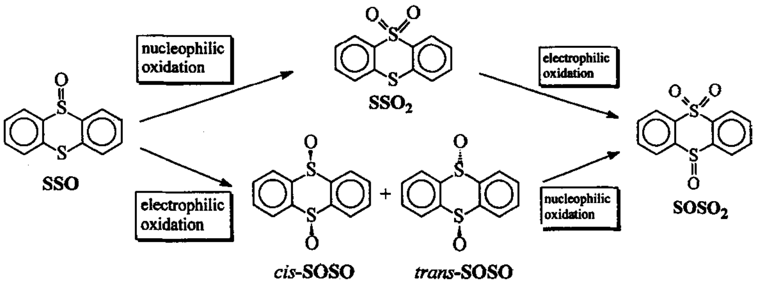
Thianthrene 5-Oxide as a Mechanistic Probe in Oxygen Transfer Reactions: The Case of Carbonyl Oxides versus Dioxiranes Revisited

Abstract: Thianthrene 5-oxide (SSO) constitutes a useful mechanistic tool for the assessment of the electronic character of oxygen transfer agents by means of their X_{SO} values, which reflect the extent of nucleophilic oxidation at the SO site in SSO. Treatment of dioxiranes **1a–d** with the SSO probe confirms that these are electrophilic oxidants ($X_{SO} < 0.15$). Dioxirane sulfoxidation is sensitive to protic solvents and acids, which implies a polar mechanism (S_N2) with nucleophilic attack of the sulfide electron pair on the dioxirane peroxide bond. In contrast, the carbonyl oxides **2a** and **b**, diethyl persulfoxide (**3**), and adamantylideneadamantane perepoxide (**4**) are nucleophilic oxidants ($X_{SO} > 0.85$). However, the cyclopentadienone carbonyl oxides **2c** and **d** show low X_{SO} values typical for electrophilic oxygen transfer agents. For these carbonyl oxides, photoisomerization to the respective dioxiranes is proposed under the photooxidation conditions of the diazoalkanes. Additionally, the *trans/cis* ratio of bissulfoxides (SOSO) formed provides valuable information on the stereochemical course of the oxygen-transfer process due to the steric requirements of the oxidant. Thus, the electrophilic dioxiranes preferentially attack the axial lone pair of SSO because of repulsion by the *peri* hydrogen atoms to afford *trans*-SOSO.

Keywords
carbonyl oxides · dioxiranes · mechanistic studies · oxidations · thianthrene 5-oxide

Introduction

During the last decade, the oxidation of thianthrene 5-oxide (SSO) has been used as a mechanistic probe to determine the electronic character of an oxidant (Scheme 1).[1–4] Valuable information on the nucleophilic (oxidation at the sulfoxide site, i.e., SO in SSO) versus electrophilic (oxidation at the sulfide site, i.e., S in SSO) nature of oxidants has been acquired by the SSO probe. Diverse oxygen transfer systems have been examined in this manner, including peroxometal complexes,[5] metalloporphyrin catalysts,[6] hemoprotein oxidizing species,[7] heteropolyoxometalate oxidants,[8] persulfoxides,[6] dimethylphenylsilyl hydrotrioxide ($R_3SiOOOH$),[9] dialkyl peroxonium intermediates ($R^1R^2O^+{-}OH$),[10a,b] and carbonyl oxides versus dioxiranes.[2]



The development of the SSO mechanistic probe was originally motivated by the desire to differentiate between in situ generated dioxiranes and carbonyl oxides on account of their expected electrophilic versus nucleophilic oxygen transfer nature. The preliminary results implied that dioxiranes and carbonyl oxides are differentiable valence isomers, separated by a substantial thermal activation barrier. This has now been unequivocally established by theoretical,[11–13] chemical-trapping,[1,2] spectral,[13–15] and most recently even by preparative[16] work. In contrast, carbonyl oxides can be photochemically cyclized to dioxiranes with visible light; however, to our knowledge, examples of the reverse thermal or photochemical isomerization are not yet known.

In view of the mechanistic significance of the actual electronic nature of the oxygen transfer step for carbonyl oxides versus dioxiranes, in this study we have reexamined[2] their oxidation of SSO by means of our new analytical protocol,[17] which takes explicit account of the *trans*-SOSO product, the bissulfoxide. Frequently *trans*-SOSO is the major oxygen transfer product, but it was previously missed because of the unusually long HPLC retention times that result from its highly polar nature. Consequently, too high a val-

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$$X_{SO} = \frac{\text{nucleophilic oxidation}}{\text{total oxidation}} = \frac{SSO_2 + SOSO_2}{SSO_2 + SOSO + 2\,SOSO_2} \qquad (1)$$

SSO to afford the sulfone SSO_2. Fortunately, our present results confirm our previous conclusions[2] that carbonyl oxides ($X_{SO} \approx 0.9$) are definitely nucleophilic oxygen transfer agents, while dioxiranes ($X_{SO} \approx 0.1$) are definitely electrophilic ones.

Results and Discussion

The results are summarized in Table 1 (entries 1–4). All oxidations of SSO by the isolated dioxiranes **1a–d** gave low X_{SO} values (<0.13) under a variety of experimental conditions. Thus, the expected[18, 19] electrophilic nature of these oxygen transfer agents is established beyond any doubt.

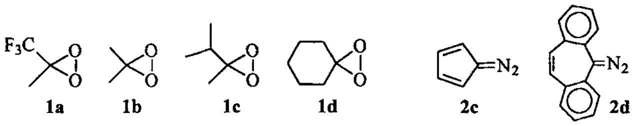
The temperature effect on the chemoselectivity is quite evident for the case of trifluorodioxirane **1a** (entries 1a,b). While the reaction at −78 °C ($X_{SO} = 0.01$, entry 1a) gave nearly exclusively SOSO, at 0 °C ($X_{SO} = 0.10$, entry 1b) a significantly higher amount of overoxidation product $SOSO_2$ (Scheme 1) was observed, while the increase in the sulfone product SSO_2 is less pronounced. This should not be construed to mean that the dioxirane **1a** becomes more nucleophilic at higher temperatures, but rather that in the latter stages of the oxidation process the accumulating bissulfoxide SOSO (major product) is competitively more effectively oxidized to the overoxidation product $SOSO_2$. Such overoxidation results in lack of selectivity and masks the true electronic nature of the oxidant [Eq. (1)]; thus, it is important to minimize overoxidation by reactive oxidants such as dioxirane **1a**.

The much less reactive (by a factor of about 1000 compared with **1a**[20]) dimethyldioxirane (DMD, **1b**) leads to an X_{SO} value of 0.07 (entry 2a) at −50 °C. At higher temperatures (0 °C) the X_{SO} value increases to 0.13, but not as the result of overoxidation, since the amount of $SOSO_2$ is negligible. Thus, the amount of nucleophilic oxidation product, namely the sulfone SSO_2, is significantly higher for dioxirane **1b** (entry 2a) than **1a** (entry 1a) and, as expected, the larger X_{SO} value implies more nucleophilic character for dioxirane **1b**.

As was done for dioxirane epoxidations[21] and CH insertions,[22a] the effect of protic solvents and acids on the heteroatom oxidation of SSO was examined. The use of a 1:1 mixture of CH_2Cl_2/MeOH as solvent (entry 2c) versus CH_2Cl_2 (entry 2b) resulted in a reduction of the amount of SSO_2 from 12 to 8.8% and a comparable change in the X_{SO} value from 0.13 to 0.09. With acetic acid instead of methanol, the amount of SSO_2 dropped to 6.5% and X_{SO} to 0.07 (entry 2d). The most effective reduction in the amount of SSO_2, to 1.6%, and X_{SO}, to 0.02 (entry 2e), was achieved with 10% trifluoroacetic acid (TFA). Similar temperature and TFA effects were observed in the oxidations of SSO by isopropyl(methyl)dioxirane (**1c**), entries 3a–c, and by cyclohexanone dioxirane (**1d**), entries 4a–c, which confirm their general nature.

To explain these results, we propose transannular oxygen transfer as an additional source of the sulfone SSO_2 product, as displayed in the mechanism of Scheme 2. S_N2 attack of the sulfide lone pair of the thianthrene oxide on the dioxirane peroxide bond leads to the dipolar intermediate **A**, analogous to the one postulated in dioxirane epoxidation reactions on the basis of solvent effects[21] and allylic oxidation.[22b] Usually the latter affords *trans*-SOSO by acetone elimination along path 1 (Scheme 2); however, we postulate that in view of the favorable

Table 1. Oxidation of thianthrene-5-oxide by dioxiranes and *O*-oxides.



Entry	Solvent [b]	*T* (°C)	Oxidant	Conv. [a] (%)	Product distribution [a] (%)				
					SSO_2	SOSO *cis*	SOSO *trans*	$SOSO_2$ [c]	X_{SO} [d]
1a	CH_2Cl_2	−78	**1a**	21	0.8	3.1	96	0.2	0.01
1b	CH_2Cl_2	0	**1a**	20	2.8	3.9	85	8.1	0.10
2a	CH_2Cl_2	−50	**1b**	52	6.8	3.1	90	0.1	0.07
2b	CH_2Cl_2	0	**1b**	56	12	3.9	84	0.3	0.13
2c	CH_2Cl_2/MeOH (1:1)	0	**1b**	35	8.8	16	75	0	0.09
2d	CH_2Cl_2/AcOH (1:1)	0	**1b**	35	6.5	13	80	0	0.07
2e	CH_2Cl_2/TFA [e] (10:1)	0	**1b**	53	1.6	5.7	93	0	0.02
3a	CH_2Cl_2	−40	**1c**	44	4.3	1.2	94	0	0.04
3b	CH_2Cl_2	0	**1c**	44	13	2.5	84	0	0.13
3c	CH_2Cl_2/TFA [e] (10:1)	0	**1c**	42	0	2.5	98	0	0.00
4a	CH_2Cl_2	−70	**1d**	46	5.8	11	82	1.9	0.08
4b	CH_2Cl_2	0	**1d**	46	12	12	76	0.9	0.12
4c	CH_2Cl_2/TFA [e] (10:1)	0	**1d**	45	1.0	13	86	0	0.01
5a	MeCN/CH_2Cl_2 (9:2)	−20	$Ph_2C{=}N_2$ (**2a**)/$^1O_2$	26	85	0	6.5	8.9	0.86
5b	MeCN/CH_2Cl_2 (9:2)	−20	*p*-$An_2C{=}N_2$ [f] (**2b**)/$^1O_2$	23	88	0	7.6	4.7	0.88
5c	MeCN/$CDCl_3$/CCl_4 (1:1:8)	−20	**2c**/$^1O_2$	2.2	30	12	57	0	0.30
5d	MeCN/$CDCl_3$/CCl_4 (1:1:7)	−20	**2d**/$^1O_2$	2.7	21	7.6	71	0	0.21
6a	MeCN/CH_2Cl_2 (9:2)	−20	Et_2S (**3**)/$^1O_2$	27	100	0	0.1	0	1.00
6b	MeCN/CH_2Cl_2 (1:1)	−20	Ad=Ad (**4**)/$^1O_2$ [g]	42	87	0	8.2	4.7	0.88

[a] Product distributions and conversions were determined by HPLC (RP-18 column, 64:34:2 MeOH/H_2O/MeCN as eluent) [17] detected at 254 nm, error ±3% of the stated values, normalized to 100% conversion. [b] For exact conditions, see Experimental Section. [c] The amount of overoxidation product, the trioxide $SOSO_2$, should be kept small (below 10%), since it masks information on the chemoselectivity, that is, electrophilic S versus nucleophilic SO oxidation in SSO (Scheme 1). [d] X_{SO} is defined in Equation (1); error ±0.03 units. [e] TFA = trifluoroacetic acid. [f] *p*-An = *para*-anisyl (*p*-$MeOC_6H_4$). [g] Ad=Ad = adamantylideneadamantane; treated with Me_2S after irradiation.

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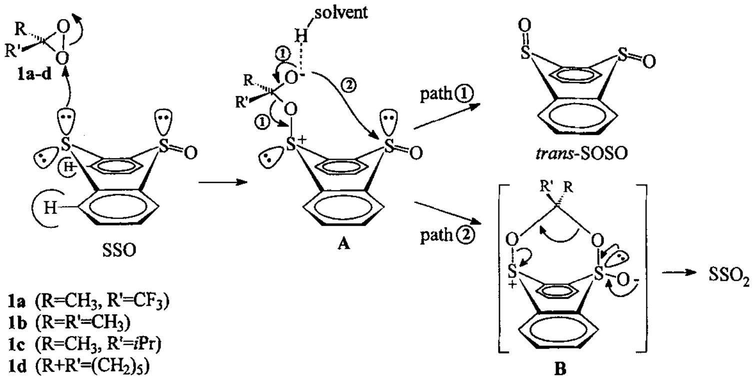


Scheme 2.

puckered geometry of the thianthrene skeleton, the negatively charged oxygen of the dipole **A** may reach across to add nucleophilically at the electrophilic sulfoxide site to generate the bridged dipole **B** (path 2). The latter fragments into sulfone SSO_2 and acetone and would explain the higher amount of SSO_2 formed in all the dioxirane oxidations even at low temperature (entries 2–4). In the presence of proton sources, particularly the strong acid TFA, the dipolar intermediate **A** is protonated at the negatively charged oxygen atom, its nucleophilic attack at the sulfoxide site thereby blocked, and the amount of SSO_2 product decreases in favor of SOSO.

PM3 calculations[23] revealed that the intermediate **B** occupies a local minimum with a heat of formation (ΔH_f) of 19.4 $kcal\,mol^{-1}$, which means that intermediate **B** is plausible. For comparison, we also calculated the ΔH_f energies of SSO (44.6), *cis*-SOSO (19.9), *trans*-SOSO (23.7), SSO_2 (10.8), DMD (−18.1), and acetone (− 53.0 $kcal\,mol^{-1}$). This means that the intermediate **B** (19.4) would lie well between the starting materials (SSO + DMD, 26.5) and the products (SSO_2 + acetone, −42.2 $kcal\,mol^{-1}$) of path 2.

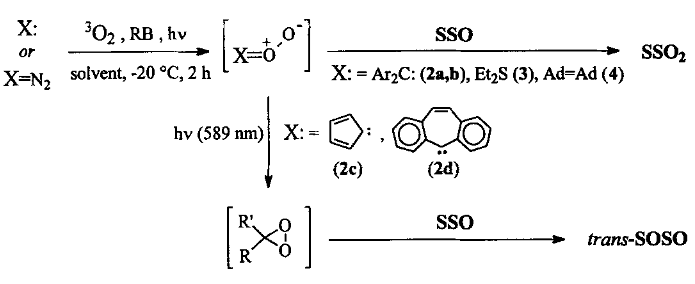
Again, such competitive transannular oxygen transfer by the dioxirane to afford sulfone SSO_2 does not signify higher nucleophilic oxidative character and masks the inherent electronic nature of the dioxirane. Nonetheless, it must be emphasized that such complications as overoxidation and transannular oxygen transfer are minor deviations, because dioxiranes are unquestionably pronounced electrophilic oxidants.

The fact that predominantly the *trans*-SOSO bissulfoxide is obtained for all dioxiranes **1a–d** (*trans*:*cis* ratio approximately 8–30:1) is of stereochemical interest. Thus, the axial lone pair at the sulfide site of SSO is attacked in preference to the equatorial one because of steric shielding by the *peri* hydrogen atoms in the thianthrene 5-oxide (Scheme 2). The *trans*/*cis* ratio, which at 0 °C covers a range from 8 to 30 (Table 1, entries 1b, 2b, 3b and 4b), reflects a clear trend in the steric demand of the dioxirane substituents, the order of *trans*/*cis* ratio is **1c** > **1a** ≈ **1b** > **1d**.

The carbonyl oxides **2a–d** were generated in situ by photooxygenation of the corresponding diazoalkanes, a well-established method.[13–15] For practical reasons (solubility, side products, etc.), rose bengal (RB) was used as a sensitizer in solvent mixtures of acetonitrile and chloromethanes (CH_2Cl_2, $CHCl_3$, and CCl_4). Control experiments confirmed that singlet oxygen alone in the absence of diazoalkanes did *not* oxidize SSO even at higher temperatures and longer reaction times.

The results in Table 1 show a definite nucleophilic selectivity for the diphenyl carbonyl oxide (**2a**) and for its *para*-anisyl-substituted derivative **2b** (entries 5a,b). Surprisingly, the cyclopentadienyl (**2c**) and the dibenzocycloheptatrienyl (**2d**) carbonyl oxides gave electrophilic X_{SO} values, with *trans*-SOSO as the main product. These low X_{SO} values for the carbonyl oxides **2c,d** are typical for dioxiranes. Presumably, the visible light (λ = 589 nm) used for the photosensitized generation of the carbonyl oxides **2c,d** photoisomerizes the latter in situ to their dioxiranes more efficiently than oxidizing SSO directly (Scheme 3).

In this context, it is known from low-temperature spectroscopic experiments[13] that the carbonyl oxide **2c** cyclizes to its dioxirane isomer on irradiation at $\lambda > 418$ nm, while for the carbonyl oxide **2a** isomerization at $\lambda > 630$ nm[13] has been reported. This agrees with our data, in that **2c** does and **2a** does not photoisomerize under irradiation with λ = 589 nm.



Scheme 3.

The photoisomerization of carbonyl oxides **2c** and **2d** under the photooxidation conditions requires a major revision of our earlier conclusions[2] that the carbonyl oxides **2c,d** also act as nucleophilic oxidants in their oxygen transfer to SSO. However, the previous analytical protocol, which failed to detect the *trans*-SOSO (major product), was responsible for this artifact. Nonetheless, the benzophenone-type derivatives **2a,b** are authentic carbonyl oxides and as expected preferentially oxidize SSO by nucleophilic oxygen transfer at the sulfoxide functionality.

For comparison with the carbonyl oxides **2a,b**, the persulfoxide **3** postulated in the photooxygenation of diethyl sulfide[6, 24, 25] (Scheme 3) was reexamined. Under the present analytical protocol,[17] the SSO probe again confirmed the highly nucleophilic character (X_{SO} = 1.00) of **3** (entry 6a). Thus, like the carbonyl oxides **2a,b**, **3** is also a nucleophilic oxidant. More significant from the mechanistic standpoint is the fact that the dipolar valence isomer rather than the cyclic dioxirane-type structure intervenes as intermediate in the oxidation of diethyl sulfide by singlet oxygen.

Similarly, reexamination of the photooxygenation of adamantylideneadamantane in the presence of the SSO probe under the new analytical protocol[17] gave predominantly SO oxidation (entry 6b, X_{SO} = 0.88). This nucleophilic oxygen transfer suggests that the postulated perepoxide **4** figures as the oxidizing species.[26a, 27]

Conclusion

In summary, the thianthrene 5-oxide probe is a useful mechanistic tool for assessment of the electronic character of oxygen transfer agents by means of the X_{SO} parameter, for which low values ($X_{SO} < 0.3$) signify electrophilic and high ones ($X_{SO} > 0.7$) nucleophilic oxidative character. In addition, the *trans*/*cis* ratio of bissulfoxides provides information on the stereochemical course of the oxygen transfer process. Of particular mechanistic import is the observation that some carbonyl oxides, for example **2c** and **d**, may photoisomerize to their respective dioxiranes, while the persulfoxide **3** of diethyl sulfide remains as the dipolar valence isomer under the photooxygenation conditions.

Experimental Section

Equipment: IR spectra were recorded on a Perkin–Elmer 1420 ratio-recording infrared spectrophotometer. ^1H and ^{13}C NMR spectra were acquired on a Bruker AC250 spectrometer. The HPLC analyses were carried out on a KONTRON analytical system (T-414 pumps, detector 430 and the data system 450MT/EMS), equipped with a C-18 reversed-phase column (250 × 4.6 mm i.d.; particle size 5 μm) with the ternary solvent mixture of $CH_3OH/H_2O/CH_3CN$ (64:34:2) as eluent. Detection was performed at $\lambda = 254$ nm and the flow rate was 1.2 mL min^{-1} [17].

Materials: All oxidations were run in distilled solvents (CH_2Cl_2 over P_2O_5, MeCN over CaH, MeOH over Mg). $CDCl_3$, acetic acid and trifluoroacetic acid were used without further purification. The concentration of the dioxiranes in the ketone solution was determined iodometrically. Caroate (potassium monoperoxysulfate, the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) for the synthesis of DMD [28], TFD [29,20], and the other dioxiranes [30a] was obtained from Peroxid Chemie (D-82049 Pullach, Germany) and used as received. 1,1,1-Trifluoroacetone, which was usually not contamined by ether, was obtained from FLUKA [30b]. Solutions of dimethyldioxirane, isopropyl(methyl)dioxirane, cyclohexanone dioxirane, and methyl(trifluoromethyl)dioxirane in their respective ketones were prepared according to the published procedures and their peroxide content was determined by iodometry. The dimethyldioxirane solutions were stored over molecular sieves (4 Å) at −20 °C, while the other dioxirane solutions were kept at −20 °C without drying agent. The diazoalkanes were prepared according to standard literature methods [31].

General Procedure for the Oxidation of Thianthrene 5-Oxide (SSO) by Dioxiranes: To a cooled, stirred solution of thianthrene 5-oxide (23.2 mg, 0.100 mmol) in the solvent (ca. 10 mL) (Table 1) was added a dioxirane solution (0.05–0.6 M, 0.2–0.5 equiv). After 1 h the peroxide had been consumed and the solvent was evaporated (40 °C, 12 Torr); the residue was taken up in ethanol/CH_2Cl_2 (1:1 v/v, 5 mL) and analysed by HPLC as described above; the results are summarized in Table 1.

General Procedure for the Oxidation of Thianthrene 5-Oxide (SSO) by *O*-Oxides: Thianthrene 5-oxide (23.2 mg, 0.100 mmol) and catalytic amounts (ca. 1 mg) of rose bengal (RB) were placed in a 25 mL test tube and dissolved in ca. 10 mL of solvent. Several equivalents of the diazoalkane, diethyl sulfide, or adamantylideneadamantane were added and cooled to −20 °C. By means of a Pasteur pipette a constant slow stream of oxygen gas was allowed to pass through the solution under irradiation with two sodium lamps (300 or 500 W). After 2 h the diazoalkane had been consumed, the solvent was evaporated (40 °C, 12 Torr), and the residue was taken up in ethanol/CH_2Cl_2 (1:1 v/v, 5 mL) and analysed by HPLC as described above. The results are summarized in Table 1.

Acknowledgments: We are grateful for generous financial support from the Deutsche Forschungsgemeinschaft (Schwerpunktprogramm "Peroxidchemie: mechanistische und präparative Aspekte des Sauerstofftransfers") and the Fonds der Chemischen Industrie. We thank F. Kita for assistance with the PM3 calculations.

Received: April 25, 1995
Revised version: July 28, 1995 [F126]

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