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Role of Hydrogen Bonding in the Oxidation of Thianthrene 5-Oxide with Peroxy Acids†

Evgen Eržen, Jože Koller, and Božo Plesničar*

Department of Chemistry, Faculty of Chemistry and Chemical Technology, University of Ljubljana,
P.O. Box 537, 1000 Ljubljana, Slovenia

bozo.plesnicar@uni-lj.si.

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The oxidation of thianthrene 5-oxide, i.e., a mechanistic probe for the assessment of the electronic character of various oxidants, with peroxybenzoic acids in various oxygen bases as solvents was investigated. The nucleophilicity (X_{SO}) of peroxy acids was increasing with increasing basicity of the oxygen base. A good linear correlation was observed by plotting X_{SO} values vs either the Kamlet−Taft β values or the OOH ^{1}H NMR chemical shifts of *m*-chloroperoxybenzoic acid (*m*-CPBA) in solvents of various basicity. These observations, together with the results of IR and ^{1}H NMR spectroscopic studies of peroxybenzoic acids, and DFT (B3LYP/6-311++G**) studies of the intramolecular hydrogen bonding in peroxyformic, peroxyacetic, and *m*-CPBA, as well as the intermolecular hydrogen bonding in the complexes of the these peroxy acids with dimethyl ether as a model oxygen base, support the involvement of the peroxy acid−oxygen base complexes in the transition states of these reactions. The increased nucleophilicity (X_{SO}) of peroxy acids in basic solvents is most likely due to the increased negative charge on the terminal “electrophilic” peroxycarboxylic oxygen atom (OH), and/or the increased LUMO and HOMO energies of the peroxy acid in the complexes, as compared to those parameters in the intramolecularly hydrogen-bonded form of peroxy acids, believed to be operative in inert solvents.

Introduction

It has already been reported that solvents with basic oxygen play a crucial role in the oxidation of various organic substrates, i.e., olefins, acetylenes, and sulfides with peroxy acids.[2−7] Whether this is a result of the reduction of concentration of the “effective” intramolecularly hydrogen-bonded form of peroxy acid,[8−10] or the basic solvent actually participates in the transition state of the reaction in the form of the peroxy acid-solvent complex, is still an open question.

We addressed this mechanistic dilemma by studying the effect of “basic” solvents on the X_{SO} values in the oxidation of thianthrene 5-oxide (SSO) with substituted peroxybenzoic acids. Namely, SSO has been introduced by Adam et al. as a mechanistic probe for the assessment of the electronic character of various oxidants.[11,12] In this molecule there are an electron-rich sulfide sulfur as well as an electron-poor sulfoxide group. The electron-rich sulfur is preferentially attacked by electrophilic oxidants to form two diastereoisomeric forms of thianthrene 5,10-dioxide, i.e., the axial approach of the oxidant resulting in more polar trans form (*trans*-SOSO) and the equatorial attack forming the less polar cis form (*cis*-SOSO). On the other hand, nucleophilic oxidants oxidize SSO predominantly to the thianthrene 5,5-dioxide (SSO_2). All these products are susceptible to overoxidation leading to thianthrene 5,5,10-trioxide ($SOSO_2$). However, the

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† Dedicated to Professor Miha Tišler on the occasion of his forthcoming 75th birthday.

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Table 1. Oxidation of Thianthrene 5-Oxide with *m*-Chloroperoxybenzoic Acid and with *m*-Chloroperoxybenzoic Acid−Triphenylphosphine Oxide Complex (*m*-CPBA−TPPO) in Various Solvents

							products[h] (%)			
no.	solvent[a]	β[b,c]	δ[d,e] (ppm)	time[f] (min)	conv	X_{SO}[g]	*trans*-SOSO	*cis*-SOSO	SSO_2	$SOSO_2$
1	CH_2Cl_2		11.50	2	0.47	0.16	66.2	17.9	14.3	1.6
2	$CHCl_3$		11.57	2	0.46	0.13	65.5	20.9	11.9	1.6
3	Me-O-Ph	0.223	11.85	5	0.47	0.19	57.6	23.4	16.9	2.1
4	*i*-Pr-O-*i*-Pr	0.466	12.18	15	0.08	0.18	38.5	43.0	17.6	0.9
5	MeCOOMe	0.454	12.24	3	0.40	0.20	60.6	18.9	17.2	3.4
6	Et-O-Et	0.466	12.39	10	0.46	0.18	55.4	25.8	13.4	5.5
7	Me-O-*t*-Bu		12.38	5	0.48	0.22	56.8	20.8	18.0	4.4
8	THF	0.550	12.82	10	0.38	0.24	55.1	19.6	19.5	5.2
9	$(EtO)_3PO$	0.774	13.37	20	0.26	0.27	49.7	20.4	17.6	12.4
10	DMAA	0.756	14.42	20	0.33	0.30	48.0	17.3	20.1	14.6
11	MeOH	0.620	13.70	10	0.31	0.18	63.9	17.5	15.3	3.3
12	CH_2Cl_2/HMPA (1:0.75)[i,j]			10	0.46	0.16	65.7	18.1	14.0	2.2
13	CH_2Cl_2/HMPA (1:1.25)[i]		13.81	30	0.52	0.16	66.0	17.4	13.9	2.7
14	CH_2Cl_2/HMPA (1:10)[i]		14.78	20	0.30	0.24	52.2	20.4	13.6	13.9
15	CH_2Cl_2/HMPA (1:51)[i]		14.79	30	0.19	0.36	31.6	20.7	15.5	32.2
16	CH_2Cl_2 *m*-CPBA−TPPO		13.21	8	0.41	0.19	60.5	19.9	14.7	5.0
17	Me-O-*t*-Bu *m*-CPBA−TPPO		12.92	20	0.44	0.26	46.4	24.2	17.6	11.7
18	MeCOOMe *m*-CPBA−TPPO		12.83	20	0.41	0.23	53.6	21.3	15.2	9.8

[a] Reaction media, 25 °C. [b] β parameter of solvent basicity (ref 13). [c] β(TPPO) = 0.942, β(HMPA) = 1.054 (ref 13). [d] Chemical shift (downfield from TMS) of peroxyacidic proton in pure nondeuterated solvent (1% solution w/w). [e] $\delta(CCl_4) = 11.61$, δ(HMPA) = 14.77. [f] Experimentally determined reaction time for 35−50% conversion. [g] X_{SO} parameter (see Scheme 1). The reported value is an average of three independent runs; error ± 0.005 units. [h] Determined by HPLC (± 0.5%). [i] Mole ratio *m*-CPBA:HMPA. [j] The OOH absorption was flattened into the baseline.

amount of the undesirable $SOSO_2$ can be minimized by using excess of SSO. On the bases of these observations, the X_{SO} parameter, i.e., mole fraction of nucleophilic-attack products (SSO_2 and $SOSO_2$), ranging from $X_{SO} = 1.00$ for the hydroperoxide anion (HOO^-) as a prototype nucleophilic oxidant to $X_{SO} = 0.05$ for protonated hydrogen peroxide ($H_3O_2^+$) as a prototype electrophilic oxidant, was proposed as a measure of the electronic nature of oxidants.

The results of the present studies showed a relatively strong influence of basic solvents (esters, ethers, amides) on the X_{SO} values. This, together with the results of IR and NMR spectroscopic studies of peroxybenzoic acids, and DFT (B3LYP/6-311++G**, ZPE) studies of the intramolecular hydrogen bonding in peroxyformic, peroxyacetic, and *m*-chloroperoxybenzoic acid, as well as the intermolecular hydrogen bonding in the complexes of these peroxy acids with dimethyl ether as a model oxygen base, supports the involvement of the peroxy acid-oxygen base complexes in the transition states of these reactions.

Results and Discussion

Oxidation of Thianthrene 5-Oxide, and IR and NMR Spectroscopic Studies of Hydrogen Bonding in Peroxybenzoic Acids. The experimental conditions, product distributions, and the calculated X_{SO} values for the oxidation of the SSO probe with *m*-chloroperoxybenzoic acid (*m*-CPBA) in various solvents are collected in Table 1.

It is evident from Table 1 that the nucleophilicity (X_{SO}) of substituted peroxybenzoic acids was increasing with the increasing basicity of the oxygen base used as a solvent. A reasonably good linear correlation was observed by plotting X_{SO} values vs either (a) the OOH ^1H NMR chemical shifts of *m*-chloroperoxybenzoic acid in various basic solvents, or (b) the Kamlet−Taft β values, reflecting hydrogen bond acceptor basicities[13] (Figure 1a and 1b). At the same time, a good linear correlation of β values vs OOH ^1H NMR chemical shifts was also observed (Figure 1c). The slope of plots of a linear dependence between solvent basicity (δ OOH or β scale) and X_{SO} parameter increased with increasing acidity of the substituted peroxybenzoic acid.

The change in the OOH proton chemical shift has already been found to be very sensitive to the change of the acidity of peroxybenzoic acids, as well as to the change of the strength of the oxygen base.[7b,14] Namely, it appears by now well established that peroxy acids exist in "inert" solvents in the form of intramolecularly hydrogen-bonded chelates.[15] On the other hand, the solvated forms of the peroxy acid were already suggested to be predominant in solution where oxygen bases (B) are used as solvents (Scheme 1).[7] Additional support for the presence of 1:1 adducts of peroxy acids in solutions with oxygen bases as solvents comes from the actual isolation of the intermolecularly hydrogen bonded 1:1 complexes between peroxybenzoic acids and triphenylphosphine oxide and triphenylarsine oxide, respectively.[16] Namely, their structure has recently been confirmed by X-ray crystallography.[17]

Although intramolecular hydrogen bonding in peroxy acids (inert solvents) has already been proven by IR spectroscopy, there are no reports found in the literature

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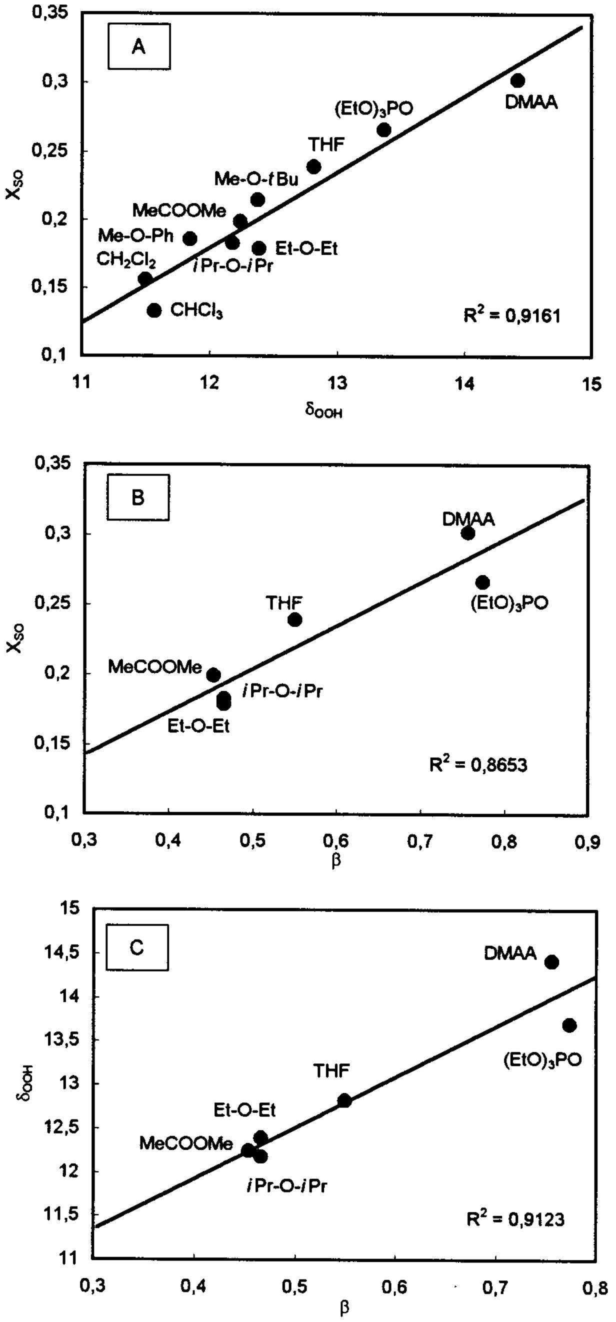

Figure 1. Plot of (A) X_{SO} values for the oxidation of thianthrene 5-oxide with *m*-chloroperoxybenzoic acid (*m*-CPBA) vs the OOH ^{1}H NMR chemical shift (δ) of *m*-CPBA in various solvents; (B) X_{SO} values vs the solvent β parameter; C) the OOH ^{1}H NMR chemical shift (δ) of *m*-CPBA in various solvents vs the solvent β parameter.

of systematic studies of the complexation of peroxy acids with oxygen bases by using this technique. Therefore, to confirm the crucial role of the complexation of peroxy acids with oxygen bases in the oxidation of SSO, we performed a series of experiments by adding various amounts of hexamethylphosphoramide (HMPA), a relatively strong oxygen base ($\beta = 1.054$), to the solutions of *m*-CPBA in CH$_2$Cl$_2$. At a molar ratio HMPA:*m*-CPBA as low as 4:1, the predominant form of the peroxy acid was the complex HMPA−PBA, as characterized by the C═O frequency shift from 1736 to 1760 cm^{-1}. At a molar ratio HMPA:*m*-CPBA of 50:1, the complexed peroxy acid was found to be the only form present in the solution. The observed OOH ^{1}H NMR chemical shift of 14.78 ppm, i.e., identical with that in pure HMPA, additionally supported these observations. The oxidation of SSO with such solutions of the peroxy acid gave the X_{SO} value of 0.36, the highest measured for *m*-CPBA in basic solvents. Similar observations were also made by studying the IR spectra of solutions of *m*-CPBA in CH$_2$Cl$_2$ with progressively increasing amounts of *N*,*N*-dimethylacetamide (DMAA) added (see Figure 2).

It is interesting to note that, when SSO was oxidized with solutions of *m*-chloroperoxybenzoic acid−triphenylphosphine oxide complex (*m*-CPBA−TPPO) in inert or basic solvents (Table 1, entries 16−18), X_{SO} values were similar to those obtained in the oxidations with *m*-CPBA in these solvents. The IR and NMR spectroscopic studies indicated that in inert solvents the hydrogen-bonded *m*-CPBA−TPPO complex partially dissociated into the intramolecuraly hydrogen-bonded form of the peroxy acid (the predominant form present in the solution), which was in equilibrium with the complexed form. In basic solvents, on the other hand, a rapid solvent-assisted equilibrium between the *m*-CPBA−TPPO complex and the intermolecularly hydrogen-bonded peroxy acid−oxygen base (solvent) complexes occurred, with the latter forms of the peroxy acid found to predominate in such solutions.

In general, longer reaction times were needed for comparable conversion of SSO to the oxidized products when stronger bases were used as solvents. However, the oxidation was much faster when methanol was used as solvent. The X_{SO} parameter was lower (0.18) than expected on the basis of the basicity of methanol alone (β = 0.62). As already reported previously,[4,9] methanol is capable of acting as a bifunctional catalyst, and thus most likely participates in the transfer of proton during the peroxy acid oxidation of SSO.

An excellent Hammett correlation for the oxidation of SSO with substituted peroxybenzoic acids (log X_{SO} vs σ) in chloroform with the reaction constant $\rho = -0.107$ was observed (Figure 3). This value is in excellent agreement with $\rho = -0.099$ (CH$_2$Cl$_2$), reported previously by Adam et al.[12] However, in *tert*-buthyl methyl ether as a basic solvent, the reaction was found to be somewhat more sensitive to the electronic effect of substituents ($\rho = -0.112$, and Table S1 in Supporting Information).

Still another feature of these reactions is worth mentioning. Namely, in a series of alkyl-substituted benzenes used as solvents, no significant variation of X_{SO} values was detected. The OOH ^{1}H NMR chemical shifts for *p*-nitroperoxybenzoic acid were completely concentration independent in all the solvents investigated, indicating the presence of the intramolecularly hydrogen-bonded form of the peroxy acid in these solvents. We found, however, that the *trans*-SOSO to *cis*-SOSO ratio, denoted as the X_{tc} parameter, was decreasing with increasing number and size of alkyl substituents on the benzene ring (Table 2). The X_{tc} parameter correlates well with both the Charton's sterical parameters (υ),[18] as well as with the recently introduced ligand repulsive energies (E_R)[19] (Figure 4a and 4b). If we anticipate that these substituent parameters are additive for polysubstituted benzenes, *p*-xylene also fits well into the correlation.

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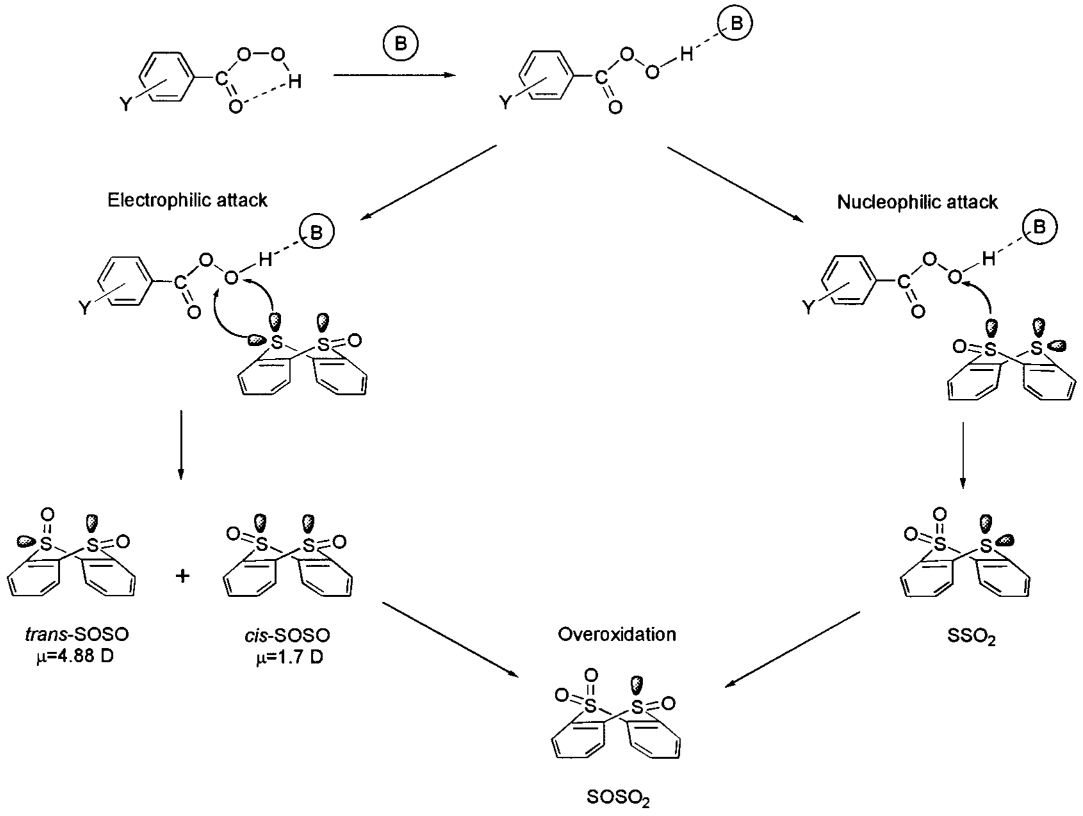
Scheme 1



$$X_{SO} = \frac{n(SO)}{n(S)+n(SO)} = \frac{n(SSO_2)+n(SOSO_2)}{(n(cis\text{-}SOSO)+n(trans\text{-}SOSO)+n(SSO_2))+(n(SSO_2)+n(SOSO_2))}$$

A plausible explanation for the above-mentioned phenomena could be a $\pi-\pi$ interaction between SSO and the benzene ring of the solvents, i.e., face-to-face (or point-to-face) orientation.[20] The former type of interaction is shown in Scheme 2. In both types of orientation of the solvent around the substrate, the axial but not the equatorial approach of the oxidant to the electron pair on the sulfide sulfur atom would be hindered. This hindrance would increase with the increasing number and size of the alkyl groups on the benzene ring.

Theoretical Studies of Hydrogen Bonding in Peroxy Acids. Several attempts have been made in the past to evaluate theoretically the strength of the intramolecular hydrogen bonding in peroxy acids. By using ab initio methods with minimal and extended basis sets as well as the calculations at the MP2/6-31G* level of theory, values ranging from 1 to 7 kcal/mol have been reported for peroxyformic and peroxyacetic acid.[21] To determine the strength of the intramolecular hydrogen bonding, we used density functional theory at the B3LYP/6-311++G** (+ZPE) level[22] to calculate the energies of the intramolecularly hydrogen-bonded and the most stable open form of peroxyformic, peroxyacetic, and *m*-CPBA, respectively. Namely, the energy difference between the two forms can be taken as a reasonable measure of the strength of the hydrogen bonding in these species.[23] The results of the calculations are collected in Table 3.

The strength of the intramolecular hydrogen bonding in the peroxy acids under investigation was increasing in going from peroxyformic to *m*-chloroperoxybenzoic acid (HCO_3H (2.01 kcal/mol) < CH_3CO_3H (3.37 kcal/mol) < *m*-CPBA (3.77 kcal/mol). The calculations at the B3LYP/6-311++G** level of theory appear to be a reliable method for treating these systems since a comparable value (2.28 kcal/mol, without ZPE) for the H-bonding energy in peroxyformic acid was calculated at the CCSD(T)/6-311++G** level. At the same time, the calculated equilibrium geometry and dipole moment of the most stable intramolecularly hydrogen-bonded form of peroxyformic acid (1.428 D, B3LYP/6-311++G**) and peroxyacetic acid (2.493 D, B3LYP/6-311++G**) were in excellent agreement with the experimentally determined values of electric dipole moments (HCO_3H, 1.398 D, MW;[21e] CH_3CO_3H, 2.384 D, MW[24]).

Some interesting observations were made by studying structural features of *m*-CPBA, i.e., at present the most widely used commercially available peroxy acid. Two

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[20] For two recent studies of this type of interactions, see: (a) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217. The gas-phase simulation revealed that, the face-to-face interaction (the sandwich arrangement) of the toluene dimer was preferred over the point-to-face interaction (the T-shaped structure) by 0.71 kcal/mol. (b) Laatikainen, R.; Ratilainen, J.; Sebastian, R.; Santa, H. *J. Am. Chem. Soc.* **1995**, *117*, 11006.

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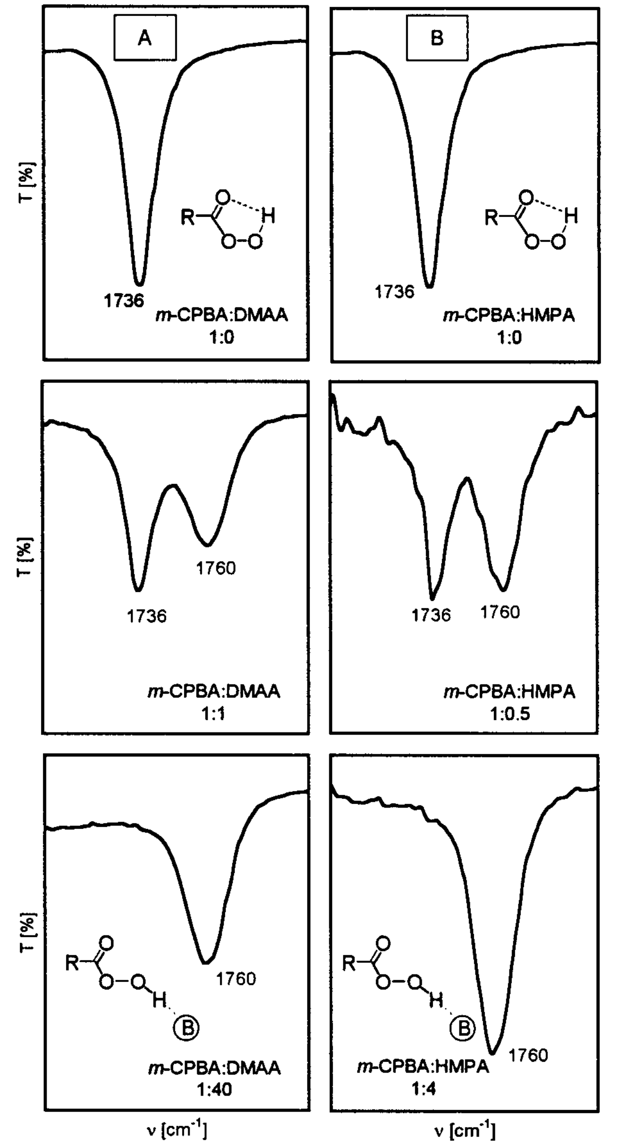

Figure 2. Infrared spectra (1700−1800 cm^{-1}) of *m*-chloroperoxybenzoic acid (*m*-CPBA) in CCl_4 (0.5%, w/w) with various amounts of oxygen base added: (A) *N*,*N*-dimethylacetamide (DMAA), (B) hexamethylphosphoramide (HMPA). Molar ratio, m-CPBA: oxygen base, is shown on each individual spectrum.

conformations of the intramolecularly hydrogen-bonded form of the peroxy acid of very similar energy (ΔE_{A-B} = 0.085 kcal/mol, see Supporting Information) were calculated, with the conformer with the lower dipole moment to be slightly more stable. The same also holds for the most stable open form of the peroxy acid (ΔE_{C-D} = 0.133 kcal/mol, see Supporting Information). Again, the experimentally determined dipole moment of 2.44 D[25] agrees well with the calculated value of 2.616 D for the intramolecularly hydrogen-bonded form.

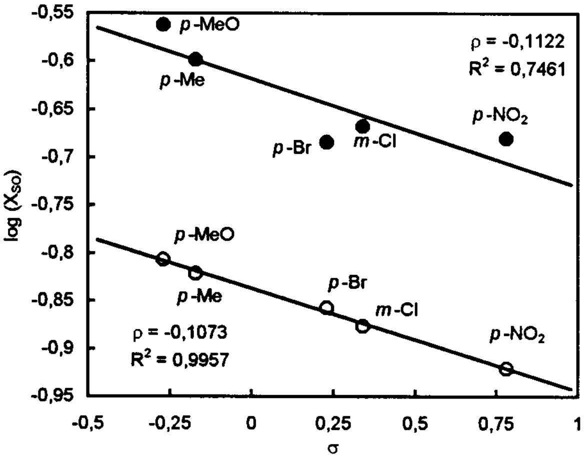

Figure 3. Plot of log(X_{SO}) values for the oxidation of thianthrene 5-oxide with substituted peroxybenzoic acids vs Hammett σ constants in $CHCl_3$ (○), and Me-O-*t*-Bu (●).

The peroxy acids under investigation form relatively strongly bonded complexes with dimethyl ether (DME), taken as a model oxygen base. The strength of the intermolecular hydrogen bond (the energy difference between the complex and the sum of energies of the most stable open form of the peroxy acid and DME) increased in the order: CH_3CO_3H (6.87 kcal/mol) < HCO_3H (7.37 kcal/mol) < *m*-CPBA (8.67 kcal/mol).[26] The optimized structures of the peroxy acid−DME complexes are shown in Figure 5. The OH···O bond distance follows the strength of the interaction with the shortest intermolecular hydrogen bonding in the complex *m*-CPBA−DME. However, when the energy of the chelated form of the peroxy acid was taken into account in the calculation of the binding energies, the following order the hydrogen-bond strength was found: CH_3CO_3H (3.49 kcal/mol) < *m*-CPBA (5.00 kcal/mol) < HCO_3H (5.36 kcal/mol). This is also the order expected on the basis of the acidity of the peroxy acids, i.e., CH_3CO_3H (pK_a, 8.2) < *m*-CPBA (7.60) < HCO_3H (7.1).[27] The calculated binding energies are also in very good agreement with experiment. Namely, the previously reported calorimetrically determined enthalpy of the hydrogen-bonded complex fomation between *p*-chloroperoxybenzoic acid (pK_a, 7.67) and di-*n*-butyl ether in carbon tetrachloride (4 kcal/mol) is the sum of two contributions, i.e., an endothermic opening of the chelate ring in the intramolecularly hydrogen-bonded form of the peroxy acid, and an exothermic contribution due to the formation of the intermolecularly hydrogen-bonded complex.[7b]

By comparing the net atomic charge (Mulliken populations) on the “electrophilic” oxygen atom (O_4, −0.257 e) of the OH group in *m*-CPBA−DME complex with that on the same atom in the intramolecularly hydrogen-bonded form of the peroxy acid (−0.084 e), it is evident that the intermolecular hydrogen bond formation forces a moderately large negative charge on the OH atom. Similar observations were also made in other peroxy acid−DME complexes under investigation.

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(26) One of the reviewers indicated that since the strength of the hydrogen bond was obtained as the energy difference between species with very different dipole moments, solvent effects could have a dramatic influence. Our preliminary studies of the effect of solvent with dielectric constant ϵ of 4.335 (diethyl ether) on the strength of the interaction between the peroxy acid and DME by using the polarized continuum model, developed by Tomasi and co-workers (Miertus, S.; Scrocco, E.; Tomasi, J. *Chem. Phys.* **1981**, *55*, 117.*GAUSSIAN98*), indicated that although the calculated binding energies (BE) were somewhat lower as compared to the values in the gas phase, the trend of the strength of the hydrogen bonds in the two peroxy acid-DME complexes under investigation remained the same. (B3LYP/6-311++G**, complete optimization: HCO_3H-DME, BE = 6.65 kcal/mol; CH_3CO_3H-DME, BE = 6.42 kcal/mol (without ZPE)).

(27) (a) Everett, A. J.; Minkoff, G. J. *Trans. Faraday Soc.* **1953**, *49*, 410. (b) Goodman, J. F.; Robson, P.; Wilson, E. R. *Trans. Faraday Soc.* **1962**, *58*, 1846.

Table 2. Charton's υ Parameters, Repulsive Energies (E'_R (Me)), X_{SO} and X_{tc} Parameters, and δ (^1H NMR) OOH Chemical Shifts of Substituted Peroxybenzoic Acids in Substituted Benzenes

	oxidant			*p*-NO$_2$-PBA			*o*-NO$_2$-PBA			*m*-Cl-PBA		
no.	solvent[a]	υ[b]	E'_R (Me)[c]	δ[d]	X_{SO}	X_{tc}[e]	δ[d]	X_{SO}	X_{tc}[e]	δ[d]	X_{SO}	X_{tc}[e]
1	C_6H_6	0.00	0	11.07	0.20	2.45	10.78	0.14	1.30	11.19	0.17	2.17
2	C_6H_5Me	0.52	20	11.04	0.20	2.07		0.15	1.12		0.18	1.89
3	$C_6H_4Me_2$	1.04	40	11.04	0.20	1.66		0.15	0.95		0.20	1.62
4	C_6H_5-*i*-Pr	0.76	34	11.07	0.21	1.81		0.15	1.00		0.20	1.62
5	C_6H_5-*t*-Bu	1.24	43		0.20	1.65		0.15	0.97		0.19	1.52
6	$C_6H_3Me_2$*t*-Bu				0.19	1.48		0.16	0.91		0.19	1.28
7	$C_6H_5CF_3$	0.91	17		0.24	2.65	11.58	0.21	1.93		0.247	2.71
8	C_6H_5Cl	0.55			0.22	2.69						

[a] Substituted benzenes used as solvents, 25 °C. [b] Charton's steric parameter (ref 18). [c] Ligand repulsive energies (in kcal/mol) for the methyl (Me) group as prototypical fragment (ref 19). [d] Chemical shift (downfield from TMS) of the peroxyacidic proton in pure nondeuterated solvent (1%, w/w). [e] X_{tc} = *trans*-SOSO/*cis*-SOSO. The reported value is an average of three independent runs; error ± 0.05 units.

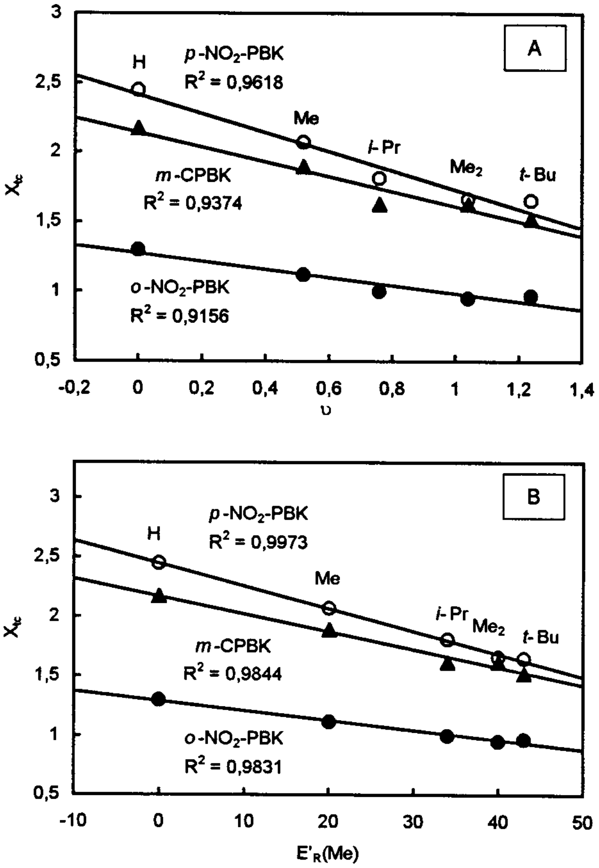
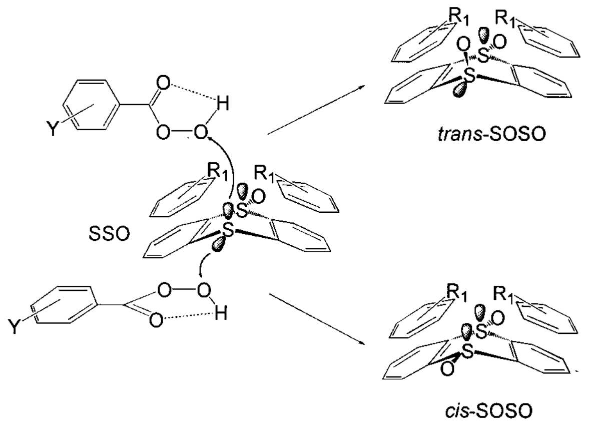


Figure 4. Plot of X_{tc} values for the oxidation of thianthrene 5-oxide with substituted peroxybenzoic acids vs (A) the Charton's steric parameter (υ) of alkyl substituents, and (B) vs the ligand repulsive energies, E'_R (kcal/mol) of alkyl substituents on the benzene ring of the solvent.

We believe that the increased nucleophilicity (X_{SO} values) in solvents of progressively increasing basicity (β) is the result of an increasing negative charge on the "electrophilic" oxygen atom of the OH group in peroxy acid−oxygen base complexes, which most likely participate in the transition states of these reactions. Although, the theoretical studies of oxidations of even the simplest substrates with such complexes are at present beyond our computational capabilities, it is nevertheless indicative to note that the LUMO and HOMO of *m*-CPBA in the complex with DME are significantly higher (LUMO, −1.969 eV; HOMO, −7.249 eV) compared to that of the free peroxy acid (LUMO, −2.406 eV; HOMO, −7.540 eV). In terms of the recently introduced quantum-chemical probe for the elucidation of the electronic character of oxygen-transfer reactions,[28] the "back-donation", i.e., the interaction among the occupied orbitals of the oxidant and the vacant orbitals of the substrate, is becoming increasingly more pronounced in more basic solvents.

Scheme 2



$$X_{tc} = \frac{trans\text{-}SOSO}{cis\text{-}SOSO}$$

Conclusions

Our IR and ^1H NMR spectroscopic and DFT (B3LYP/6-311++G**) studies revealed that *m*-chloroperoxybenzoic acid exists in inert solvents exclusively in the form of the intramolecularly hydrogen bonded chelates. Esters, ethers, and amides (oxygen bases) used as solvents are capable of disrupting the chelated peroxycarboxyl ring to form intermolecularly hydrogen-bonded peroxy acid−oxygen base complexes as the only entities detected in such solutions.

The increased nucleophilicity (X_{SO}) of peroxybenzoic acids in the oxidation of SSO, when going from inert solvents to solvents of increasing basicity, is most likely due to the increased negative charge on the "electrophilic" oxygen atom of the OH group of the peroxy acid−oxygen base complexes and/or the increased LUMO and HOMO energies of the peroxy acid in such complexes, as compared to those parameters in the intramolecularly hydrogen-bonded form of the peroxy acid present in inert solvents. Therefore, the reduced reactivity of peroxy acids against thianthrene 5-oxide (and most likely other substrates as well) in oxygen bases as solvents is most prob-

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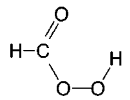
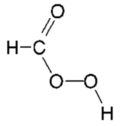
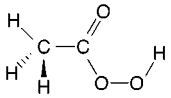
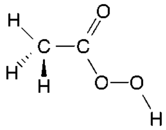
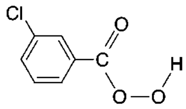
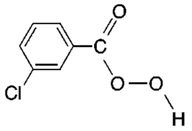
Table 3. The B3LYP/6-311++G Optimized Equilibrium Geometries (bond lengths (Å) and angles (deg)), Total Energies (au, ZPE), and Dipole Moments of Peroxyformic, Peroxyacetic, and *m*-Chloroperoxybenzoic Acid**

bond lengths (Å) and angles (deg)					 (A)	 (D)
H−C (C−C)	1.096 (1.098)[b]	1.101 (1.103)[b]	1.501	1.511	1.483[a]	1.496[a]
C=O	1.202 (1.207)[b]	1.189 (1.195)[b]	1.209	1.194	1.212	1.197
C−O	1.343 (1.348)[b]	1.357 (1.363)[b]	1.355	1.371	1.356	1.370
O−O	1.441 (1.448)[b]	1.453 (1.458)[b]	1.441	1.452	1.436	1.447
O−H	0.982 (0.979)[b]	0.969 (0.967)[b]	0.984	0.969	0.985	0.969
OH···O	1.950		1.893		1.875	
∠HCO	127.2 (127.3)[b]	127.3 (127.3)[b]			126.2	125.9
∠OCO	124.4 (124.5)	127.6 (127.3)	121.7	124.5	121.4	124.2
∠COO	111.8 (110.7)	110.5 (109.0)	111.7	110.3	111.5	109.8
∠OOH	100.8 (101.6)	97.9 (97.4)	100.9	97.9	101.0	97.9
∠OCOO	0	0	0	0	0	0
E	−264.936026 (−264.371248)[c]	−264.932825 (−264.367615)[c]	−304.247101	−304.241723	−955.607114	−955.601105
Δ*E* [kcal/mol][d]	2.01 (2.28)		3.37		3.77	
μ [D]	1.428 (1.680)	3.106	2.493	3.465	2.616	1.940

[a] For complete geometrical parameters, see Figure S1 in Supporting Information. [b] CCSD(T)/6-311++G**. [c] CCSD(T)/6-311++G** total energies without zero point energy correction. [d] The energy difference between the intramolecularly hydrogen-bonded and the most stable open form of the peroxy acid.

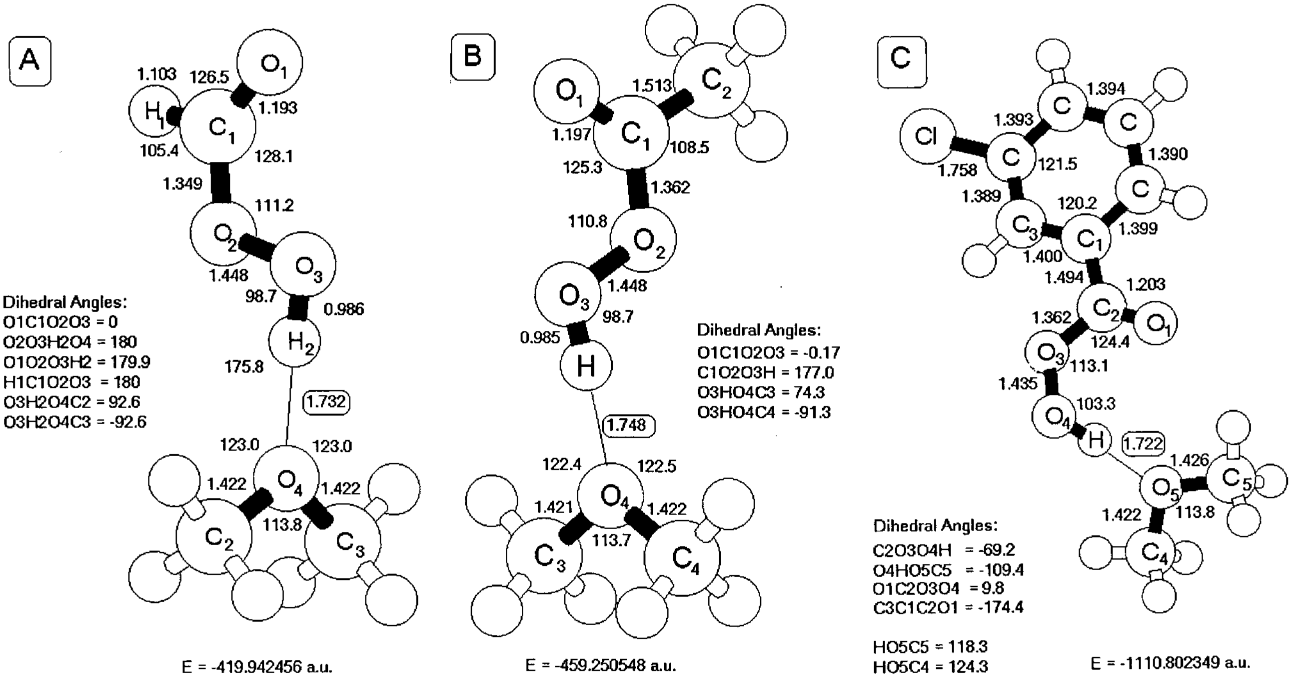


Figure 5. The B3LYP/6-311++G** optimized structures of the peroxy acid−dimethyl ether (DME) complexes: (A) peroxyformic acid−DME, (B) peroxyacetic acid−DME, (C) *m*-chloroperoxybenzoic acid−DME. Dimethyl ether (DME): C−O, 1.413 Å; C−O−C, 112.7 °; *E* = −154.997881 au.

ably not the result of the reduced concentration of the "effective" intramolecularly hydrogen-bonded form of peroxy acid in basic solvents, but is rather due the decreased reactivity (increased nucleophilicity) of the peroxy acid-oxygen base complexes, believed to be involved in the transition states of these reactions. Since there are often many "basic" entities present in oxidations of various substrates with peroxy acids, it is quite probable that in all such systems the Bartlett ("butterfly")[29] mechanism (involving the intramolecular 1,4-proton transfer in the chelated peroxy acid) is not the only (or even a necessary) mechanistic possibility available.

Experimental Section

Instrumentation and Materials. Gas chromatography was performed on a GC/MS instrument (electron-impact ion source) equipped with HP5-MS capillary column (30 m). ^{1}H NMR spectra were obtained at 300.1 MHz and 302 K on a spectrometer equipped with variable-temperature probe (IBB probe, temperature stability ±0.1K). Infrared (IR) spectra of solutions under investigation were recorded with the use of demountable liquid cell (0.2 mm path length, NaCl windows).

The HPLC analysis were performed on an isocratic HPLC chromatograph equipped with a C-18 reversed-phase column (Spherisorb S10 ODS2, 250 × 4.6 mm). Elution and detection of the oxidation products were carried out by following literature procedure (mobile phase: MeOH/H_2O/MeCN: 64/32/2, flow rate 1.25 mL/min, UV detector at 254 nm).[11f] Retention times and relative absorption coefficients of SSO and its oxidation products (*trans*-SOSO, *cis*-SOSO, SSO_2, $SOSO_2$) were determined with authentic samples kindly provided by Professor Waldemar Adam. X_{so} values, relative proportions of the oxidation products and *trans*-SOSO/*cis*-SOSO ratios (X_{tc} values) were calculated according to the equations cited in Schemes 1 and 2.

All the solvents used were the purest commercial products and were purified according to the literature procedures. Their purity was checked by GC/MS. Solvents used in IR spectroscopic studies were kept over molecular sieves (5 Å).

Thianthrene 5-oxide (SSO) was prepared by the oxidation of the commercially available thianthrene (99%, Aldrich) with acidified H_2O_2 (70% water solution) in methanol according to the following procedure. A solution of H_2O_2 (3.50 g, 72.06 mmol) in methanol (150 mL), acidified with catalytic amount of $HClO_4$ (ca. 1 mL), was slowly added to a cold (0 °C) stirred suspension of thianthrene (12.53 g, 58.01 mmol) in methanol (230 mL). The reaction mixture was stirred at room temperature for 3 days. Reaction progress was monitored twice a day by HPLC with a mixture of MeOH/H_2O/Et_2O (85/13/2, flow rate 1.25 mL/min) used as a mobile phase (retention times: SSO_2, *cis*-SOSO, *trans*-SOSO, $SOSO_2$ 2.15−2.55 min; SSO 3.31 min; SS 6.44 min). Suspension was then refluxed for 1 day until all the suspended thianthrene disappeared. The precipitate, which was formed during cooling to room temperature, was dissolved with addition of diethyl ether (200 mL). The solution was then washed with water (100 mL), saturated solution of $NaHCO_3$ (100 mL), diluted solution of $NaHSO_3$ (100 mL), and again with water (2 × 100 mL). The organic phase was separated and dried over anhydrous Na_2SO_4. The solvent was evaporated at rotary evaporator. The purification of a crude product (92% pure by HPLC) was performed on a medium-pressure liquid chromatograph ("flash" chromatograph) under isocratic conditions with a silica gel normal-phase column (Aldrich, 70−270 mesh, 230 × 36 mm). Dichloromethane was used as a mobile phase (flow rate 14.5 mL/min, UV detector at 254 nm). SSO was collected as a medium section of a broad peak with initial retention time of around 30 min. Starting from 0.4100 g of crude SSO, dissolved in 10 mL of CH_2Cl_2, 0.1910 g of pure SSO (99.5% by HPLC) was obtained.

m-Chloroperoxybenzoic acid (*m*-CPBA) and *p*-nitroperoxybenzoic acid (*p*-NO_2-PBA) were commercial products (Fluka). *o*-Nitroperoxybenzoic acid (*o*-NO_2-PBA) and *p*-bromoperoxybenzoic acid (*p*-Br−PBA) were prepared by the procedure of Silbert et al.[30] *p*-Methoxyperoxybenzoic acid (*p*-MeO-PBA) and *p*-methylperoxybenzoic acid (*p*-Me-PBA) were prepared from the corresponding benzoyl chlorides and sodium peroxide according to the literature procedure.[31] All peroxybenzoic acids were purified by washing with phosphate buffer (pH ca. 7.5) and distilled water and by subsequent crystallization from pentane/diethyl ether (3 /1). The purity of the peroxy acids was always over 99% (by iodometry).

Complexes of *m*-chloroperoxybenzoic acid and *p*-nitroperoxybenzoic acid with triphenylphosphine oxide (*m*-CPBA−TPPO and *p*-NO_2-PBA−TPPO) were prepared and purified as described previously.[16]

General Procedures for the Oxidation of Thianthrene 5-Oxide with Substituted Peroxybenzoic Acids and the *m*-Chloroperoxybenzoic Acid−Triphenylphosphine Oxide Complex (*m*-CPBA−TPPO). To a stirred solution of SSO (11.5 mg, 0.05 mmol) in 3 mL of the selected solvent was added 0.025 mmol of substituted peroxybenzoic acid or the complex (mole ratio of 2:1). The solution was vigorously stirred at room temperature until ca. 25−50% conversion of SSO. The reaction mixture was neutralized with saturated aqueous solution of $NaHCO_3$ (15 mL), and the oxidation products were then extracted with CH_2Cl_2 (15 mL). The organic layer was dried over anhydrous Na_2SO_4. After the solvent was evaporated, the residue was taken up in methanol and analyzed by HPLC.

Methods of Calculation. Ab initio density functional calculations were performed using the B3YLP hybrid functional as implemented in *GAUSSIAN98* with 6-311++G** basis set to fully optimize the various conformers of molecules under investigation.[32,33] The nature of each critical point was characterized by computing the harmonic vibrational frequencies. The calculated zero-point energy (ZPE) corrections were used without scaling. CCSD(T) theory[32,34] was used for the geometry optimization of the various conformers of peroxyformic acid.

Acknowledgment. Financial support for this project by the Ministry of Science and Technology of the Republic of Slovenia is gratefully acknowledged.

Supporting Information Available: Tables S1 and S2, containing additional experimental data on the oxidation of thianthrene 5-oxide (SSO) with substituted peroxybenzoic acids, and Figure S1, containing the B3LYP/6-311++G** optimized energies and geometries of four conformers of *m*-chloroperoxybenzoic acid (*m*-CPBA). This material is available free of charge via the Internet at http://pubs.acs.org.

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