

## Molecular Modeling Studies on Aromatic Sulfonation. 1. Intermediates Formed in the Sulfonation of Toluene

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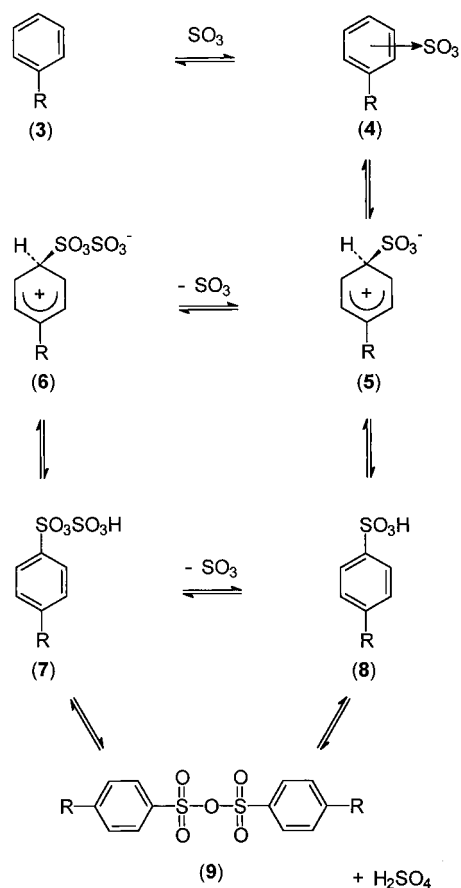
Molecular modeling studies suggest that the mechanism of the sulfonation of toluene with sulfur trioxide proceeds via the formation of a  $\pi$ -complex (**4b**) which rearranges to form a Wheland intermediate (**5**). This structure is unable to form toluenesulfonic acid (**8**) directly and prefers to react with a further molecule of sulfur trioxide to form a pyrosulfonate intermediate (**6a**) which undergoes a facile prototropic rearrangement involving the transfer of the ring hydrogen at the  $sp^3$  carbon of **6a** to the sulfonate oxygen atom to form the corresponding acid (**7**). The formation of toluenesulfonic acid (**8**) appears to arise from an exothermic reaction of between the pyrosulfonic acid (**7**) and toluene. The overall calculated thermodynamic change in moving from the reaction of one molecule of sulfur trioxide with toluene to the sulfonic acid (**8b**) is fully consistent with an estimated experimental value of  $-33.5 \text{ kcal mol}^{-1}$  for the same reaction using simple alkylbenzenes.

### Introduction

The mechanism of aromatic sulfonation is complex and is thought to involve several intermediate species which are not readily accessible by experiment.<sup>1–4</sup> In the case of sulfonation with sulfur trioxide a number of intermediate structures (**4–6**) have been proposed (Scheme 1),<sup>4</sup> but few, if any, have been properly characterized. The reaction appears to proceed with the absence of a kinetic isotope effect for the ring hydrogen. It has been proposed that the rate-limiting step of aromatic sulfonation with sulfur trioxide (**1**) in fluorotrichloromethane involves the addition of the reagent to the substrate such as toluene (**3**) to give the Wheland intermediate (**5**), but the corresponding rate-limiting step for the same reaction in nitromethane apparently involves the addition of sulfur trioxide to intermediate **5** to give the pyrosulfonate intermediate **6**.<sup>2,3</sup> A molecular rearrangement of the intermediate **5** or **6** then gives either toluenesulfonic acid (**8**) or toluene pyrosulfonic acid (**7**), respectively. In the latter case, although it is possible that toluenesulfonic acid (**8**) is formed by loss of sulfur trioxide (Scheme 1), it seems more likely that the acid **7** once formed will be a highly reactive sulfonating agent which attacks toluene to form 2 equiv of toluenesulfonic acid (**8**).<sup>4</sup> While the sulfonation proceeds with high selectivity and in very high yield, the main byproduct of the reaction is toluenesulfonic anhydride (**9**) which is presumed to be formed from a reaction between the sulfonic acids **7** and **8** with the liberation of sulfuric acid (Scheme 1).<sup>4</sup>

The present theoretical studies, which are concerned solely with the thermodynamic aspects of these very complex processes, have been carried out to probe the structures, electronic properties, and energies of some of

Scheme 1. Postulated Mechanism of Aromatic Sulfonation with  $\text{SO}_3$



these unstable species in an attempt to gain a greater understanding of the fundamental reactions which are occurring during aromatic sulfonation.

There are a number of theoretical methods which have been used to explore the mechanism of electrophilic aromatic substitution. These range from the simple Huckel method<sup>5</sup> to semiempirical treatments such as the MNDO,<sup>6</sup> AM1,<sup>7</sup> and PM3<sup>8</sup> methods through to more complex ab initio treatments using extended basis sets.<sup>9</sup> While the semiempirical methods generally give a rea-

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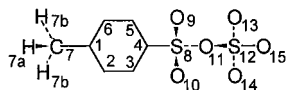
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**Scheme 2. Numbering Convention Adopted for the Aromatic Structures 3–9**



sonable account of the geometry and electronic properties of simple aromatic systems and have been used to study electrophilic substitution reactions involving first row elements, in sulfur-containing systems, they suffer from the disadvantage that the binding energy of the sulfur atom is represented by the valence 3s and 3p orbitals only. Although the sulfur parameterization<sup>10</sup> has been adapted to represent the vacant 3d orbitals, the absence of these functions often have a pronounced effect on the molecular geometry and energies of many organic sulfur-containing systems.

Both semiempirical and *ab initio* methods have been used here to probe the enthalpies of the various processes (Scheme 1) using toluene as a typical substrate. No account has been taken of the entropy changes involved in the sulfonation reaction which would be expected to be significantly negative for the formation of intermediates **5** and **6**, though smaller and less important for the formation of toluenesulfonic acid (**8**) and sulfonic anhydride **9** from the pyrosulfonic acid **7**.

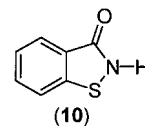
### Methods of Calculation

Initial calculations were carried out on sulfur trioxide (**1**) and sulfuric acid (**2**) using the MNDO,<sup>6</sup> AM1,<sup>7</sup> and PM3<sup>8</sup> methods of the MOPAC package.<sup>11</sup> Because the results from these calculations were considered unsatisfactory (see later), the 4-31G basis set<sup>9</sup> of the GAMESS program<sup>12</sup> was used for all subsequent calculations. The atom numbering convention used for these studies are shown below (Scheme 2). While there are many different conformations possible for most of the aromatic structures considered here, in most cases only one of these was assessed in order to reduce and simplify the number of calculations. For example, in toluene (**3**) and its sulfonic acids **7** and **8**, hydrogen atom H7a was placed perpendicularly above the ring plane (torsion angle C2–C1–C7–H7a = 90°) with H7b and H7c below the plane, and in a *trans* conformation in the sulfonic acids to oxygen atom O11, which was placed perpendicularly below the plane (torsion angle C5–C4–S8–O11 = –90°), with O9 and O11 above the plane as shown (Scheme 2). However, the position of the hydrogen (H11) attached to O11 in toluenesulfonic acid (**8**) will have an impact on the properties of the molecule as it can point either away from the ring or toward it. Both possibilities were explored, where the torsion angle C4–S8–O11–H11 was

set at 0° to correspond to the direct product **8a** which would result in one mechanism from the transfer of the ring proton, H4, from the Wheland intermediate **5** to the sulfonate oxygen atoms O11, and also at 180° to correspond to the most stable product **8b**. All the structures were prepared and analyzed using the SYBYL molecular modeling program,<sup>13</sup> and calculations were carried out on a cluster of Silicon Graphics Indigo workstations.

### Discussion

There have been few previous studies of aromatic sulfonation at a reasonable level of theory with the exception of a STO-3G study of substrate and positional selectivity in toluene based on frontier orbital theory.<sup>14</sup> In this study, the selectivity of electrophilic substitution was related to a frontier rate factor which was equated to both the charges and the reciprocal of the energies of the frontier orbitals of the substrate alone. In the present work, the energies of the substrate, intermediates, and products were probed using the more accurate 4-31G basis set for all first row elements with additional d functions added to the sulfur atom only (subsequently referred to as the 4-31G/S\* basis set). This approach is justified by our recent studies on isothiazolinones which showed a marked improvement in the key carbon–sulfur and sulfur–nitrogen bond lengths when additional d orbitals were added to the sulfur atom in this way.<sup>15</sup> For example, in 4,5-benzo-3-isothiazolinone (**10**), while calculations using the standard 4-31G basis set gave C–S and C–N bond lengths of 1.83 and 1.78 Å, respectively, versus experimental values of 1.76 and 1.70 Å, respectively, the addition of d orbitals to the sulfur atom alone gave markedly improved values of 1.76 and 1.71 Å, respectively.<sup>15</sup>



**1. Structural Aspects.** An examination of the Cambridge Structural Database (CSD)<sup>16</sup> shows few experimental reference structures available to check the accuracy of the calculations on the sulfur-containing systems reported here though there are data available from other sources on sulfur trioxide (**1**)<sup>17</sup> and sulfuric acid (**2**).<sup>18,19</sup> Initial calculations on **1** and **2** using the MNDO method gave S=O and S–O bond lengths which are far too long by comparison with experimental data, while the AM1 and PM3 methods gave values which are too short for the former and too long for the latter (Table 1). However, although all three methods give satisfactory angles (Table 1), the discrepancy between the calculated and experimental bond lengths was considered to be too large, and

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**Table 1. Geometric and Electronic Properties of Sulfur Trioxide (1) and Sulfuric Acid (2) Calculated at the Semiempirical and ab Initio 4-31G/S\* Level Compared with Experimental Data and That for Dimethyl Sulfate (11)**

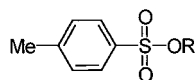
method	bond lengths (Å)			bond angles (deg)			atomic charges <sup>a</sup>			
	S=O	S-OH	O-H	O=S=O	O-S-O	S-O-H	S	Od	Os	H
<b>Structure 1</b>										
MNDO	1.491			120.0			1.600	-0.533		
AM1	1.350			120.0			2.838	-0.946		
PM3	1.384			120.0			2.543	-0.848		
4-31G/S*	1.407			120.0			1.467	-0.489		
expt <sup>b</sup>	1.43 ± 0.02			120.0						
<b>Structure 2</b>										
MNDO	1.515	1.629	0.947	122.4	100.2	117.2	1.748	-0.639	-0.484	0.249
AM1	1.398	1.573	0.938	119.8	94.4	117.9	2.858	-0.952	-0.772	0.294
PM3	1.397	1.669	0.955	121.8	89.1	110.3	2.537	-0.883	-0.629	0.244
4-31G/S*	1.417	1.551	0.957	118.8	95.0	118.6	1.598	-0.581	-0.703	0.485
expt <sup>c</sup>	1.43	1.54								
<b>Structure 11</b>										
expt <sup>d</sup>	1.410	1.535		119.9	105.5					

<sup>a</sup> Od and Os are oxygen atoms at the double and single bond positions, respectively. <sup>b</sup> Reference 17. <sup>c</sup> References 18 and 19. <sup>d</sup> Reference 20.

all subsequent calculations were carried out using the ab initio method.

The 4-31G/S\* results for sulfur trioxide (**1**) show a marked improvement over the semiempirical results with the S=O bond length at 1.407 Å almost falling within the experimental error range (Table 1). In sulfuric acid (**2**) a similar calculated value of 1.417 Å is obtained for the same bond which is slightly shorter than that found experimentally at 1.43 Å (Table 1), but the latter is almost certainly longer than expected because of intermolecular hydrogen bonding of the oxygen atom to an adjacent sulfuric acid molecule. Indeed, the corresponding experimental bond lengths for dimethyl sulfate (**11**) which cannot hydrogen bond are shorter with values of 1.410 and 1.535 Å for the S=O and S-O bonds, respectively,<sup>20</sup> and more compatible with the calculated 4-31G/S\* results obtained for sulfuric acid. The O=S=O and O-S-O angles also show a good correlation between experiment and theory with values of 119.9° and 105.5° in the former versus values of 118.8° and 95.0° in the latter, respectively.

Although there are no experimental data on toluene-sulfonic acid (**8**) or the pyrosulfonic acid **7**, there are many examples of alkyl toluenesulfonates (**12**) present in the CSD.<sup>16</sup> An analysis of typical examples such as the 2-phenylethyl (**12a**),<sup>21</sup> cyclohexyl (**12b**),<sup>22</sup> and 3-chloro-2-oxopropyl (**12c**)<sup>23</sup> *p*-toluenesulfonates show bond lengths ranging from 1.74–1.76 Å (Ar-SO<sub>3</sub>R), 1.41–1.43 Å (S=O), and 1.56–1.58 Å (S-O).

**(12)**

- a R = C<sub>2</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>  
 b R = C<sub>6</sub>H<sub>11</sub>  
 c R = CH<sub>2</sub>COCH<sub>2</sub>Cl  
 d R = CH<sub>3</sub>

The calculated values of 1.73, 1.43, and 1.58 Å, respectively, for the same bonds in **8b**, therefore, show a

**Table 2. Bond Lengths of the Reactants, Intermediates, and Products (3–9) Involved in the Sulfonation of Toluene Calculated at the ab Initio 4-31G/S\* Level**

bond lengths (Å)	structure						
	3	4	5	6a	7	8b	9
C1–C2	1.387	1.389	1.406	1.408	1.390	1.389	1.390
C2–C3	1.383	1.382	1.358	1.353	1.378	1.379	1.379
C3–C4	1.382	1.388	1.450	1.457	1.386	1.384	1.385
C1–C7	1.508	1.507	1.497	1.493	1.506	1.507	1.507
C7–H7a	1.085	1.085	1.085	1.087	1.085	1.085	1.085
C2–H2	1.073	1.072	1.070	1.069	1.071	1.071	1.072
C3–H3	1.072	1.072	1.071	1.070	1.070	1.071	1.070
C4–H4	1.072	1.071	1.092	1.137			
C4–S8		2.962	1.967	1.831	1.728	1.734	1.736
S8–O9		1.408	1.435	1.425	1.417	1.428	1.420
S8–O11		1.409	1.436	1.506	1.652	1.582	1.636
O11–H11						0.958	
O11–S12				1.813	1.609		1.635
S12–O13				1.412	1.408		1.420
S12–O15				1.449	1.547		
O15–H15					0.954		

very good correlation with the experimental data; a similar result is obtained for **7** with calculated values here of 1.73 and 1.42 Å for the first two bonds (Table 2). Although there are no experimental geometric data available for the unstable Wheland intermediates **5** and **6a**, the calculated S=O bond lengths of 1.43–1.44 Å (Table 2) are longer than those found in sulfur trioxide (**1**) at 1.407 Å (Table 1) though fully compatible with those found in the loosely related triphenylphosphine-sulfur trioxide complex<sup>24,25</sup> which shows values for the same bond ranging from 1.42 to 1.44 Å.

The calculated angles also show a very good correlation with expected values. For example, the O9–S8–O10 angles in the sulfonic acids **7** and **8b** and sulfone **9** at 121.5°, 119.3°, and 120.7° (Table 3) compare favorably with values of 119.8°, 120.1°, and 120.0° found in the crystal structures of **12a**, **12b**, and **12c**, respectively. However, the corresponding angle C4–S8–O11 is smaller and ranges from 100.3° to 102.2° for the calculated structures (Table 3) versus 103° to 104° in the related crystal structures.

The experimental structures for **12a**, **12b**, and **12c** are generally spatially arranged so that the oxygen contain-

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**Table 3. Bond Angles and Torsion Angles of the Reactants, Intermediates, and Products (3–9) Involved in the Sulfonation of Toluene Calculated at the ab Initio 4-31G/S\* Level**

angles (deg)	structure						
	3	4	5	6a	7	8b	9
C1–C2–C3	120.9	120.9	119.9	120.3	121.0	121.0	121.0
C2–C3–C4	120.2	120.2	121.5	121.1	119.3	119.4	119.4
C3–C4–C5	119.5	119.3	115.4	116.0	120.8	120.6	120.5
C2–C1–C6	118.4	118.6	120.2	120.6	118.8	118.7	118.7
C2–C1–C7	120.9	120.8	119.9	119.7	120.6	120.7	120.7
C1–C2–H2	119.4	119.6	119.3	119.3	119.7	119.7	119.6
C2–C3–H3	119.8	119.9	120.9	121.2	120.5	120.6	120.5
C3–C4–H4	120.3	120.3	108.6	103.7			
C3–C4–S8		93.6	114.3	114.6	119.4	119.7	119.5
C4–S8–O9		96.3	101.8	105.6	110.3	110.3	109.4
O9–S8–O10		120.1	117.1	119.9	121.5	119.3	120.7
O9–S8–O11		119.8	115.9	110.6	105.6	107.5	106.7
C4–S8–O11			100.2	102.9	101.5	100.3	102.2
S8–O11–H11							122.6
S8–O11–S12				144.5	130.2		129.7
O11–S12–O13				100.7	109.0		106.5
O11–S12–O15				97.2	96.4		
S12–O15–H15					123.4		
C2–C3–C4–H4		–177.3	–111.1	–103.5			
C2–C3–C4–S8		96.9	146.7	146.5	172.1	177.3	172.7
C3–C4–S8–O9		–120.5	–128.3	–132.2	–154.4	–155.2	–153.2
C3–C4–S8–O11		120.1	112.3	111.8	94.0	91.7	94.0
C4–S8–O11–H11						–180.0	
C4–S8–O11–S12				–0.2	–179.6		–179.6
S8–O11–S12–O13				117.9	–66.2		–65.1
S8–O11–S12–O15				–0.1	–179.1		
O11–S12–O15–H15					–4.8		

ing the ester group, O11, lies below the ring plane with the torsion angle C3–C4–S8–O11 ranging from 75° to 112° broadly in line with the calculated angles of 94.0° and 91.7° in **7** and **8b**, respectively (Table 3).

**2. Electronic Properties.** There is little experimental data available on the electronic properties of the molecules considered here with the exception of data for the dipole moment of toluene (**3**) which varies from 0.31 D as a liquid<sup>26</sup> to 0.38 D in the vapor phase<sup>27</sup> and for the methyl ester **12d** of toluenesulfonic acid, which would be expected to be similar to the free acid **8**, with values of 4.89 to 5.22 D in benzene<sup>28,29</sup> and 5.26 D in dioxane.<sup>30</sup> The calculated results of 0.31 D for the former (**3**) (Table 4) shows a good correlation with the experimental data though the calculated value for toluenesulfonic acid (**8**) is highly dependent on the molecular conformation of the sulfonic acid group adopted. Thus a calculation on the conformer **8a** with the acidic hydrogen of the sulfonate group, H11, placed *cis* to the aromatic ring, which is the product in one reaction mechanism, resulting from the transfer of the ring proton, H4, from the Wheland intermediate **5** to oxygen, O11, shows a very large dipole moment of 8.31 D. However, in the preferred alternative conformer **8b**, where oxygen O11 has been rotated 180° around the S8–O11 bond to make H11 *trans* to the aromatic ring, the calculated dipole moment reduces to 4.70 D, which is now fully compatible with the data on methyl tosylate (**12d**).

The calculations suggest that sulfur trioxide (**1**) is able to react with toluene (**3**) to form a loose  $\pi$ -complex when the starting structure is arranged so that the oxygen atoms are positioned over carbon atoms C2, C4, and C6

and the sulfur over the central ring. The resulting optimized structure **4a** shows each oxygen at an average distance of 3.45 Å from the respective carbon, and there is a small negative charge of –0.009 on the SO<sub>3</sub> component of the molecular complex which contributes to the overall dipole moment of 0.61 D. However, a more stable  $\pi$ -complex results when the sulfur is positioned over C4 with the three oxygens over C3, C5, and H4, respectively, at the starting position of the structure optimization. The resulting structure **4b** shows a bond distance of 2.96 Å between S8 and C4 with an overall charge now of –0.041 on the SO<sub>3</sub> component of the complex to give a much larger dipole moment of 1.74 D (Table 4).

In moving from the more stable  $\pi$ -complex **4b** to the Wheland intermediate **5**, the aromatic carbon C4 changes from a trigonal sp<sup>2</sup> conformation to a tetrahedral sp<sup>3</sup> conformation with both C4–C3 and C4–C5 bond lengths now at 1.45 Å versus 1.38 Å in toluene, the C4–S8 distance at 1.967 Å (Table 2), an angle at C3–C4–H4 of 108.6°, and a torsion angle C2–C3–C4–H4 of –115.5° (Table 3). The overall charge at the aromatic ring and at the SO<sub>3</sub> group is now  $\pm 0.500$ , and the molecule is highly polarized with an overall dipole moment of 13.6 D (Table 4) in line with the classical concept of a  $\sigma$ -bonded complex. A subsequent reaction with a further molecule of sulfur trioxide gives the pyrosulfonate Wheland intermediate **6** which can be spatially arranged in a number of ways so that the torsion angle C4–S8–O11–S12 for the incoming sulfur atom, S12, ranges from 0° in the *cis* conformer **6a**, where the attached oxygen, O15, faces the aromatic ring, through to 180° in the *trans* conformer **6b** where it points away from the ring (see Scheme 2 and Figure 1). Electronically, there are significant differences between these two conformers. In the latter, **6b**, which is likely to be formed first, the terminal oxygens, O13 (or the equivalent O14) and O15 have approximately the same charges with values of –0.569 and –0.571, respectively, with the ring hydrogen H4 showing a positive value of 0.348. However, in the former, **6a**, O13 shows

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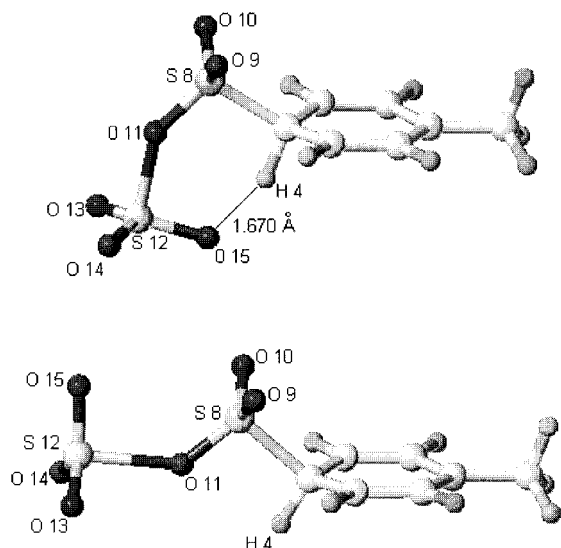
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**Table 4.** Partial Atomic Charges, and Dipole Moments ( $\mu$ ) of the Reactants, Intermediates, and Products (3–9) Involved in the Sulfonation of Toluene Calculated at the *ab Initio* 4-31G/S\* Level

atomic charge <sup>a</sup>	structure						
	3	4	5	6a	7	8b	9
C1	-0.031	-0.024	0.075	0.082	0.002	-0.002	-0.001
C2	-0.197	-0.193	-0.241	-0.233	-0.208	-0.208	-0.209
H2	0.185	0.198	0.232	0.246	0.215	0.206	0.208
C3	-0.182	-0.166	0.028	0.051	-0.094	-0.099	-0.097
H3	0.188	0.208	0.284	0.301	0.265	0.255	0.261
C4	-0.197	-0.321	-0.660	-0.749	-0.338	-0.323	-0.324
H4	0.187	0.224	0.341	0.469			
C7	-0.450	-0.453	-0.490	-0.495	-0.460	-0.458	-0.458
H7a	0.173	0.182	0.223	0.232	0.195	0.188	0.190
H7b	0.164	0.169	0.203	0.211	0.180	0.176	0.177
S8		1.466	1.455	1.532	1.450	1.416	1.454
O9		-0.498	-0.648	-0.596	-0.557	-0.612	-0.572
O11		-0.511	-0.659	-0.832	-0.835	-0.724	-0.796
H11						0.466	
S12				1.627	1.677		1.453
O13				-0.567	-0.534		-0.572
O15				-0.704	-0.724		
H15					0.496		
$\mu$	0.31	1.74	13.58	16.80	11.16	4.70	10.81

<sup>a</sup> In the structure as drawn (Scheme 2), the atom pairs C2 and C6, H2 and H6, C3 and C5, H3 and H5, O9 and O10, O13 and O14 are equivalent. H7a is perpendicular to the ring plane; H7b represents the two equivalent hydrogens which lie below the ring plane and attached to the tetrahedral carbon C7.

**Figure 1.** Conformations of the pyrosulfonate Wheland intermediate: *cis* conformer (**6a**, top); *trans* conformer (**6b**, bottom).

a similar charge of  $-0.567$ , but O15 is considerably more negative with a value of  $-0.704$  with H4 now strongly positive with a value of  $0.469$  (Table 4). These two atoms, O15 and H4, form a hydrogen bond with a bond length of  $1.670$  Å. As a result of the structural differences, the dipole moments change from  $19.65$  to  $16.80$  D in moving from **6b** to **6a**. Overall, the more stable structure **6a** (see later) is more polarized than **5** with an overall charge at the aromatic ring and at the  $S_2O_6$  group of  $\pm 0.694$  (Table 4).

**3. Thermodynamics of the Sulfonation Processes.** The results obtained suggest that toluene will react exothermically with sulfur trioxide to form stable  $\pi$ -complexes such as **4a** and **4b** which are  $3.59$  and  $4.09$  kcal mol<sup>-1</sup> lower in energy than the reactants, respectively (Table 5). The subsequent formation of the Wheland intermediate **5** from the most stable  $\pi$ -complex **4b**, which is thought to be close to the rate controlling step of the sulfonation via a nearby transition state on the reaction coordinate, is an endothermic process as ex-

**Table 5.** Molecular Energies of the Reactants, Intermediates, and Products (1–9) Involved in the Sulfonation of Toluene Calculated at the *ab Initio* 4-31G/S\* Level

structure	molecular energy <sup>a</sup>	reaction <sup>b</sup>	relative energy <sup>c</sup>
<b>1</b>	-621.260830		
<b>2</b>	-697.218879		
<b>3</b>	-269.358158		
<b>1 + 3</b>	-890.618988		
<b>4a</b>	-890.624710	<b>1 + 3</b> → <b>4a</b>	-3.59
<b>4b</b>	-890.625507	<b>1 + 3</b> → <b>4b</b>	-4.09
<b>5</b>	-890.587056	<b>4b</b> → <b>5</b>	24.13
<b>5 + 1</b>	-1511.847886	<b>1 + 3</b> → <b>5</b>	20.03
<b>6a</b>	-1511.896934	<b>5 + 1</b> → <b>6a</b>	-30.78
<b>6b</b>	-1511.884947	<b>5 + 1</b> → <b>6b</b>	-23.25
<b>7</b>	-1511.958679	<b>6a</b> → <b>7</b>	-38.74
<b>8a</b>	-890.663207		
<b>8b</b>	-890.671708	<b>5</b> → <b>8b</b>	-53.12
<b>7 + 8</b>	-2402.630387	<b>7</b> → <b>8b + 1</b>	16.40
<b>7 + 3</b>	-1781.316837	<b>7 + 3</b> → <b>8b + 8b</b>	-16.68
<b>9</b>	-1705.410958		
<b>9 + 2</b>	-2402.629837	<b>7 + 8b</b> → <b>9 + 2</b>	0.35

<sup>a</sup> In Hartrees. <sup>b</sup> See Scheme 1. <sup>c</sup> In kcal mol<sup>-1</sup> (1 Hartree =  $627.46$  kcal mol<sup>-1</sup>).

pected by  $24.1$  kcal mol<sup>-1</sup>. However, sulfur trioxide is predicted to react exothermically with the Wheland intermediate **5** to form the pyrosulfonate Wheland intermediates **6a** or **6b** which are  $30.8$  and  $23.3$  kcal mol<sup>-1</sup> lower in energy than the reactant (Table 5). It follows that in a situation where free sulfur trioxide is in the vicinity of the Wheland intermediate **5**, the formation of the pyrosulfonate intermediate **6** will predominate over its reaction with toluene (**3**). These results are fully consistent with the experimental results in the inert solvent fluorotrichloromethane where the rate-limiting step is the formation of the Wheland intermediate **5**, but not with the results obtained in nitromethane where the rate-limiting step is the formation of the pyrosulfonate intermediate **6**.<sup>2,3</sup> However, in the latter, the sulfonating species is probably a sulfur trioxide-nitromethane complex, and the formation of the pyrosulfonate intermediate **6** from the solvated Wheland intermediate **5** becomes the rate-limiting step of the process because this process is sterically hindered by complexed solvent molecules.

Although the mechanism of the formation of the sulfonic acids **8** and **7** has not been completely resolved, it seems likely in one favored process that the ring hydrogen, H4, which is positively charged (0.341) in intermediate (**5**) is able to transfer via an intramolecular mechanism to the negatively charged sulfonate oxygen, O11 (-0.659), in its vicinity possibly via hydrogen bonding (Table 4). A similar process can operate for intermediate **6a** where H4 is even more positively charged (0.469) and is able to bind more tightly to the nearby more negatively charged (-0.659) sulfonate oxygen, O15 (Table 4). Thermodynamically, the rearrangement of Wheland intermediate **6a** to toluene pyrosulfonic acid (**7**) is strongly exothermic by 38.74 kcal mol<sup>-1</sup> (Table 5). Overall, the thermodynamic change in moving from the reaction of two molecules of sulfur trioxide with toluene to the pyrosulfonic acid product **7**, is exothermic by 49.5 kcal mol<sup>-1</sup>.

Although the calculated results suggest that a similar process for the rearrangement of Wheland intermediate **5** directly to toluenesulfonic acid (**8b**), via **8a**, is even more strongly exothermic by 53.1 kcal mol<sup>-1</sup> (Table 5), an examination of the structure of intermediate **5** reveals an H4-O11 distance of 2.30 Å, and there seems no facile process involving bond rotation or angle bending that could bring the two atoms into closer contact for hydrogen bonding and thence for rearrangement to toluenesulfonic acid (**8**). If the latter **8** is indeed formed from intermediate **5**, then it seems more likely that this process will occur via an intermolecular mechanism involving the transfer of hydrogen, H4, as a proton to another adjacent electron rich species.

In contrast, as sulfur trioxide reacts with intermediate **5**, the sulfur atom, S12, of the terminal SO<sub>3</sub> group in the pyrosulfonate intermediate (**6b**) is likely to point away from the aromatic ring (a torsion angle C4-S8-O11-S12 of 180°, see Figure 1), because there is less steric hindrance involved in the addition process. This initial process is exothermic by 23.3 kcal mol<sup>-1</sup> (Table 5). However, a simple rotation of this SO<sub>3</sub> group around the S8-O11 bond easily moves the negatively charged oxygen O15 into hydrogen bonding distance of the ring hydrogen H4. For example, at the original torsion angle C4-S8-O11-S12 of 180°, atom O15 is in a *trans* conformation to ring hydrogen, H4, at a distance of 4.97 Å, but at reduced torsion angles of 90° and 45° corresponding to rotations of 90° and 135° around the S8-O11 bond, the O15-H4 distance falls to 3.64 and 2.29 Å, respectively. This rotation is beneficial as a full optimization on a structure resulting from a rotation of 180° around the S8-O11 bond corresponding to a *cis* arrangement between atom O15 and ring hydrogen H4 (Figure 1) gives another Wheland intermediate (**6a**) which is 7.52 kcal mol<sup>-1</sup> lower in energy than **6b** and shows a strong hydrogen bond between O15 and H4 at an interatomic distance of 1.670 Å. It seems highly likely, therefore, that the formation of the pyrosulfonic acid **7** occurs via the rearrangement of **6a**.

The possibility that toluenesulfonic acid (**8b**) is formed by decomposition of toluenepyrosulfonic acid (**7**) to liber-

ate free sulfur trioxide seems very unlikely (see Scheme 1) because the process is endothermic by 16.4 kcal mol<sup>-1</sup> (Table 5). However, the postulated reaction of toluene (**3**) with the pyrosulfonic acid (**7**) is an exothermic process by 16.7 kcal mol<sup>-1</sup>, and this seems to be the preferred thermodynamic pathway to the desired product, though the precise mechanism is unclear and remains to be explored. The formation of the main byproduct, toluenesulfonic anhydride (**9**), which is thought to occur from a reaction between the sulfonic acid **8** and the pyrosulfonic acid **7** leading to the liberation of sulfuric acid, is predicted to be a slightly endothermic process by 0.35 kcal mol<sup>-1</sup> (Table 5).

**4. A Comparison with Experimental Data.** Experimentally, the enthalpy of reaction of gaseous sulfur trioxide with liquid monoalkylbenzenes to form the corresponding 4-alkylbenzene sulfonic acid is around -40.7 kcal mol<sup>-1</sup> for simple straight alkyl chains.<sup>31</sup> However, to compare this data with the calculated results for toluene, it is necessary to subtract the enthalpy of dissolution of sulfur trioxide from the gas into the reaction medium. A good estimate of this process is available by calculating the latent heat of sulfur trioxide vaporization using a modified Trouton constant of 22. This gives an enthalpy of -7.2 kcal mol<sup>-1</sup> for the experimental process, which when subtracted from the overall reaction enthalpy gives a value for the gas phase process of -33.5 kcal mol<sup>-1</sup>. The overall calculated thermodynamic change of -33.1 kcal mol<sup>-1</sup> in moving from the reaction of one molecule of sulfur trioxide with toluene to the sulfonic acid **8b** is therefore fully consistent with the experimental data, and we conclude that the choice of basis set adopted for the calculations is entirely adequate.

## Conclusions

The ab initio 4-31G/S\* basis set appears to give a good account of the geometry, electronic properties, and energies of the species involved in aromatic sulfonation. The results of the calculations suggest that the reaction proceeds via the formation of a  $\pi$ -complex (**4b**). The subsequent rearrangement of this complex to form a Wheland intermediate **5** appears to be the rate-controlling step of the reaction. Molecular modeling studies suggest that this intermediate is unable to form toluenesulfonic acid by a prototropic rearrangement and prefers to react exothermically with a further molecule of sulfur trioxide to form a pyrosulfonate intermediate (**6a**). This process is followed by a facile prototropic rearrangement to form the corresponding acid **7** which then reacts exothermically with toluene to form toluenesulfonic acid (**8**). A competing reaction between the same acid **7** and the product **8** is slightly endothermic and leads to the formation of toluenesulfonic anhydride (**9**).

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