

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231527328>

# Experimental and ab Initio Computational Evidence for New Peroxidic Intermediates (Iminopersulfonic Acids). Substituent Effects in the Photooxidations of Sulfenic Acid Derivatives

ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · MAY 1997

Impact Factor: 12.11 · DOI: 10.1021/ja964295l

---

CITATIONS

13

---

READS

31

## 4 AUTHORS, INCLUDING:



Frank Jensen

Aarhus University

153 PUBLICATIONS 6,236 CITATIONS

SEE PROFILE



Edward L Clennan

University of Wyoming

134 PUBLICATIONS 2,425 CITATIONS

SEE PROFILE

# Experimental and *ab Initio* Computational Evidence for New Peroxidic Intermediates (Iminopersulfonic Acids). Substituent Effects in the Photooxidations of Sulfenic Acid Derivatives

Alexander Greer,<sup>†</sup> Ming-Fang Chen,<sup>†</sup> Frank Jensen,<sup>\*,‡</sup> and Edward L. Clennan<sup>\*,†</sup>

Contribution from the Departments of Chemistry, University of Wyoming, Laramie, Wyoming 82071, and Odense University, DK-5230 Odense M., Denmark

Received December 13, 1996<sup>⊗</sup>

**Abstract:** A detailed *ab initio* study of the structures and energetics of the persulfoxides and thiadioxiranes derived from sulfenic acid derivatives (RSX) is reported. The persulfoxides adopt structures in which the O–O bond bisects the RSX angle while the thiadioxiranes prefer a distorted trigonal bipyramidal geometry. The thiadioxiranes are more stable in every case than their persulfoxide isomer. The exothermicities of the interconversions of the persulfoxide to the thiadioxirane increase in the substituent (X) order  $\text{CH}_3 < \text{NH}_2 < \text{Cl} < \text{OCH}_3 < \text{SCH}_3 < \text{F}$  from a low of 3 kcal/mol to a high of 31 kcal/mol. The activation barriers, on the other hand, decrease in the substituent order  $\text{Cl} > \text{CH}_3 \approx \text{NH}_2 > \text{OCH}_3 \approx \text{SCH}_3 > \text{F}$  from 27 to 10 kcal/mol. Only those persulfoxides which do not have a hydrogen on a heteroatom X exist in well-defined minima on the potential energy surface. Attempted minimization with tight convergence criteria of persulfoxides with heteroatom X–H bonds resulted in collapse via ene-like reactions to give hydroperoxy sulfonium ylides. In the case where X–H is N–H, the resulting hydroperoxysulfonium ylide (iminopersulfonic acid) adopts a hydrogen-bonded structure reminiscent of peracids. Experimental evidence for the formation of these new peroxides was obtained by photooxidations of *N*-methyl-, *N*-*n*-butyl-, and *N*-*tert*-butylbenzenesulfenamides.

## Introduction

The three-membered ring peroxide, thiadioxirane, is a potentially novel oxidizing agent which has yet to be isolated and identified. For this reason, and because of its topographical similarity to dimethyldioxirane,<sup>1</sup> there is recent interest surrounding the viability of this chemically unusual molecule. In 1983 Foote and co-workers<sup>2</sup> suggested that diethylthiadioxirane (**1B**) is an intermediate formed from diethyl persulfoxide (**1A**) during the photooxidation of diethyl sulfide ( $\text{Et}_2\text{S}$ ) (Scheme 1). Cophotooxidations of  $\text{Et}_2\text{S}$  with electrophilic diaryl sulfoxide (*p*-X- $\text{Ph}_2\text{SO}$ ) or nucleophilic diaryl sulfide (*p*-X- $\text{Ph}_2\text{S}$ ) trapping agents provided the kinetic evidence for both **1A,B** and simultaneously information on their electronic character.

The experimental observation that diethyl persulfoxide prefers to decompose to the extent of 95% or greater via a physical quenching rather than via a chemical quenching channel (Scheme 1) suggests that **1A,B** are separated by a large barrier.<sup>3</sup> This speculation was confirmed by *ab initio* calculations at the MP2/6-31G\* level of theory which revealed that dimethyl persulfoxide (**2A**) and thiadioxirane (**2B**) are virtually isoenergetic and connected by a substantial 20 kcal/mol barrier.<sup>4–6</sup> The origin of this large barrier is undoubtedly related to the large reorganization energy associated with collapse of the tetrahedral persulfoxide to a distorted trigonal bipyramidal (TBP) thiadioxirane.

We have recently reported the results from photooxidations of substrates designed to modify the relative energies of these important intermediates. Two different strategies were employed: (1) the sulfur was sterically confined within a small ring<sup>7</sup> and (2) an electron-withdrawing substituent was directly attached to sulfur (RSX).<sup>4,7–11</sup>

The first strategy was designed because it was envisioned that steric confinement of the sulfur within a small ring would prevent the attainment of a preferred tetrahedral persulfoxide geometry and hence promote rearrangement to a trigonal bipyramidal (TBP) thiadioxirane which can accommodate a small ring with little if any cost in energy. To our delight, the chemical reaction channel is dramatically enhanced in the four-membered ring sulfide, thietane, in comparison to  $\text{Et}_2\text{S}$ . However, careful examination of this reaction revealed that the enhanced rate of chemical reaction was the result of a novel self-catalysis route (Scheme 2) rather than a result of the lowering of the persulfoxide–thiadioxirane activation barrier.<sup>7</sup>

Unfortunately, recent *ab initio* calculations reveal that even in the absence of substrate catalysis (Scheme 2) that the ring strain strategy 1 is unlikely to be successful since the calculated persulfoxide–thiadioxirane interconversion barriers for the three-, four-, and five-membered ring systems<sup>12</sup> are virtually identical to that for the acyclic substrate dimethyl sulfide. We have suggested that the anticipated increase in ring strain in the persulfoxides was circumvented by a decrease in the sulfur–oxygen interaction and a corresponding relaxation in the need to adopt a tetrahedral geometry at sulfur.

<sup>†</sup> University of Wyoming.

<sup>‡</sup> Odense University.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, May 1, 1997.

(1) Clennan, E. L. In *Trends in Organic Chemistry*; Council of Scientific Information: Trivandrum, India, 1995; pp 231–252.

(2) Liang, J.-J.; Gu, C.-L.; Kacher, M. L.; Foote, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 4717–4721.

(3) Clennan, E. L. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. IV, pp 49–80.

(4) Jensen, F.; Foote, C. S. *J. Am. Chem. Soc.* **1988**, *110*, 2368–2375.

(5) Jensen, F. *J. Org. Chem.* **1992**, *57*, 6478–6487.

(6) Jensen, F. In *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; JAI Press: Greenwich, CT, 1995; Vol. 4, pp 1–48.

(7) Clennan, E. L.; Dobrowolski, P.; Greer, A. *J. Am. Chem. Soc.* **1995**, *117*, 9800–9803.

(8) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1994**, *116*, 809–810.

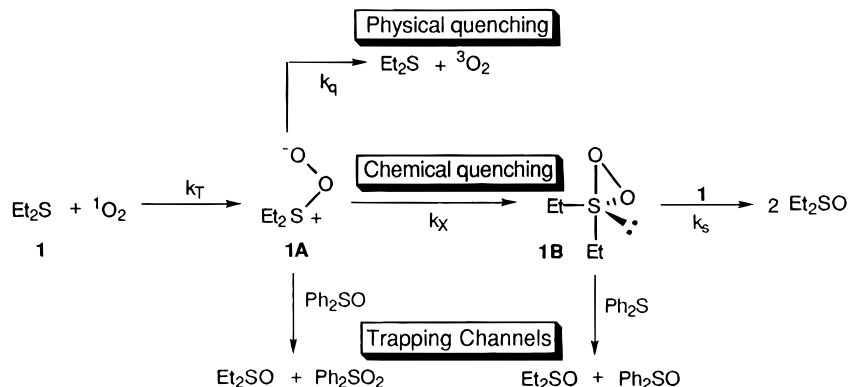
(9) Clennan, E. L.; Wang, D.; Zhang, H.; Clifton, C. H. *Tetrahedron Lett.* **1994**, *35*, 4723–4726.

(10) Clennan, E. L.; Zhang, H. *J. Org. Chem.* **1994**, *59*, 7952–7954.

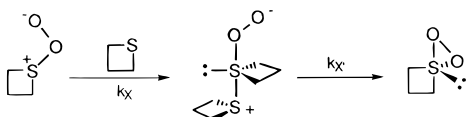
(11) Clennan, E. L.; Zhang, H. *J. Am. Chem. Soc.* **1995**, *117*, 4218–4227.

(12) Greer, A.; Jensen, F.; Clennan, E. L. *J. Org. Chem.* **1996**, *61*, 4107–4110.

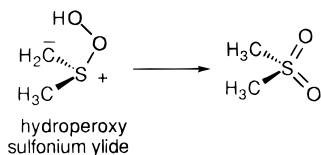
## Scheme 1



## Scheme 2



## Scheme 3



The second strategy was designed because it was anticipated that an electron-withdrawing group adjacent to the sulfenyl sulfur would destabilize the persulfinate (persulfoxide, **A**) by intensifying the positive charge at the sulfonium sulfur and at the same time stabilize the pseudo TBP thiadioxirane by the well-established apical substituent effect.<sup>13</sup> Photooxidations of sulfenamides ( $X = NR_2$ ) demonstrated that this strategy was partially successful.<sup>8,11</sup> The diminished  $^1O_2$  reactivities of sulfenamides relative to sulfides are consistent with destabilization of the persulfoxide; unfortunately, only tentative evidence for the population of the thiadioxirane was obtained.

We now report on an *ab initio* computational study of the persulfoxide–thiadioxirane interconversion in a series of sulfenic acid derivatives ( $CH_3SX$ ;  $X = CH_3$  (**2**),  $N(CH_3)_2$  (**3**),  $F$  (**4**),  $Cl$  (**5**),  $OCH_3$  (**6**),  $SCH_3$  (**7**),  $NH_2$  (**8**),  $NHCH_3$  (**9**),  $OH$  (**10**), and  $SH$  (**11**)), which was designed to assess the likelihood of success of strategy 2 (*vide supra*). As a byproduct of this study we also detected formations of hydroperoxysulfonium ylides (persulfenic acids) in those substrates bearing hydrogen(s) on a heteroatom (N, O, S) directly attached to sulfur. The observation of hydrogen abstraction  $\alpha$  to the sulfonium sulfur is important in light of the recent suggestion that the resulting hydroperoxysulfonium ylides can rearrange to sulfones<sup>14</sup> (Scheme 3).

## Experimental Section

**General Aspects.** Gas chromatographic data were collected on a Hewlett-Packard GC/MS instrument consisting of a 5890 series II GC and a 5971 series mass selective detector or on a Perkin-Elmer Autosystem. A HP-5 (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m (length  $\times$  inside diameter  $\times$  film thickness)) capillary column was used on the GC/MS, and a 5% diphenylpolysiloxane–95% dimethylpolysiloxane (30

m  $\times$  0.32 mm  $\times$  1.0  $\mu$ m (length  $\times$  inside diameter  $\times$  film thickness)) fused silica column was used on the Perkin Elmer Autosystem. *N*-Methyl-, *N*-*n*-butyl-, and *N*-*tert*-butylbenzenesulfenamides (PhSNHMe, PhSNH*n*Bu, and PhSNH*t*Bu) were synthesized, isolated, and purified as described in the literature.<sup>15</sup> Norbornene oxide was synthesized as reported in the literature<sup>16</sup> and purified by slow sublimation at 70  $^\circ$ C to give needle-like crystals. Tetraphenylporphyrin (TPP), 4-*tert*-butylcyclohexanone, and norbornene were obtained from Aldrich, dodecane was obtained from JT Baker, and 75% MCPBA was obtained from ACROS, and all were used without further purification.

**Computational Methods.** *Ab initio* calculations were performed using the Gaussian-94 program package<sup>17</sup> incorporating standard notations and procedures.<sup>18</sup> All geometry optimizations were done at the MP2/6-31G\* level of theory. The qualities of the geometry optimizations were excellent as assessed by comparison of calculated and experimentally available geometries of the sulfenic acid derivatives<sup>19–21</sup> (Table 2, *vide infra*). The nature of the stationary points were verified by harmonic vibrational frequency calculations. A previous theoretical study has demonstrated that electron correlation is necessary to adequately describe the sulfide– $^1O_2$  potential energy surface (PES).<sup>5,6</sup> Sensitivity toward inclusion of additional electron correlation was tested by running single point calculations on optimized geometries up to either the fourth-order perturbation (MP4) or coupled cluster (CCSD(T)) level. Basis set dependence was tested by comparing the 6-31G(1d), 6-311G(2d), and 6-311+G(2df) basis sets.

**Photooxidations.** Tubes containing 1 mL of an oxygen-saturated benzene solution of 2.3 mM sulfenamides (PhSNHR; R = Me, *n*Bu, and *t*Bu),  $5 \times 10^{-5}$  M TPP, 1–50 mM norbornene, and an internal standard (4-*tert*-butylcyclohexanone or dodecane) were irradiated for 20–25 min with a 500 W tungsten halogen lamp through a 1 cm 75% (w/v) NaNO<sub>2</sub> filter solution. The reaction mixtures were analyzed immediately by gas chromatography, and the norbornene oxide concentrations were measured by reference to calibration curves constructed with authentic samples of the epoxide.

## Results and Discussion

The results for **2–11** are discussed using the nomenclature presented in Scheme 4. Calculated geometries are shown in Tables 1–6 and will be discussed first, followed by the energetic results.

(15) Armitage, D. A.; Clark, M. J.; Kinsey, A. C. *J. Chem. Soc. (C)* **1971**, 3867–3869.

(16) Budnik, R. A.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 1384–1389.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1994.

(18) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley & Sons: New York, 1986.

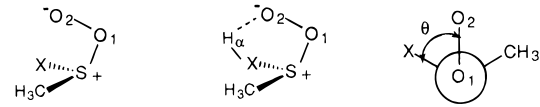
(19) Pierce, L.; Hayashi, M. *J. Chem. Phys.* **1961**, *35*, 479–485.

(20) Penn, R. E.; Block, E.; Revelle, L. K. *J. Am. Chem. Soc.* **1978**, *100*, 3622–3623.

(21) Steudel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 655–664.

(13) Hayes, R. A.; Martin, J. C. In *Organic Sulfur Chemistry. Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, The Netherlands, 1985; Vol. 19, pp 408–483.

(14) Ishiguro, K.; Hayashi, M.; Sawaki, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7265–7271.

**Table 1.** Selected Persulfoxide Structural Parameters<sup>a</sup>


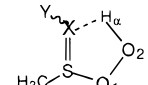
	substituent <sup>e</sup>	S-X	S-O <sub>1</sub>	S-O <sub>2</sub>	O <sub>1</sub> -O <sub>2</sub>	H <sub>α</sub> -O <sub>2</sub>	X-S-C	S-O <sub>1</sub> -O <sub>2</sub>	O <sub>2</sub> -O <sub>1</sub> -S-X	NBO charge <sup>b</sup>
<b>2A</b>	CH <sub>3</sub>	1.787	1.651	2.517	1.434	2.098	99.7	109.1	51.0	1.20, <sup>c</sup> -0.60, <sup>d</sup> -0.90 <sup>e</sup>
<b>3A</b>	NMe <sub>2</sub>	1.666	1.599	2.495	1.470		100.8	108.6	58.2	1.42, <sup>c</sup> -0.64, <sup>d</sup> -0.70 <sup>e</sup>
<b>4A</b>	F	1.643	1.546	2.525	1.449		94.0	114.9	70.3	1.57, <sup>c</sup> -0.57, <sup>d</sup> -0.49 <sup>e</sup>
<b>5A</b>	Cl	2.386	1.713	2.650	1.303		90.9	122.4	86.7	0.89, <sup>c</sup> -0.11, <sup>d</sup> -0.46
<b>6A</b>	OCH <sub>3</sub>	1.644	1.579	2.500	1.463		94.7	110.5	52.9	1.52, <sup>c</sup> -0.61, <sup>d</sup> -0.73 <sup>e</sup>
<b>7A</b>	SCH <sub>3</sub>	2.104	1.618	2.524	1.437		97.5	111.2	54.7	1.05, <sup>c</sup> -0.60, <sup>d</sup> +0.07 <sup>e</sup>
<b>8A</b>	NH <sub>2</sub>	1.665	1.651	2.490	1.442	1.649	104.3	107.0	42.5	1.39, <sup>c</sup> -0.58, <sup>d</sup> -1.11 <sup>e</sup>
<b>8A'</b>	NH <sub>2</sub>	1.655	1.646	2.465	1.454	1.710	97.9	105.2	36.9	1.38, <sup>c</sup> -0.59, <sup>d</sup> -1.10 <sup>e</sup>
<b>9A</b>	NHMe	1.665	1.621	2.474	1.463	1.800	106.3	106.6	48.5	1.42, <sup>c</sup> -0.60, <sup>d</sup> -0.91 <sup>e</sup>
<b>9A'</b>	NHMe	1.666	1.599	2.495	1.470	1.821	100.8	108.6	58.2	1.39, <sup>c</sup> -0.61, <sup>d</sup> -0.90 <sup>e</sup>
<b>10A</b>	OH	1.660	1.572	2.527	1.454	3.471	93.4	113.2	60.2	1.50, <sup>c</sup> -0.59, <sup>d</sup> -0.89 <sup>e</sup>
<b>11A</b>	SH	2.087	1.589	2.419	1.459	3.995	100.4	105.0	47.2	1.09, <sup>c</sup> -0.60, <sup>d</sup> -0.10 <sup>e</sup>

<sup>a</sup> Distances in Å, angles in deg. <sup>b</sup> NBO = natural bond orbital analyses. <sup>c</sup> Charge at sulfur. <sup>d</sup> Charge at O<sub>2</sub>. <sup>e</sup> Charge at X. <sup>f</sup> **8A**, **9A** = out conformations; **8A'**, **9A'** = in conformations.

**Table 2.** Calculated and (Experimental) Values of Sulfenic Acid (CH<sub>3</sub>SXY<sub>n</sub>) Structural Parameters<sup>a</sup>

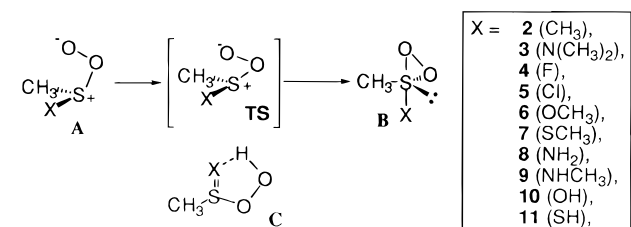
X	Y <sub>n</sub>	C-S	S-X	H <sub>3</sub> C-S-X	CSXY	X-Y	S-X-Y
<b>2</b>	C H <sub>3</sub>	1.806	1.806 (1.802) <sup>b</sup>	98.5 (98.5) <sup>b</sup>	180.0, 61.1, -61.1	1.092, 1.093, 1.093(1.091) <sup>b</sup>	107.6, 111.3, 111.3(110.4) <sup>b</sup>
<b>3</b>	N (CH <sub>3</sub> ) <sub>2</sub>	1.803	1.735	98.3	116.7	1.464	112.3
<b>4</b>	F	1.787	1.656	97.4			
<b>5</b>	Cl	1.801	2.049	99.3			
<b>6</b>	O CH <sub>3</sub>	1.798	1.690	99.6	88.9	1.437	112.9
<b>7</b>	S CH <sub>3</sub>	1.814 (1.81) <sup>d</sup>	2.055 (2.03) <sup>d</sup>	102.1 (103) <sup>d</sup>	85.0 (84) <sup>d</sup>		
<b>8</b>	N H <sub>2</sub>	1.802	1.731	98.6	120.1	1.017	110.1
<b>9</b>	N H, CH <sub>3</sub>	1.803	1.729	98.7	119.4, <sup>e</sup> 116.6 <sup>f</sup>	1.018, <sup>e</sup> 1.466 <sup>f</sup>	108.6, <sup>e</sup> 114.2 <sup>f</sup>
<b>10</b>	O H	1.797	1.696 (1.658) <sup>c</sup>	99.6 (100.1) <sup>c</sup>	92.2 (93.9) <sup>c</sup>	0.976 (0.957) <sup>c</sup>	106.3 (107.7) <sup>c</sup>
<b>11</b>	S H	1.812	2.063	102.0	87.5		

<sup>a</sup> Experimental values in parentheses. <sup>b</sup> Reference 17. <sup>c</sup> Reference 18. <sup>d</sup> Reference 19. <sup>e</sup> Y = H. <sup>f</sup> Y = C.

**Table 3.** Selected Persulfenic acid Structural Parameters<sup>a</sup>


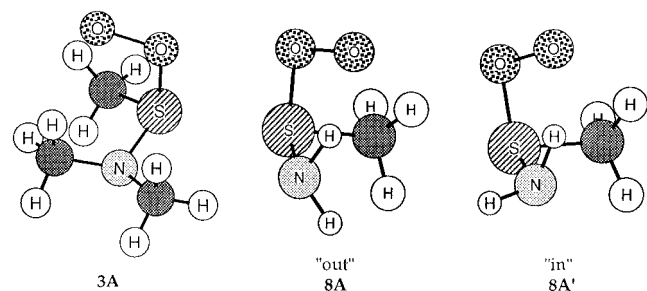
substituent		S-X	S-O <sub>1</sub>	H <sub>α</sub> -X	X-S-C	S-O <sub>1</sub> -O <sub>2</sub>	SO <sub>1</sub> -O <sub>2</sub> -H <sub>α</sub>	MeS-X-Y	MeSO <sub>1</sub> -O <sub>2</sub>
<b>10C</b>	O Lp <sup>b</sup>	1.490	1.716	2.561	106.3	108.1	75.0		61.8
<b>11C</b>	S Lp <sup>b</sup>	1.938	1.744	2.883	107.3	109.4	80.6		61.5
<b>12C<sup>c</sup></b>	N H	1.571	1.763	2.882	99.7	106.8	80.6	165.8	43.3

<sup>a</sup> Distances in Å; angles in deg; the dihedral angles, WXYZ, are positive for a clockwise movement from W to Z as you look from X to Y down bond XY. <sup>b</sup> LP = lone pair. <sup>c</sup> Peracid derived from HSNH<sub>2</sub>.

**Scheme 4**

**A. Persulfoxides (A in Scheme 4).** The persulfoxides fall in two computationally distinct classes which are distinguished by the presence and/or absence of a hydrogen attached to a heteroatom directly bonded to the sulfonium-ion like sulfur (*vide infra*).

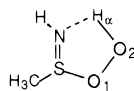
Persulfoxides **2A–7A** have no hydrogen on an adjacent heteroatom and optimize to well-defined minima. Structure **2A** has C<sub>s</sub> symmetry<sup>5</sup> while **3A–7A** have no symmetry (Table 1). In each case, however, the O–O bond in the optimized structures bisects or nearly bisects the X–S–CH<sub>3</sub> bond angle

**Scheme 5**

as illustrated by persulfoxide **3A** in Scheme 5. These persulfoxides adopt a distorted tetrahedral geometry, somewhat similar to that of a sulfonium salt,<sup>22</sup> with a C–S–X bond angle of ca. 100° and a substantial positive charge on sulfur.

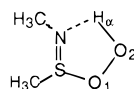
Several features indicate that the electronic and steric character of the substituent X plays an important role in

(22) Lopez-Castro, A.; Truter, M. R. *Acta. Crystallogr.* **1964**, *17*, 465–471.

**Table 4.** Selected Iminopersulfonic Acid, 8C, Structural Parameters<sup>a</sup>

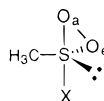
conformer	S–N	S–O <sub>1</sub>	H <sub>α</sub> –N	N–S–C	S–O <sub>1</sub> –O <sub>2</sub>	SO <sub>1</sub> –O <sub>2</sub> –H <sub>α</sub>	MeS–N–H	MeSO <sub>1</sub> –O <sub>2</sub>	ΔE <sup>b</sup>
<b>8CI</b>	1.573	1.769	2.264	101.3	106.4	52.2	162.2	63.6	0
<b>8CII</b>	1.566	1.787	3.994	100.0	109.7	–120.7	166.1	55.1	3.59
<b>8CIII</b>	1.550	1.781	4.024	109.4	108.3	–125.0	–34.2	60.0	4.44
<b>8CIV</b>	1.554	1.790	3.052	109.3	106.6	97.2	–30.3	66.4	1.72
<b>8CV</b>	1.565	1.800	4.085	100.4	102.9	–106.2	–166.9	178.5	1.41
<b>8CVI</b>	1.568	1.793	3.160	101.3	102.7	99.0	–163.4	–175.1	2.61
<b>8CVII</b>	1.554	1.781	3.159	109.9	104.1	91.3	31.0	170.5	2.54
<b>8CVIII</b>	1.550	1.790	4.030	109.7	104.5	–103.5	32.6	174.5	3.89

<sup>a</sup> Distances in Å; angles in deg; the dihedral angles, WXYZ, are positive for a clockwise movement from W to Z as you look from X to Y down bond XY. <sup>b</sup> Relative MP2/6–31G\* energies in kcal/mol.

**Table 5.** Selected Iminopersulfonic Acid, 9C, Structural Parameters<sup>a</sup>

conformer	S–N	S–O <sub>1</sub>	H <sub>α</sub> –N	N–S–C	S–O <sub>1</sub> –O <sub>2</sub>	SO <sub>1</sub> –O <sub>2</sub> –H <sub>α</sub>	MeS–N–Me	MeSO <sub>1</sub> –O <sub>2</sub>	ΔE <sup>b</sup>
<b>9CI</b>	1.566	1.808	2.876	100.9	108.2	79.7	166.3	55.6	0
<b>9CII</b>	1.563	1.816	4.029	100.0	109.5	–120.0	169.6	55.0	2.46
<b>9CIII</b>	1.546	1.804	4.126	111.3	109.5	–127.1	–34.5	57.6	2.68
<b>9CIV</b>	1.550	1.805	3.337	111.4	108.2	106.9	–31.0	61.6	0.94
<b>9CV</b>	1.563	1.827	4.073	100.5	102.2	–105.5	–170.0	–178.6	1.41
<b>9CVI</b>	1.565	1.819	3.338	100.9	102.1	106.0	–167.2	–177.1	0.72
<b>9CVII</b>	1.552	1.803	3.254	111.2	104.2	95.0	33.0	166.7	0.72
<b>9CVIII</b>	1.548	1.812	4.023	111.3	104.6	–102.7	34.8	173.7	1.58

<sup>a</sup> Distances in Å; angles in deg; the dihedral angles, WXYZ, are positive for a clockwise movement from W to Z as you look from X to Y down bond XY. <sup>b</sup> Relative MP2/6–31G\* energies in kcal/mol.

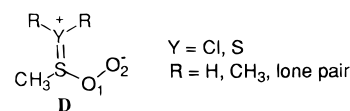
**Table 6.** Selected Thiadioxirane Structural Parameters<sup>a</sup>

substituent	S–X	S–O <sub>axial</sub>	S–O <sub>equatorial</sub>	O <sub>e</sub> –O <sub>a</sub>	O <sub>a</sub> –S–O <sub>e</sub>	X–S–O <sub>a</sub>	CH <sub>3</sub> –S–X	X–S–O <sub>e</sub>	NBO charges		
									S	O <sub>a</sub>	O <sub>e</sub>
<b>2B</b> CH <sub>3</sub>	1.854	1.811	1.652	1.556	53.2	143.5	94.1	92.6	1.32	–0.55	–0.46
<b>3B</b> NMe <sub>2</sub>	1.757	1.797	1.666	1.547	52.9	150.2	94.5	98.3	1.45	–0.55	–0.46
<b>4B</b> F	1.706	1.747	1.634	1.555	54.6	146.5	90.1	92.9	1.59	–0.51	–0.41
<b>5B</b> Cl	2.252	1.753	1.639	1.555	54.4	146.5	91.9	92.5	1.34	–0.47	–0.39
<b>6B</b> OCH <sub>3</sub>	1.735	1.771	1.650	1.549	53.7	147.9	88.9	95.9	1.52	–0.52	–0.44
<b>7B</b> SCH <sub>3</sub>	2.224	1.786	1.649	1.551	53.5	147.9	92.6	95.1	1.20	–0.52	–0.42
<b>8B</b> NH <sub>2</sub>	1.754	1.803	1.649	1.546	53.0	149.9	92.2	98.3	1.45	–0.55	–0.46
<b>9B</b> NHMe	1.749	1.800	1.659	1.546	52.9	149.8	92.4	98.3	1.45	–0.55	–0.46
<b>10B</b> OH	1.742	1.773	1.642	1.549	53.8	147.8	89.0	95.7	1.52	–0.52	–0.43
<b>11B</b> SH	2.261	1.780	1.643	1.552	53.7	147.4	91.6	94.4	1.22	–0.51	–0.41

<sup>a</sup> Distances in Å, angles in deg.

determining the structure of the persulfoxide intermediate. The atomic charges at the sulfonium-ion like sulfur as revealed by Mulliken, electrostatic (ESP), or natural bond order (NBO)<sup>23</sup> analysis are remarkably different in persulfoxides bearing substituents with 2p and 3p lone pairs (Table 1). It is tempting to suggest that the significantly reduced atomic charges at the sulfonium sulfur in **5A**, **7A**, and **11A** reflect the  $\pi$ -donating ability of substituents with 3p lone pairs as depicted in resonance structure **D**. On the other hand, the longer S–X bond length in persulfoxides **5A**, **7A**, and **11A** in comparison to their sulfenic acid precursors is inconsistent with a dominant role of  $\pi$ -donation (compare Tables 1 and 2).

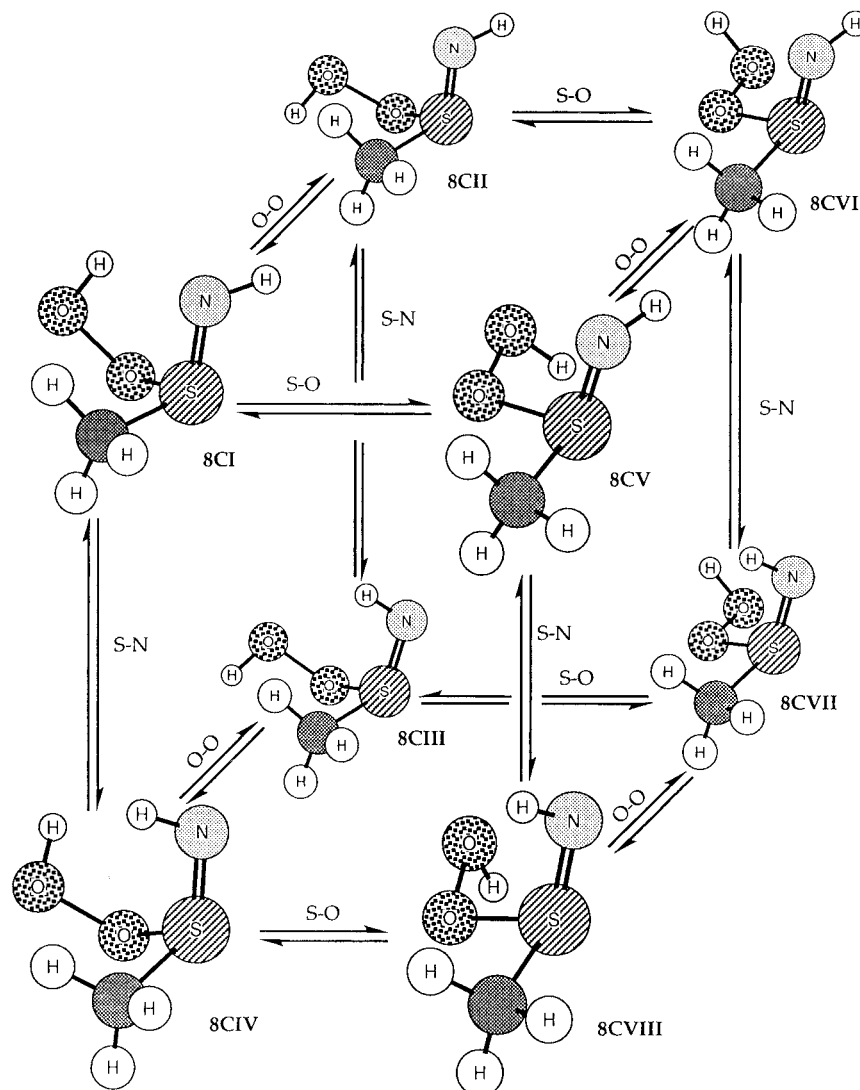
It is the repulsive electrostatic interaction between the terminal oxygen and the substituent X which plays the major role in



determining the electronic and structural character of the persulfoxide. This repulsive interaction is a direct result of the proximity of the substituent X and the outer oxygen (O<sub>2</sub>) which optimizes in every persulfoxide to a location bisecting the methyl–S–X angle. In the case of **5A** with the large 3p substituent Cl, this repulsive interaction manifests itself in a compromise structure exhibiting a dramatic increase in the O<sub>2</sub>–O<sub>1</sub>–S–X dihedral angle and an increase in the S–O<sub>1</sub> bond length. The increased S–O<sub>1</sub> bond length is accompanied by a smaller transfer of electron density from sulfur to oxygen as revealed by significant decreases in the negative NBO charges at O<sub>1</sub> and O<sub>2</sub> and positive NBO charge at sulfur in comparison

(23) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.

Scheme 6



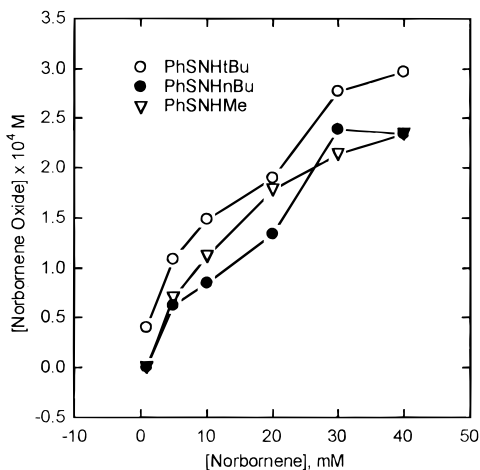
to the other persulfoxides (Table 1). We also believe that this repulsive interaction is responsible in part for the increase in the S-X distance as **5** is converted to the persulfoxide. The effect of this repulsive interaction is also observed to a reduced extent in other persulfoxides bearing substituents with 3p lone pairs. The structural integrity of the persulfoxide is also influenced by steric effects. An increase in the size of the substituent X (e.g., **8A**  $\Rightarrow$  **9A**  $\Rightarrow$  **3A**) leads to small increases in the O<sub>2</sub>-O<sub>1</sub>-S-X dihedral angle and in the O<sub>1</sub>-O<sub>2</sub> bond distance and a decrease in the S-O<sub>1</sub> bond distance.

Persulfoxides **8A**–**11A**, in contrast to **2A**–**7A**, all have a hydrogen attached to an adjacent heteroatom and have at least one rotomer which either spontaneously collapses or collapses when stringent (tight) convergence criteria are imposed to persulfonic acids, **8C**–**11C** (Scheme 4). For example, at the MP2/6-31G\* level with normal convergence criteria (i.e., forces of  $<10^{-4}$ ; displacements of  $<10^{-3}$ ), minima for both an “out”, **8A**, and an “in”, **8A'**, rotomer of the persulfoxide derived from sulfenamide **8** can be located. These “in” and “out” rotomers as depicted in Scheme 5 represent different rotational conformations around the N-S bonds. The nitrogen lone pair is syn to the S-C bond in the “in” isomer but anti to the S-C bond in the “out” rotomer. Only the “out” rotomer exists when tight convergence criteria are imposed (i.e., forces of  $<10^{-5}$ ; displacements of ca.  $10^{-6}$ ). Even the out rotomer, **8A**, however,

has little chemical significance because its barrier to collapse to iminopersulfonic acid **8CI** (*vide infra*) is only 0.0015 kcal/mol.<sup>24</sup> In the case of sulfenamide **9**, neither the “out” nor “in” rotomer, **9A** or **9A'**, survives under stringent convergence criteria, suggesting the possibility of a concerted formation of the iminopersulfonic acid.

**B. Iminopersulfonic Acids (C in Scheme 4).** Eight different conformers for the iminopersulfonic acids have been identified by a careful search of conformational space (Tables 4 and 5). The energies of these conformers all lie within 3.89 kcal/mol of each other for **8C** and within 2.68 kcal/mol of each other for **9C**. Each conformer is related to three other conformers by rotations about the O-O, S-O, and S-N bonds. Consequently, each of the conformations of iminopersulfonic acid (**8C**) occupy a corner of a conformational interconversion cube (Scheme 6). The vertical equilibria represent rotations about the S-N bond, the horizontal equilibria rotations about the S-O bond, and the diagonal equilibria rotations around the O-O bond. In the pairs of conformers related by rotations about the S-O bond, the structure with the peroxy hydrogen on the same face of the S-O-O plane as the nitrogen, **8CI**, **8CIV**, **8CVI**, and **8CVII**, are the most stable with **8CI** representing the global minimum (Table 4). The nitrogen-peroxy hydrogen distance in these four conformers is less than 3.2 Å in comparison to greater than

(24) Greer, A.; Jensen, F.; Clennan, E. L. Unpublished results.



**Figure 1.** Norbornene oxide concentrations as a function of the concentration of norbornene in the photooxidations of 2.3 M sulfenamide.

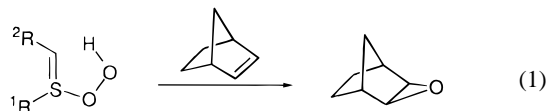
3.9 Å in their rotameric partners. The very short N–HOO distance of 2.264 Å found in **8CI** is even shorter than the hydrogen-bond length of 2.74 Å reported for *p*-nitroperoxybenzoic acid.<sup>25</sup>

The eight conformers located for **9C** are very similar to those located for **8C** (Table 5). The conformer with the shortest N–HOO distance, **9CI** (2.876 Å), is also the global minimum. In the case of **9C**, however, the energy difference between the global minimum and the next most energetically stable conformer is only 0.72 kcal/mol in comparison to 1.41 kcal/mol for **8C**. This difference undoubtedly reflects the destabilizing methyl–methyl interaction in **9CI**.

In comparison to the persulfonides, **8A**, **9A**, **10A**, and **11A**, the corresponding persulfonic acids, **8C**, **9C**, **10C**, and **11C**, have shorter S–X bond lengths, as anticipated for increased  $\pi$ -bond character, and longer S–O<sub>1</sub> bond lengths (Tables 3, 4, and 5). The S–X (O) bond length in **10C** (1.49 Å) is very similar to S–O bond lengths reported in alkyl sulfoxides (ca. 1.48–1.51 Å).<sup>26,27</sup>

To provide experimental evidence for the existence of iminopersulfonic acids, the photooxidations of PhSNHMe, PhSNHnBu, and PhSNHtBu in the presence of norbornene have been examined. Gas chromatographic analyses of these reactions revealed formation of norbornene epoxide in concentrations which are directly dependent upon the initial concentration of norbornene<sup>28</sup> (Figure 1). These results are compelling evidence for formation of iminopersulfonic acids and are consistent with the fact that the nitrogen in **8CI** is spatially close and in the proper position to pick up the persulfonic proton in the classic butterfly epoxidation transition state. In addition, Ando and co-workers<sup>29</sup> have reported that *S*-hydroperoxysulfonium ylides, the carbon analogues of the iminopersulfonic acids, convert norbornene to its epoxide (eq 1).

**C. Thiadioxiranes (B in Scheme 4).** The thiadioxiranes, **2B–11B**, optimize to asymmetric structures with two non-equivalent S–O bonds (Table 6). The geometry is best described as distorted trigonal bipyramidal (TBP), where the ligands reside in either apical or equatorial positions. In all



cases, the substituent X and an oxygen occupy the apical positions (X, O<sub>a(axial)</sub>) leaving the remaining oxygen and methyl carbon to occupy the equatorial positions (C, O<sub>e(equatorial)</sub>). The S–O<sub>a</sub> bonds are longer than the S–O<sub>e</sub> bonds, and natural bond order analyses reveal more negative charge at O<sub>a</sub> than O<sub>e</sub> (Table 6). The distortion from idealized TBP geometry is best seen by examination of the O<sub>a</sub>–S–O<sub>e</sub> angle which should be 90° and the X–S–O<sub>a</sub> angle which should be 180° (Table 6) in a perfect TBP environment.

The S–X bond is substantially longer in the thiadioxirane than in the persulfonide (compare Tables 1 and 6) for all substituents X with the sole exception of compound **5** (X = Cl). In **5** the S–X bond length is 0.13 Å shorter in the thiadioxirane than in the persulfonide. This, however, is consistent with the fact the bond-lengthening repulsive interaction between the terminal oxygen and the chlorine in the persulfonide (*vide supra*) is absent in the thiadioxirane. The apical S–Cl distance in the thiadioxirane is 0.20 Å longer than in its sulfonyl chloride precursor, **5** (compare Tables 2 and 6), as anticipated from the molecular orbital description of the very long 4-electron 3-centered apical–apical bonds in trigonal bipyramidal sulfuranes.

As the electronic character of the apical substituent X is altered, it has only a minor effect on the overall pseudo TBP geometry. Thiadioxiranes **2B–11B** bear a remarkable resemblance to each other in many of the basic geometric features. For example, the bond distances S–O<sub>a</sub>, S–O<sub>e</sub>, and O<sub>a</sub>–O<sub>e</sub> are identical to within 0.05, 0.03, and 0.01 Å, respectively. Bond angles are also insensitive to the identity of X and only fluctuate by ca. 5° and 2° for X–S–C and S–O<sub>e</sub>–O<sub>a</sub>, respectively. The only exception to this insensitivity to the identity of X is the S–X bond length which changes from 1.706 Å in **4B** to 2.261 Å in **11B**. Changes in the steric requirements of the substituents also provide only a minimal perturbation to the distorted TBP geometry. Only small, albeit systematic, decreases in S–O<sub>a</sub>, S–O<sub>e</sub>–O<sub>a</sub>, and O<sub>a</sub>–O<sub>e</sub>–S–C, and increases in S–O<sub>e</sub> and X–S–C, are observed as the size of the amino substituent increases (e.g., **8B**  $\Rightarrow$  **9B**  $\Rightarrow$  **3B**).

**D. Transition State Structures (TS in Scheme 4).** Saddle points connecting the persulfonide and thiadioxirane have been located for seven of the nine substituents (Table 7). Structure **2TS** has C<sub>s</sub> symmetry while **3TS**, **4TS**, **5TS**, **6TS**, **7TS**, and **8TS** have no symmetry. Calculations were not done for the NHCH<sub>3</sub> **9TS** system since we believe it is not necessary due to the very similar geometry and energy relative to that of X = NH<sub>2</sub>, **8TS**. All attempts at transition state optimizations for the sulfenic acid **10** and hydrodisulfide **11** resulted in the collapse to the peracid structures **10C** and **11C**, respectively.

The interconversions of the persulfonides to the thiadioxiranes are characterized by several events on the potential energy surfaces including (1) substantial decreases in the S–O<sub>1</sub>–O<sub>2</sub> angles; (2) increases in the S–X bond distances (with the exception of X = Cl, **5**); (3) increases in the O<sub>1</sub>–O<sub>2</sub> bond distances; and (4) reductions in the S–O<sub>2</sub> distances.

**E. Energetic Results.** The relative energies of the stationary points on the reaction surfaces are given in Table 8 and Scheme 7 using the nomenclature depicted in Scheme 4. These energies are for the most part insensitive to an extension of basis set or theoretical level. The same through-bond and through-space electronic interactions and steric effects of the substituents which

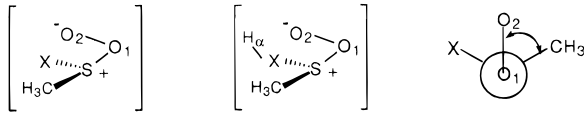
(25) Kim, H. S.; Chu, S.-C.; Jeffrey, G. A. *Acta Crystallogr.* **1970**, B26, 896–900.

(26) Carey, F. A.; Smith, P. M.; Maher, R. J.; Bryan, R. F. *J. Org. Chem.* **1977**, 42, 961–967.

(27) *The Chemistry of the Sulfonium Group. Part 1*; Stirling, C. J. M., Ed.; John Wiley & Sons: Salisbury, U.K., 1981.

(28) Clennan, E. L.; Chen, M.-F. Unpublished results.

(29) Akasaka, T.; Sakurai, A.; Ando, W. *J. Am. Chem. Soc.* **1991**, 113, 2696–2701.

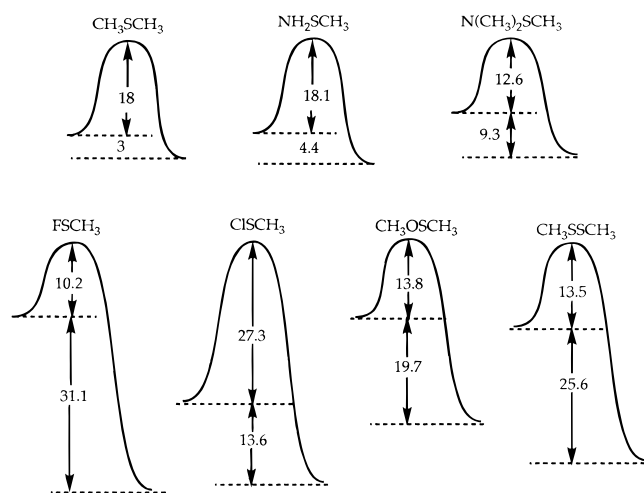
**Table 7.** Selected Transition State Structural Parameters<sup>a</sup>


	substituent	S-X	S-O <sub>1</sub>	S-O <sub>2</sub>	O <sub>1</sub> -O <sub>2</sub>	H <sub>α</sub> -O <sub>2</sub>	X-S-C	S-O <sub>1</sub> -O <sub>2</sub>	O <sub>2</sub> -O <sub>1</sub> -S-C
<b>2TS</b>	CH <sub>3</sub> <sup>b</sup>		1.636	1.926	1.541				
<b>3TS</b>	NMe <sub>2</sub>	1.687	1.627	2.001	1.533		101.4	78.5	69.9
<b>4TS</b>	F	1.631	1.561	2.066	1.521		99.0	84.2	61.4
<b>5TS</b>	Cl	2.105	1.565	2.073	1.517		100.6	84.5	60.6
<b>6TS</b>	OCH <sub>3</sub>	1.670	1.593	2.039	1.525		95.1	81.6	66.1
<b>7TS</b>	SCH <sub>3</sub>	2.107	1.597	1.987	1.532		105.6	78.8	65.3
<b>8TS</b>	NH <sub>2</sub>	1.693	1.633	1.956	1.538	2.282	100.0	76.1	68.4

<sup>a</sup> Distances in Å, angles in deg. <sup>b</sup> Reference 5.**Table 8.** Relative Energies (kcal/mol) of Species on the RSX + <sup>1</sup>O<sub>2</sub> Reaction Surface<sup>a</sup>

	substituent X	$\Delta E^{AB} = E(\mathbf{B}) - E(\mathbf{A})$			$\Delta E^* = E(\mathbf{TS}) - E(\mathbf{A})$		$\Delta E^{AC} = E(\mathbf{C})^b - E(\mathbf{A})$			$\Delta E^c = E(\mathbf{A}) - E(\mathbf{S})$
		1	2	3	1		1	2	3	
<b>2</b>	CH <sub>3</sub>	-3.0	2.6	-2.7	18.0					ca. 4
<b>3</b>	N(CH <sub>3</sub> ) <sub>2</sub>	-9.3			12.6					ca. -5
<b>4</b>	F	-31.1	-24.3	-30.1	10.2					ca. -4
<b>5</b>	Cl	-13.6	-15.9	-14.4	27.3					ca. -8
<b>6</b>	OCH <sub>3</sub>	-19.7			13.8					ca. -6
<b>7</b>	SCH <sub>3</sub>	-25.6			13.5					ca. 9
<b>8</b>	NH <sub>2</sub>	-12.2	-7.2	-10.8	10.3	-25.1	-20.8	-25.7		ca. -9
<b>8'</b>	NH <sub>2</sub>	-4.4	0.03	-3.2	18.1	-17.3	-13.5	-18.1		ca. -1
<b>9</b>	NHCH <sub>3</sub>	-11.8				-23.5				ca. -9
<b>9'</b>	NHCH <sub>3</sub>	-4.5				-16.2				ca. -2
<b>10</b>	OH	-22.9	-16.7	-21.6		-48.7	-44.0	-48.9		ca. -2
<b>11</b>	SH	-18.0	-10.9	-16.5		-49.0	-43.8	-48.1		ca. 11

<sup>a</sup> **8**, **9** = "out" conformations; **8'**, **9'** = "in" conformations; **A** = persulfoxide; **B** = thiadioxirane; **TS** = transition state; **C** = peracid; **S** = substrate (RSX + <sup>1</sup>O<sub>2</sub>); 1 = MP2/6-31G\*; 2 = CCSD(T)/6-31G\*; 3 = MP2/6-311G(2d). <sup>b</sup> Energy of global minimum rotomer. <sup>c</sup> Reflects a 10 kcal/mol correction factor derived from the H<sub>2</sub>S + <sup>1</sup>O<sub>2</sub> system in ref 5 where the basis set has been reasonably converged with the 6-311+G(3d2flg) extension.

**Scheme 7**

we argued influenced the geometries of the stationary points on the persulfoxide–thiadioxirane energy surface undoubtedly also affect their energetics.

In all cases, the thiadioxiranes are thermodynamically stabilized in the gas phase relative to the persulfoxides. The interconversion of the persulfoxides to the thiadioxiranes (**A** to **B** in Scheme 4) get increasingly exothermic in the substituent order CH<sub>3</sub> < NH<sub>2</sub> < Cl < OCH<sub>3</sub> < SCH<sub>3</sub> < F. This trend, with the glaring exception of sulfur, follows the  $\sigma$ -electron-withdrawing ability of X as predicted by the Pauling electronegativity scale.<sup>30</sup> This observation is consistent with destabi-

lization of the persulfoxides by the  $\sigma$ -withdrawing character of the substituents and/or the stabilization of the thiadioxiranes by the apical substituent effect. The abnormal behavior of sulfur is consistent with the electronic (electron repulsion between X and O<sub>2</sub>) destabilization of the persulfoxide discussed earlier. The formations of the sulfur-substituted persulfoxides, **7A** and **11A**, are also endothermic by ca. 9 and 11 kcal/mol, respectively. In contrast, all the other persulfoxides are formed in exothermic processes with the exception of **2A** which has a moderate reaction endothermicity of ca. 4 kcal/mol (Table 8).

The activation energies for interconversions of the persulfoxides and thiadioxiranes span the range from 10.2 for X = F to 27.3 kcal/mol for X = Cl. The activation barriers decrease in the substituent order Cl > CH<sub>3</sub>  $\approx$  NH<sub>2</sub> > OCH<sub>3</sub>  $\approx$  SCH<sub>3</sub> > F. This substituent-induced trend is the same as that observed for the exothermicities of the reactions with the exception of Cl. We suggest that the unanticipated behavior of Cl is a result of the increasing importance of the repulsive interaction between the negatively charged oxygen and the 3p electrons on chlorine as the oxygen approaches sulfur (and closer to Cl) in the transition state for closure to the thiadioxirane.

The iminopersulfonic acids are clearly, with the exceptions of the sulfones, the most stable species on the potential energy surfaces. At the MP2/6-31G\* level, the iminopersulfonic acid **8C** is 25.1 and 17.3 kcal/mol more stable than the "out" and "in" persulfoxides, **8A** and **8A'**, respectively, and 12.9 kcal/mol more stable than the thiadioxirane, **8B**.

## Conclusion

A computational examination of the reaction surfaces for the interconversions of a series of persulfinate (persulfoxide)

(30) Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*, 3rd ed.; Harper & Row: New York, 1983.



derivatives has demonstrated the viability of strategy 2 which envisioned that electron-withdrawing groups would increase the energy gap and decrease the activation barrier separating the persulfinate and corresponding thiadioxirane. Consequently, the inability to directly observe the thiadioxiranes in the reactions of the sulfenic acid derivatives **2–7** is a kinetic phenomenon related to their rapid reaction with substrate. Therefore, direct detection of these thiadioxiranes may be possible on a solid support (e.g., silica) where the sulfenic acid molecules are spatially isolated from one another. In contrast, the reactions of sulfenic acid derivatives **8–11** with singlet oxygen to give thiadioxiranes are unlikely to be observed. In these reactions formations of the persulfenic acids appear to be the preferred pathways. Compelling experimental verification of iminopersulfenic acid formation is provided by the observation of

epoxidation of norbornene during photooxidations of N-substituted benzenesulfenamides.

**Acknowledgment.** This work is supported by Grants from the Danish National Science Research Council (F.J.). We also thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research (E.L.C.).

**Supporting Information Available:** Optimized geometries for **2–11**, conformational interconversion cube for **9C**, and charge distributions in the persulfoxides and thiadioxiranes (18 pages). See any current masthead page for ordering and Internet access instructions.

JA964295L