explained in terms of percolation theory by using the model "ants in a labyrinth" proposed by de Gennes. The diffusing radicals play the role of the ants and the disposition of the reactant in the regular zeolite topology determines the nature of the labyrinth. This model implies that the diffusion coefficient of the radicals is larger than the diffusion coefficient of the starting ketone. The model is supported by trapping experiments with an oxygen scavenger and by experiments carried out at -20 °C where the diffusion of the radicals is largely diminished.

### Introduction

Zeolites are microporous crystalline materials possessing molecular-sized and geometrically well defined interconnecting channels and cavities.<sup>1</sup> The adsorption and intracrystalline diffusion of organic compounds with kinetic diameters smaller than those of the critical zeolite dimensions give zeolites their sieving abilities. While the use of zeolites as active reaction catalysts has been well studied over the last few decades,<sup>2</sup> their properties as organizing reaction media for photochemical reactions have been explored only recently.<sup>3-5</sup> It has been shown, however, that both unimolecular<sup>3</sup> and bimolecular<sup>4</sup> photochemical reactions can be influenced by the structural arrangement and restrictions imposed on the reactants by the zeolite environment.

**Local and Global Effects.** The selectivity of photochemical reactions in zeolites is often very different than that observed in solution.<sup>3-5</sup> Unimolecular effects usually result from conformational restrictions<sup>3</sup> giving rise to reactant and transition-state selectivity control.<sup>2</sup> Bimolecular reactions, in contrast, depend on the distribution and transport of the reactants within the various sites of the zeolite environment.<sup>4</sup> Interestingly, these factors can be drastically influenced by relatively simple experimental manipulations such as ion exchange<sup>6</sup> and the use of small amounts of unreactive additives.<sup>7</sup> Recent photochemical investigations have demonstrated some of these effects on the product distribution of radical-mediated reactions.<sup>4-6,8</sup> In these particular cases, both the size/shape and binding interactions with the local environment as well as the connectivity of the internal zeolite channels may induce specific effects on the dynamics of recombinant radicals and radical pairs. Cage effects may originate at *locally* restricted sites where escape of the geminate radical pairs may be unfavorable, or within the *global* spaces given by extended and interconnected intracrystalline pore structures.<sup>9</sup> A distinction

between these two possibilities is of significant interest in order to understand the mechanisms that control chemical reactivity in these media. Local effects are expected to result from isolated reactant-zeolite site interactions, while global effects, involving diffusion and molecular transport, are expected to depend on the distribution of the reactants and be susceptible to cooperative interactions and critical phenomena. Local effects should be independent of the amount of reactant present in the zeolite, while global effects should depend on the amount of material present and its distribution in the intracrystalline reaction spaces. Here we report an investigation addressing the relative importance of local and global effects in a model system. With this in mind,

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