

# A Theoretical Study on the Reaction of Phosphadioxiranes and Thiadioxiranes; Disproportionation versus Epoxidation

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The transition structures for the epoxidations of ethylene and the disproportionations by the dioxiranes of phosphines, phosphites and sulfides were studied with density function theory methods using the Becke3LYP functional and 6-311+G(2d,p) basis set. When the dioxiranes have methyl substituents rather than hydrogen substituents, the reaction barriers ( $E_{TS}$ ) become higher in their epoxidations of ethylene by the steric hindrance, but become lower in their disproportionations of phosphines, phosphites and sulfides, which indicates that the nature of the dioxiranes seems to be electrophilic and in their disproportionations the reaction barriers are effected both by the electrophilicity and the steric hindrance. The steric factors in the disproportionations were calculated and more bulky substituents at dioxiranes may be necessary to retard the disproportionation and to enhance the epoxidation.

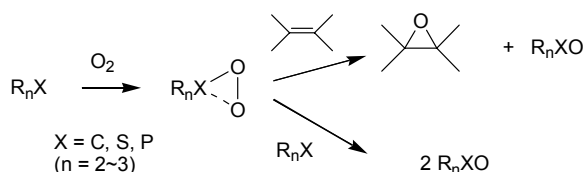
**Key Words:** Phosphadioxiranes, Thiadioxiranes, Computation, Disproportionation, Epoxidation

## Introduction

Dioxiranes of phosphines, phosphites and sulfides are reactive organic peroxides.<sup>1</sup> Structures of the dioxiranes  $XO_2$  are either cyclic triangular forms or acyclic forms. Dioxiranes of phosphines and phosphites are cyclic forms<sup>2</sup> and those of sulfides are expected to be both cyclic and acyclic forms.<sup>3</sup> They are easily formed from phosphines, phosphites and sulfides with singlet molecular oxygen, and are intermediates in reactions; during the generation process they further disproportionate *in situ* and share one oxygen with phosphines, phosphites and sulfides to form phosphine oxides, phosphates, and sulfoxides, respectively<sup>1</sup> (Scheme I). Some of them were isolated and characterized via the spectroscopic ways.<sup>1a,4c</sup>

Another reaction pathway of dioxiranes is the epoxidation of olefins, which competes with the *in situ* disproportionation.<sup>4</sup> Similar epoxidation by carbodioxiranes (C-O-O) are well studied and they are widely used in the synthetic chemistry,<sup>5</sup> probably because the carbodioxiranes are rather stable and do not undergo the *in situ* disproportionation. However, the reactivity of dioxiranes of phosphorous and sulfur molecules in the disproportionation and the epoxidation is not clearly elucidated.

If the epoxidations by the dioxiranes are utilized, they would be useful organic oxidants in synthetic chemistry. Here we present a theoretical study on the *in situ* disproportionation and the epoxidation of olefins with the dioxiranes of phosphines, sulfides and phosphites. We will compare the reactivities of both reactions and discuss the possibility of the dioxiranes as the epoxidizing agents.



Scheme 1

## Computational Details

All calculations were performed with GAUSSIAN 03 package.<sup>6</sup> Geometry optimizations were carried out by using density functional theory, the Becke3LYP functional and the 6-31G\*, 6-311+G(2d,p) basis sets. The target molecules are  $H_3P$  and  $(CH_3)_3P$ ,  $(HO)_3P$ ,  $(CH_3O)_3P$ ,  $H_2S$ , and  $(CH_3)_2S$  and their dioxiranes.

Calculations with MP2 method and the same basis sets were repeated for the disproportionation and the epoxidation of ethylene by dioxiranes of sulfides which give the acyclic peroxide intermediates rather than the cyclic dioxiranes at B3LYP.<sup>1</sup>

The target transition states were located for the disproportionation between the dioxiranes and the corresponding phosphines or phosphites or sulfides and for epoxidation of ethylene with the dioxiranes. Frequency calculations have been carried out for all the transition structures to ensure the presence of only one imaginary frequency corresponding to the bond forming and bond breaking. By the analysis of certain bond lengths of the transition structures which compares with the products, the conversions were estimated; ethylene to ethylene oxide, phosphines to phosphine oxides, *etc.* The optimized reactants were also checked by frequency calculations to confirm that they are minima.

## Results and Discussion

The RHF results are slightly different from those of B3LYP and MP2, but the differences depending on the basis sets are not significant. We will discuss the geometries and energetics at B3LYP/6-311+G(2d,p) (Table 1). The dioxiranes have previously been calculated and the present calculation also gave nearly the same results.<sup>1</sup> The dioxiranes of phosphorous and sulfur are calculated to have a cyclic  $H_3P-O-O$  (**PINHO**),  $(HO)_3P-O-O$  (**PITHO**) or  $H_2S-O-O$  (**SIDHO1**) structures (about 60 ~ 70 degree angles of X-O-O) similar to the cyclic  $H_2C-O-O$  of carbodioxiranes (**DHDO**), except sulfides have

**Table 1.** Geometric parameters of various dioxiranes and their transition states at B3LYP/6-311+G(2d,p). (lengths in Å, angles in degree).

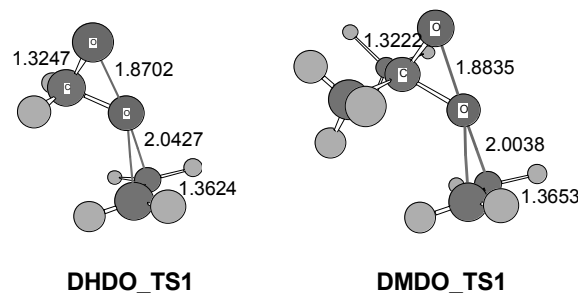
Dioxiranes	TS	d(X-O)	d(O-O)	d(O--X)	a(X-O-O)
$\text{H}_2\text{CO}_2$		1.3896	1.5028	-	57.3
	<b>DHDO_TS1</b>	1.3247	1.8702	2.0427	50.6
$\text{Me}_2\text{CO}_2$		1.4028	1.5025	-	57.6
	<b>DMDO_TS1</b>	1.3222	1.8835	2.0038 <sup>a</sup>	52.7
$\text{H}_3\text{PO}_2$		1.5996	1.5629	-	65.2
	<b>PINH_TS1</b>	1.5499	1.8260	2.1389 <sup>a</sup>	65.0
	<b>PINH_TS2</b>	1.5712	1.7334	2.2709	64.2
$\text{Me}_3\text{PO}_2$		1.6081	1.5443	-	67.7
	<b>PINM_TS1</b>	1.5395	1.7686	2.1381 <sup>a</sup>	80.4
	<b>PINM_TS2</b>	1.5823	1.6859	2.3933	67.2
$(\text{HO})_3\text{PO}_2$		1.5856	1.5541	-	66.0
	<b>PITH_TS1</b>	1.5268	1.8147	2.1610 <sup>a</sup>	72.6
	<b>PITH_TS2</b>	1.5611	1.6895	2.2378	69.4
$(\text{MeO})_3\text{PO}_2$		1.5924	1.5496	-	65.7
	<b>PITM_TS1</b>	1.5382	1.8004	2.1479 <sup>a</sup>	66.1
	<b>PITM_TS2</b>	1.5565	1.7076	2.2964	67.7
$\text{H}_2\text{SO}_2$	<b>(dioxirane)</b>	1.5824	1.5383	-	77.6
	<b>SIDH1_TS1</b>	1.5615	1.7172	2.2851 <sup>a</sup>	78.2
	<b>SIDH1_TS2</b>	1.5605	1.7404	2.3309	77.1
$\text{Me}_2\text{SO}_2$	<b>(dioxirane)</b>	1.5798	1.5295	-	84.2
	<b>SIDM1_TS1</b>	1.5568	1.7022	2.2835 <sup>a</sup>	87.7
	<b>SIDM1_TS2</b>	1.5669	1.6602	2.5138	82.6
$\text{H}_2\text{SO}_2$	<b>(peroxy)</b>	1.5645	1.4655	-	101.9
	<b>SIDH2_TS1</b>	1.5405	1.6404	2.1647 <sup>a</sup>	99.8
	<b>SIDH2_TS2</b>	1.5362	1.6740	2.2035	99.0
$\text{Me}_2\text{SO}_2$	<b>(peroxy)</b>	1.6084	1.4465	-	109.4
	<b>SIDM2_TS1</b>	1.5552	1.6407	2.1274 <sup>a</sup>	106.8
	<b>SIDM2_TS2</b>	1.5567	1.6360	2.2482	105.6

<sup>a</sup>averaged values of two d(O--X).

one additional intermediate, persulfoxides, of the angle of ~110 degree (**SIDHO2**).

### Geometries

**Carbodioxiranes.** The carbodioxiranes have  $C_{2v}$  symmetry and both oxygen atoms are equivalent. The C-O bond of and dihydrogendioxirane (**DHDO**) and dimethyldioxirane (**DMDO**) is 1.3896 Å and 1.4028 Å.<sup>7</sup> The transition state (**DHDO\_TS1**) for the epoxidation of ethylene with **DHDO** has a d(C-O) of

**Figure 2.** Transition states of the epoxidation of **DHDO** and **DMDO** with ethylene (length in Å).

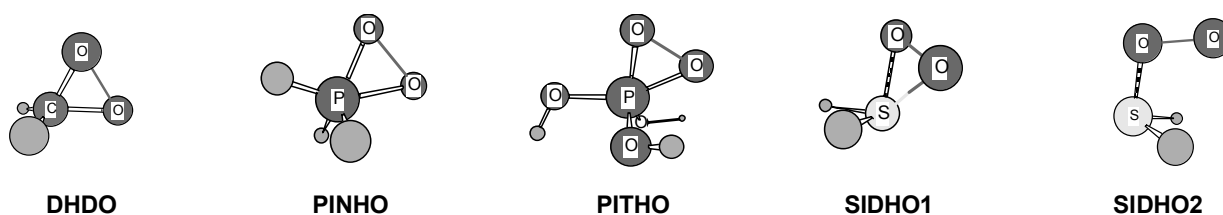
1.3247 Å, an d(O-O) of 1.8702 Å, an d(O-C<sub>ethylene</sub>) of 2.0466 Å and 2.0389 Å (i.e., slightly distorted) and a d(C=C) of 1.3624 Å.

Analyzing the C=C bond of ethylene which changes to a single bond from ethylene to TS to an epoxide, the conversion of the epoxidation can be estimated; these d(C-C) are 1.3255 Å, 1.3624 Å, and 1.4646 Å, respectively, and the conversion is 27%. And the d(C-O) of **DHDO** which becomes to a double bond of formaldehyde changes from 1.3896 Å to 1.3247 Å of TS to 1.2005 Å, the conversion to formaldehyde is estimated to be 34%.

The TS (**DMDO\_TS1**) of the epoxidation by **DMDO** and the approaching ethylene have a C-O of 1.3222 Å, an O-O of 1.8835 Å, an O-C<sub>ethylene</sub> of 2.0038 Å, and a C=C of 1.3653 Å. Comparing the C-C bond of ethylene to those of TS and the epoxide, the bonds change from 1.3255 Å to 1.3653 Å to 1.4646 Å, respectively, which indicate about 30% conversion to the epoxide. Considering the change in the C-O bonds from **DMDO** to TS to acetone which has the bond of 1.2109 Å, the TS is about 40% conversion.

**Phosphadioxiranes.** Phosphadioxiranes have the  $C_s$  symmetry with a symmetry plane containing the P-O-O triangle.  $\text{H}_3\text{PO}_2$  (**PINHO**) has two different d(P-O) of 1.5991 Å and 1.7041 Å and d(O-O) of 1.5629 Å, and  $(\text{CH}_3)_3\text{PO}_2$  (**PINMO**) has d(P-O) of 1.6081 Å and 1.7573 Å and d(O-O) of 1.5443 Å, respectively.<sup>2</sup>

The epoxidation of ethylene with both phosphadioxiranes occurs as the ethylene approaches toward the loose oxygen in a slightly distorted mode. The d(O-C<sub>ethylene</sub>) of both TS (**PINH\_TS1** and **PINM\_TS1**) are similar (2.1389 Å and 2.1381 Å) but the angles (P-O-O) are 65 and 85 degree and the d(P-O<sub>epoxide</sub>) are 1.8278 Å and 2.1432 Å, respectively, which indicates that **PINM\_TS1** is a more product-like TS than **PINH\_TS1**, and the steric hindrance by the methyl groups is prominent in the epoxidation. The C-C bonds of ethylene in the TS (**PINH\_TS1**,

**Figure 1.** Structures of various dioxiranes ( $\text{H}_2\text{C-O-O}$ ,  $\text{H}_3\text{P-O-O}$ ,  $(\text{HO})_3\text{P-O-O}$ ,  $\text{H}_2\text{S-O-O}$  and a persulfoxide).

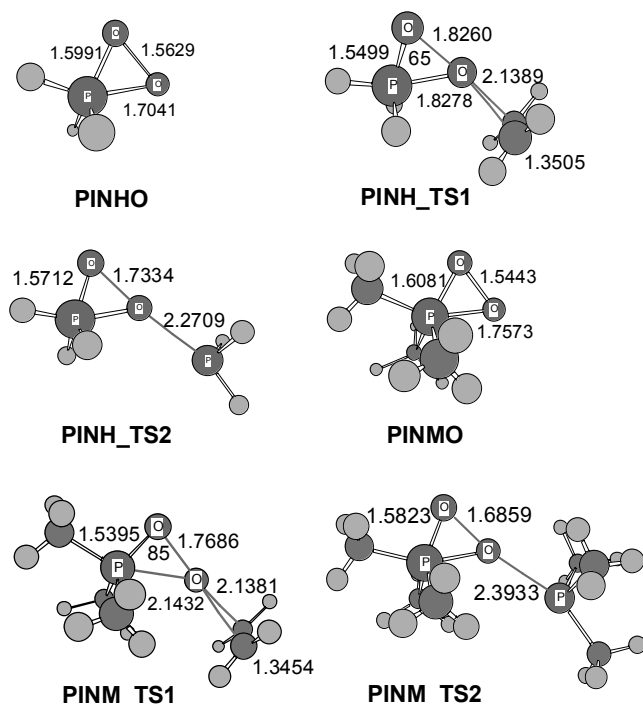


Figure 3. Phosphadioxiranes and their transition states for the epoxidations and the disproportionations (lengths in Å).

**PINM\_TS1**) with  $\text{H}_3\text{PO}_2$  and  $(\text{CH}_3)_3\text{PO}_2$  are 1.3505 Å and 1.3454 Å, i.e., 18% and 15% conversion to the epoxide. The  $d(\text{P}-\text{O})$  of  $\text{H}_3\text{PO}$  and  $(\text{CH}_3)_3\text{PO}$  are 1.4839 Å and 1.4896 Å and the corresponding lengths of TS are 1.5499 Å and 1.5395 Å; 43 % and 58% conversion.

The disproportionation reaction of a phosphadioxirane with a phosphine occurs in a similar way to the epoxidation, but the TS is more product-like; the lengths  $d(\text{O}-\text{O})$  and  $d(\text{O}-\text{P})$  of **PINH\_TS2** are 1.7334 Å and 2.2709 Å and the lengths  $d(\text{O}-\text{O})$  and  $d(\text{O}-\text{P})$  of TS **PINM\_TS2** are 1.6859 Å and 2.3933 Å, respectively.<sup>2</sup> The lengths  $d(\text{P}-\text{O})$  of dioxiranes of two TS are 1.5712 Å and 1.5823 Å; 25% and 22% conversion.

#### Trihydroxyphosphadioxirane and trimethoxyphosphadioxi-

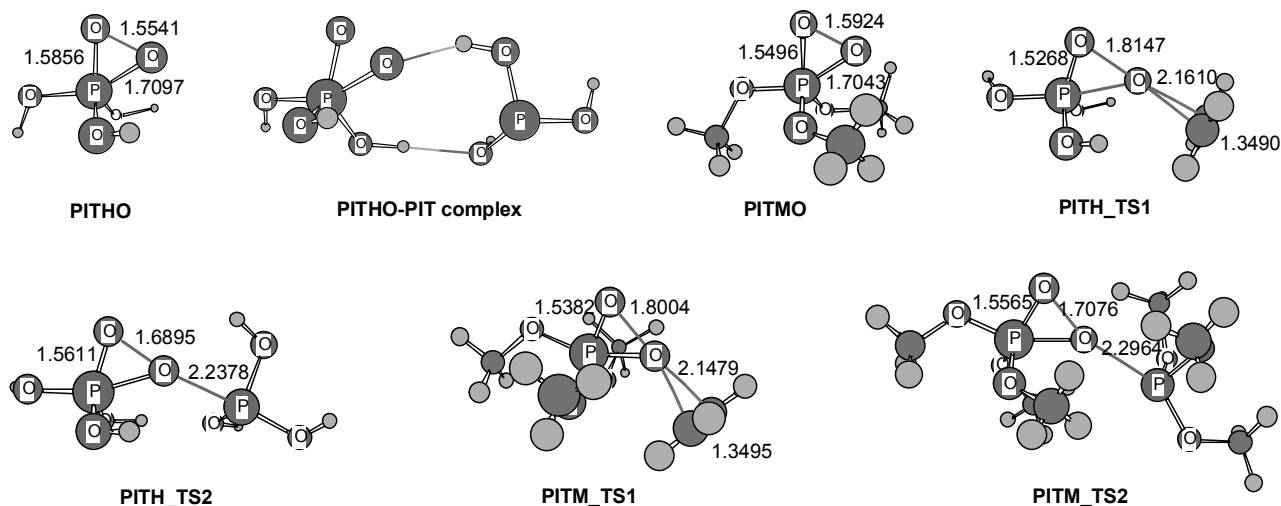


Figure 4. Hydroxyphosphadioxiranes and their transition states of the epoxidations and the disproportionations (lengths in Å).

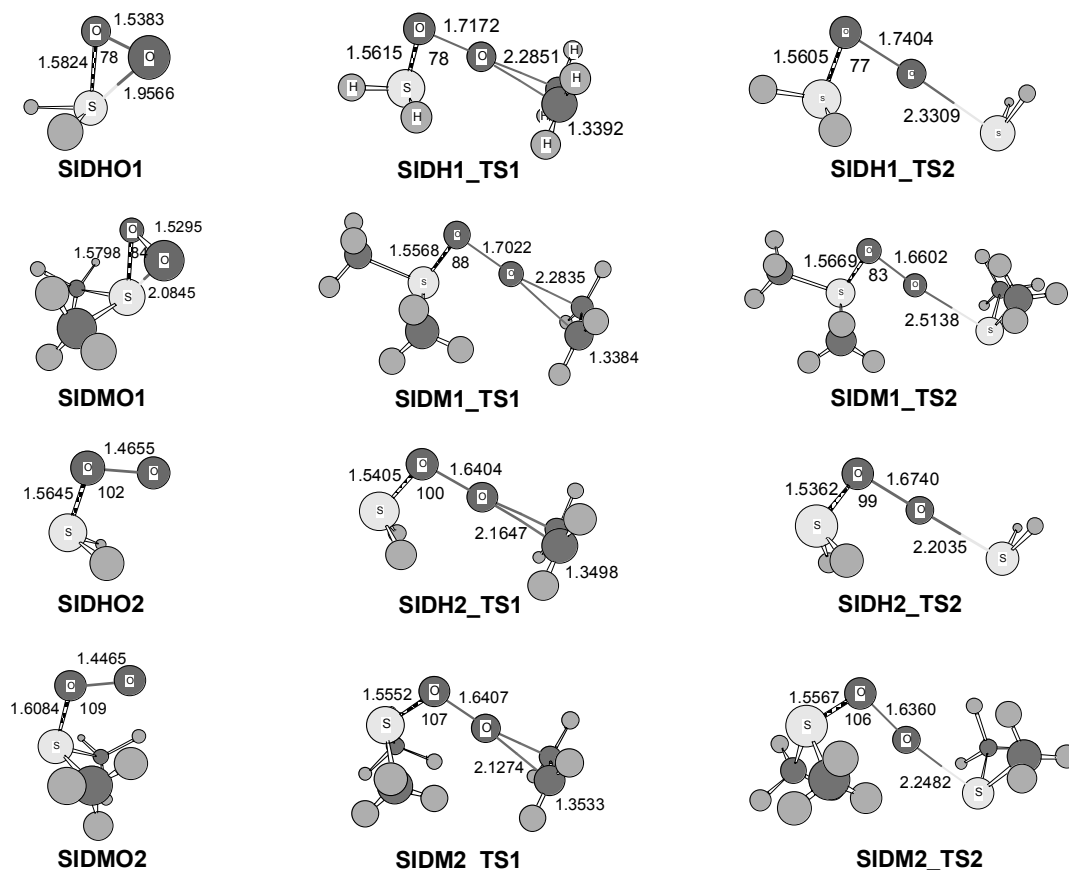
**rane.** Geometries of peroxyphosphites and TS of epoxidation and disproportionation are similar to those of phosphine adducts. A difference is that the dioxiranes of phosphites do not have a plane symmetry because of alkoxy substituents. Two substituents of the phosphites near to the reaction side are rather symmetric, but not the third substituents.

The TS (**PITH\_TS1**, **PITM\_TS1**) for the epoxidation of  $(\text{HO})_3\text{PO}_2$  and  $(\text{CH}_3\text{O})_3\text{PO}_2$  have  $d(\text{O}-\text{C}_{\text{ethylene}})$  of 2.1610 Å and 2.1479 Å and the  $d(\text{C}-\text{C})$  of ethylene of 1.3490 Å and 1.3495 Å, respectively.<sup>4</sup> Conversions to the epoxides are estimated to be 17 % for both TS. The  $d(\text{P}-\text{O})$  of  $(\text{HO})_3\text{PO}$  and  $(\text{CH}_3\text{O})_3\text{PO}$  are 1.4670 Å and 1.4705 Å and those of **PITH\_TS1** and **PITM\_TS1** are 1.5268 Å and 1.5382 Å, and those of dioxiranes (**PITHO**, **PITMO**) are 1.5996 Å and 1.6081 Å, hence the conversions to the phosphates are 45% and 49%, respectively, from the comparison of those  $d(\text{P}-\text{O})$ .

And the trihydroxyphosphadioxirane (**PITHO**) and a trihydroxyphosphite are expected to form a complex with two hydrogen-bonds, which proceeds to the corresponding TS for the disproportionation. The lengths  $d(\text{O}-\text{P})$  of TS (**PITH\_TS2**, **PITM\_TS2**) of  $(\text{HO})_3\text{PO}_2-\text{P}(\text{OH})_3$  and  $(\text{CH}_3\text{O})_3\text{PO}_2-\text{P}(\text{OCH}_3)_3$  are 2.2378 Å and 2.2964 Å, respectively. The lengths  $d(\text{P}-\text{O})$  of dioxiranes of the TS are 1.5611 Å and 1.5565 Å; 29% and 38% conversion to the phosphates.

**Thiadioxiranes and persulfoxide.** Dioxygen adducts of sulfides are known to be calculated as either a cyclic thiadioxiranes or an acyclic persulfoxides depending on the calculation methods.<sup>1,5</sup> We studied the epoxidation and disproportionation of both adducts with B3LYP/6-311+G(2d,p) and MP2/6-311+G(2d,p).

Cyclic thiadioxiranes (**SIDHO1**, **SIDMO1**) of hydrogen sulfide and methylsulfide have the triangles of S-O-O of the short  $d(\text{S}-\text{O})$  of 1.5824 Å and 1.5798 Å and the long  $d(\text{S}-\text{O})$  of 1.9566 Å and 2.0845 Å at B3LYP/6-311+G(2d,p). The further apart oxygen from the sulfur of both dioxysulfides participates in the epoxidation and disproportionation. The TS (**SIDHI\_TS1**, **SIDMI\_TS1**) for the epoxidation of the thiadioxiranes,  $\text{H}_2\text{SO}_2$  and  $(\text{CH}_3)_2\text{SO}_2$ , have  $d(\text{O}-\text{C}_{\text{ethylene}})$  of 2.2851 Å and 2.2835 Å and the  $d(\text{C}-\text{C})$  of ethylene of 1.3392 Å and 1.3384 Å, respec-



**Figure 5.** Thiadioxiranes and their transition states of the epoxidations and the disproportionations (lengths in Å, angles in degree).

tively. The conversions to the epoxides are estimated to be 10% for both TS. The  $d(\text{S-O})$  of  $\text{H}_2\text{SO}$  and  $(\text{CH}_3)_2\text{SO}$  are 1.4978 Å and 1.5013 Å and those of TS are 1.5615 Å and 1.5568 Å, and those of dioxiranes are 1.5824 Å and 1.5798 Å at B3LYP/6-311+G(2d,p), hence the conversions to the sulfoxides are 25% and 29%, respectively. The TS (**SIDH1\_TS2**, **SIDM1\_TS2**) for the disproportionation of thiadioxiranes with sulfides,  $\text{H}_2\text{SO}_2\text{-SH}_2$  and  $(\text{CH}_3)_2\text{SO}_2\text{-S}(\text{CH}_3)_2$ , have the intermolecular  $d(\text{O-S})$  of 2.3309 Å and 2.5138 Å, and the  $d(\text{S-O})$  of dioxiranes are 1.5605 Å and 1.5669 Å, which are equivalent to 26% and 16% conversion to the sulfoxides.

At MP2/6-311+G(2d,p), dioxiranes of sulfides have acyclic peroxide S-O-O structures. Persulfoxides (**SIDHO2**, **SIDMO2**),  $\text{H}_2\text{SO}_2$  and  $(\text{CH}_3)_2\text{SO}_2$ , have the short  $d(\text{S-O})$  of 1.5645 Å and 1.6084 Å and the long  $d(\text{S-O})$  of 2.3541 Å and 2.4950 Å, and the angle  $\angle\text{S-O-O}$  are 101.9 and 109.4 degree, respectively.<sup>3</sup> The TS (**SIDH2\_TS1**, **SIDM2\_TS1**) for the epoxidation of the persulfoxides,  $\text{H}_2\text{SO}_2$  and  $(\text{CH}_3)_2\text{SO}_2$ , have  $d(\text{O-C}_{\text{ethylene}})$  of 2.1647 Å and 2.1274 Å and the  $d(\text{C-C})$  of ethylene of 1.3498 Å and 1.3533 Å, respectively. Since the  $d(\text{C-C})$  of ethylene and its epoxide at MP2/6-311+G(2d,p) are 1.3340 Å and 1.4650 Å, The conversions to the epoxides are estimated to be 12% and 15% for both TS. The TS (**SIDH2\_TS2**, **SIDM2\_TS2**) for the disproportionation have the  $d(\text{S-O})$  of 1.5362 Å and 1.5567 Å, and those of  $\text{H}_2\text{SO}$  and  $(\text{CH}_3)_2\text{SO}$  are 1.4995 Å and 1.5025 Å, and those of dioxiranes (**SIDHO2**, **SIDMO2**) are 1.5645 Å and 1.6084 Å, hence the conversions to the sulfoxides are

44% and 49%, respectively.

### Energetics

Comparing the  $E_{\text{TS}}$  at B3LYP and MP2 levels, those at RHF are overestimated. (Table 2) However, the energy trends at the comparison of the TS of their reactions are same and all energetics discussed here are from B3LYP/6-311+G(2d,p).

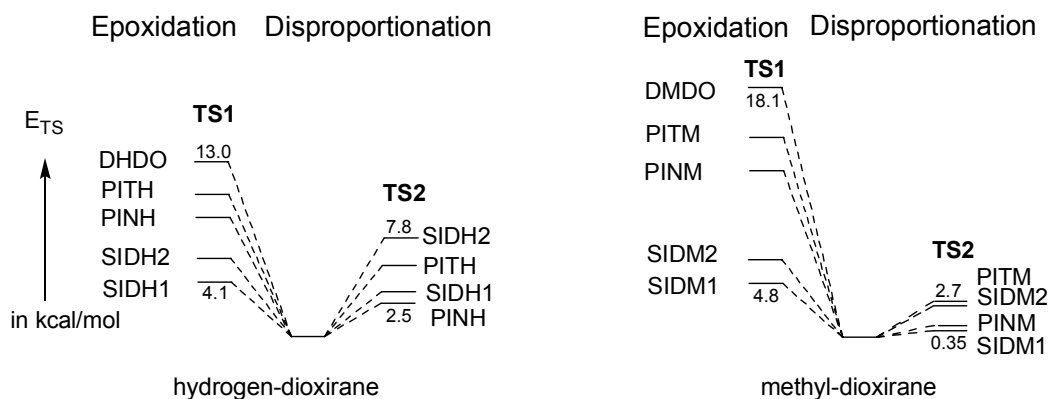
The activation energies ( $E_{\text{TS}}$ ) for the epoxidation of ethylene with **DHDO\_TS1** and **DMDO\_TS1** are 12.96 and 18.11 kcal/mol.<sup>7</sup> The energy increment by 5.2 kcal/mol is expected to be caused by the steric hindrance with methyl groups of **DMDO**.

The  $E_{\text{TS}}$  for the epoxidation with  $\text{H}_3\text{PO}_2$  (**PINH\_TS1**) and  $(\text{CH}_3)_3\text{PO}_2$  (**PINM\_TS1**) are 8.6 and 12.8 kcal/mol, and those  $E_{\text{TS}}$  with  $(\text{HO})_3\text{PO}_2$  (**PITH\_TS1**) and  $(\text{CH}_3\text{O})_3\text{PO}_2$  (**PITM\_TS1**) are 10.8 and 15.5 kcal/mol, respectively. The increments of  $E_{\text{TS}}$  by the methyl steric hindrance are 4.2 and 4.7 kcal/mol, which is similar to those of carbodioxiranes.

However, the energetics for the epoxidation by thiadioxiranes and peroxy sulfoxides are different from those by the phosphadioxiranes. The  $E_{\text{TS}}$  for the epoxidation are lower in general, and those with **SIDH1\_TS1** and **SIDH2\_TS1** are 4.1 and 5.6 kcal/mol, and those  $E_{\text{TS}}$  with **SIDM1\_TS1** and **SIDM2\_TS1** are 4.8 and 6.2 kcal/mol, respectively, probably because of the wider angle of  $\angle\text{S-O-O}$  (80 - 90 or 100 - 105 degree) than those angles  $\angle\text{P-O-O}$  of TS of phosphadioxiranes. The increments of  $E_{\text{TS}}$  are 0.7 and 0.6 kcal/mol with methyl substituents. The

Table 2. Heats of reactions of the epoxidations and the disproportionations of various dioxiranes (in kcal/mol).

Epoxidation or Disproportionation	RHF	B3LYP	
	6-31G*	6-31G*	6-311+G(2d,p)
$\text{H}_2\text{CO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{DHDO\_TS1}$	40.92	12.94	12.96
$\text{Me}_2\text{CO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{DMDO\_TS1}$	38.68	17.87	18.11
$\text{H}_3\text{PO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{PINH\_TS1}$	19.73	7.42	8.55
$\text{PMe}_3\text{O}_2 + \text{C}_2\text{H}_4 \rightarrow \text{PINM\_TS1}$	13.86	12.67	12.79
$\text{H}_3\text{PO}_2 + \text{PH}_3 \rightarrow \text{PINH\_TS2}$	17.91	2.82	2.52
$\text{PMe}_3\text{O}_2 + \text{PMe}_3 \rightarrow \text{PINM\_TS2}$	9.11	0.31	1.00
$(\text{HO})_3\text{PO}_2 + \text{C}_2\text{H}_4 \rightarrow \text{PITH\_TS1}$	15.07	9.50	10.79
$\text{P}(\text{OMe})_3\text{O}_2 + \text{C}_2\text{H}_4 \rightarrow \text{PITM\_TS1}$	16.83	14.64	15.54
$(\text{HO})_3\text{PO}_2\text{-P}(\text{OH})_3\text{-dimer} \rightarrow \text{PITH\_TS2}$	16.50	6.95	5.34
$\text{P}(\text{OMe})_3\text{O}_2 + \text{P}(\text{OMe})_3 \rightarrow \text{PITM\_TS2}$	7.27	-0.33	2.69
$\text{H}_2\text{SO}_2^a + \text{C}_2\text{H}_4 \rightarrow \text{SIDH1\_TS1}$	8.29	4.07	4.13
$\text{SMe}_2\text{O}_2^a + \text{C}_2\text{H}_4 \rightarrow \text{SIDM1\_TS1}$	9.53	4.77	4.81
$\text{H}_2\text{SO}_2^a + \text{SH}_2 \rightarrow \text{SIDH1\_TS2}$	9.10	6.50	3.59
$\text{SMe}_2\text{O}_2^a + \text{SMe}_2 \rightarrow \text{SIDM1\_TS2}$	6.51	0.52	0.35
$\text{H}_2\text{SO}_2^b + \text{C}_2\text{H}_4 \rightarrow \text{SIDH2\_TS1}$	8.90	6.31	5.64
$\text{SMe}_2\text{O}_2^b + \text{C}_2\text{H}_4 \rightarrow \text{SIDM2\_TS1}$	11.22	7.68	6.17
$\text{H}_2\text{SO}_2^b + \text{SH}_2 \rightarrow \text{SIDH2\_TS2}$	9.85	10.34	7.75
$\text{SMe}_2\text{O}_2^b + \text{SMe}_2 \rightarrow \text{SIDM2\_TS2}$	7.80	5.02	2.64

<sup>a</sup>cyclic thiadioxiranes. <sup>b</sup>peroxysulfoxides at MP2.Figure 6. Comparison of  $E_{\text{TS}}$  of the epoxidation and the disproportionation of various dioxiranes (in kcal/mol).

steric hindrance in the epoxidation with the thiadioxirane and peroxydimethylsulfoxide seems to be a minor factor.

In the disproportionation, it is noticed that the methyl substituents do not increase but lower the TS barrier ( $E_{\text{TS}}$ ) comparing to the hydrogen-substituents. The  $E_{\text{TS}}$  is decreased in  $(\text{CH}_3)_3\text{PO}_2$  by 1.5 kcal/mol than in  $\text{H}_3\text{PO}_2$  (**PINH\_TS2** vs. **PINM\_TS2**), and with  $(\text{HO})_3\text{PO}_2$  and  $(\text{CH}_3\text{O})_3\text{PO}_2$  by 2.7 kcal/mol (**PITH\_TS2** versus **PITM\_TS2**), and with cyclic  $\text{H}_2\text{SO}_2$  and  $(\text{CH}_3)_2\text{SO}_2$  by 3.2 kcal/mol (**SIDH1\_TS2** versus **SIDM1\_TS2**), and with peroxy  $\text{H}_2\text{SO}_2$  and  $(\text{CH}_3)_2\text{SO}_2$  by 5.1 kcal/mol (**SIDH2\_TS2** versus **SIDM2\_TS2**), respectively.

To study further the steric hindrance and the electronic effect, we assume the mixed disproportionations with phosphine dioxiranes ( $\text{H}_3\text{PO}_2$ ,  $(\text{CH}_3)_3\text{PO}_2$ ) and phosphines ( $\text{PH}_3$ ,  $\text{P}(\text{CH}_3)_3$ ). (Table 3) When  $\text{H}_3\text{PO}_2$  disproportionates with  $\text{P}(\text{CH}_3)_3$ , the  $E_{\text{TS}}$  is calculated to be -1.52 kcal/mol, which is lower by 4.0

kcal/mol than that with  $\text{PH}_3$  (2.52 kcal/mol). And when  $(\text{CH}_3)_3\text{PO}_2$  disproportionates with  $\text{P}(\text{CH}_3)_3$ , the  $E_{\text{TS}}$  is calculated to be 1.00 kcal/mol, which is also lower by 3.7 kcal/mol than that with  $\text{PH}_3$  (4.66 kcal/mol). Considering that methyl group is more electron-donating than hydrogen, the lower  $E_{\text{TS}}$  by methyl substituents indicates the nature of the phosphadioxiranes is electrophilic.<sup>8</sup>

When  $E_{\text{TS}}$  of  $\text{H}_3\text{PO}_2\text{-PH}_3$  is compared with  $E_{\text{TS}}$  of  $(\text{CH}_3)_3\text{PO}_2\text{-PH}_3$ , the  $\Delta E_{\text{TS}}$  is 2.14 kcal/mol, and when  $E_{\text{TS}}$  of  $\text{H}_3\text{PO}_2\text{-P}(\text{CH}_3)_3$  is compared with  $E_{\text{TS}}$  of  $\text{Me}_3\text{PO}_2\text{-P}(\text{CH}_3)_3$ , the  $\Delta E_{\text{TS}}$  is 2.52 kcal/mol. Those  $\Delta E_{\text{TS}}$  increases are caused by the steric hindrance of methyl groups. The steric effect in  $E_{\text{TS}}$  for the disproportionation will intensified with bulkier substituents.

**Epoxidation versus disproportionation.** The disproportionation has a lower TS barrier ( $E_{\text{TS}}$ ) than the epoxidation in general (Figure 6). The  $\Delta E_{\text{TS}}$  between the epoxidation and

**Table 3.** Mixed disproportionations of  $\text{H}_3\text{PO}_2$  and  $(\text{CH}_3)_3\text{PO}_2$  with  $\text{PH}_3$  and  $\text{P}(\text{CH}_3)_3$  (in kcal/mol).

Heat of Reaction	B3LYP	
	6-31G*	6-311+G(2d,p)
$\text{H}_3\text{PO}_2 + \text{PH}_3 \rightarrow \text{H}_3\text{PO}_2\text{-PH}_3\text{ TS}$	2.82	2.52
$\text{Me}_3\text{PO}_2 + \text{PMe}_3 \rightarrow \text{Me}_3\text{PO}_2\text{-PMe}_3\text{ TS}$	0.31	1.00
$\text{H}_3\text{PO}_2 + \text{PMe}_3 \rightarrow \text{H}_3\text{PO}_2\text{-PMe}_3\text{ TS}$	-2.35	-1.52
$\text{Me}_3\text{PO}_2 + \text{PH}_3 \rightarrow \text{Me}_3\text{PO}_2\text{-PH}_3\text{ TS}$	5.22	4.66

disproportionation is 6.1 kcal/mol with  $\text{H}_3\text{PO}_2$  (PINH\_TS1 vs. PINH\_TS2) and 11.8 kcal/mol with  $(\text{CH}_3)_3\text{PO}_2$  (PINM\_TS1 vs. PINM\_TS2). And the  $\Delta E_{\text{TS}}$  with  $(\text{HO})_3\text{PO}_2$  (PITH\_TS1 vs. PITH\_TS2) is 5.5 kcal/mol and that with  $(\text{CH}_3\text{O})_3\text{PO}_2$  (PITM\_TS1 vs. PITM\_TS2) is 12.8 kcal/mol. The TS energy gaps are not high in thiadioxiranes; the  $\Delta E_{\text{TS}}$  with  $\text{H}_2\text{SO}_2$  are 0.5 (SIDH1\_TS1 vs. SIDH1\_TS2) and -2.1 kcal/mol (SIDH2\_TS1 vs. SIDH2\_TS2), those with  $(\text{CH}_3)_2\text{SO}_2$ , are 4.5 kcal/mol (SIDM1\_TS1 vs. SIDM1\_TS2) and 3.5 kcal/mol (SIDM2\_TS1 vs. SIDM2\_TS2), respectively. The disproportionation of the dioxiranes is expected to be the main reaction.

In conclusion, the geometry analysis shows the epoxidation and disproportionation of dioxiranes of phosphorous and sulfide have slightly early TS (reactant-like) than the carbodioxiranes. The nature of the dioxiranes is expected to be electrophilic. And from the mixed disproportionation of phosphadioxiranes, the increment of  $E_{\text{TS}}$  by steric hindrance of methyl groups is estimated to be about 2.1 - 2.5 kcal/mol. The steric hindrance of methyl substituent increases the  $E_{\text{TS}}$  of both the epoxidation and the disproportionation. However, in disproportionation with more bulky alkyl or aryl substituents, both dioxiranes and their precursors will have steric factors and the steric hindrance will be doubly intensified. Therefore when both reactions occurs in situ, introduction of the bulky substituents in the dioxiranes may retard the disproportionation and favor the epoxidation. Experimentally dioxiranes of triphenylphosphines are known to undergo the epoxidation rather than the disproportionation.<sup>4(b),(c)</sup> The increased steric hindrance will slow down the disproportionation process and induce the epoxidation to yield epoxide products. We are continuing the studies on the more bulky system.

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