

## Enthalpy of Formation of $\text{CH}_3\text{SO}$ and $\text{CH}_3\text{SO}_2$ : A Difficult Case in Quantum Chemistry

Stella M. Resende and Fernando R. Ornellas\*

Instituto de Química, Universidade de São Paulo, CP 26077, 05513-970 São Paulo - SP, Brazil

As entalpias de formação do  $\text{CH}_3\text{SO}$  e  $\text{CH}_3\text{SO}_2$  a 298,15 K foram determinadas num alto nível de correlação eletrônica, CCSD(T), e com o uso do procedimento de Woon e Dunning para se alcançar o limite de um conjunto de base completo. Este estudo forneceu valores de  $-16,7 \text{ kcal mol}^{-1}$  e  $-53,1 \text{ kcal mol}^{-1}$ , respectivamente, para  $\text{CH}_3\text{SO}$  e  $\text{CH}_3\text{SO}_2$ , que se espera serem os mais exatos até hoje. A análise dos cálculos existentes em vários níveis de teoria claramente mostra a necessidade de conjuntos de bases muito grandes e de um alto nível de tratamento da correlação eletrônica para se produzirem resultados confiáveis e exatos.

The enthalpies of formation of  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$  at 298.15 K were determined at a high level of electronic correlation, CCSD(T), and with the use of Woon and Dunning's procedure to reach the complete basis set limit. This study led to values of  $-16.7 \text{ kcal mol}^{-1}$  and  $-53.1 \text{ kcal mol}^{-1}$ , respectively, for  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ , which are expected to be the most accurate ones to date. Analysis of existing calculations at various levels of theory clearly shows the need of large basis sets and a high level of electronic correlation treatment to produce reliable and accurate results.

**Keywords:** thermochemistry, heat of formation, enthalpy, sulfur-reduced compounds, *ab initio*

### Introduction

The complexity of environmental chemical processes with several reactions occurring simultaneously poses a great challenge to scientists involved in the modelling of reaction cycles. The identification of intermediates and products that can play a significant role in the overall reaction is thus of great relevance. In this context, the availability of thermochemical data is very important in helping to provide information about the stability and reactivity of the chemical species involved and may be decisive in answering questions about endothermicity and feasibility of various atmospheric processes.

Theoretically, empirical group additivity methods such as those developed by Benson and co-workers<sup>1</sup> provide an easy way to estimate the thermochemistry of gas-phase reactions for species whose thermochemistry has not been measured. However, its weakness lies in its requirement to apply corrections for steric effects that are not always well determined, as well as for groups not experimentally studied. On the other hand, *ab initio* methods represent today an important tool to generate thermochemical data, but the final accuracy is dependent on the level of

calculation used. Procedures such as G2, G2(MP2) and G3 methods have been reported frequently, with accuracies in the range of 1 to 2  $\text{kcal mol}^{-1}$ .<sup>2-4</sup> The CBS-Q approach gives an accuracy of about 1  $\text{kcal mol}^{-1}$ ,<sup>5</sup> reaching the complete basis set limit and making use of a high level of electronic correlation treatment such as CCSD(T). The use of isodesmic reactions,<sup>6</sup> where systematic computational errors may cancel between the right and left sides of a chemical reaction, is also a common useful practice. Besides, molecules containing second row atoms such as sulfur often need a higher theoretical description than molecules containing only first row atoms.<sup>7</sup> In the context of atmospheric reactions, the determination of important thermochemical data such as the enthalpy of formation for molecules containing sulfur can thus be a challenge. The sulfur-reduced species  $\text{H}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ , derived from the atmospheric decomposition of dimethyl sulfide,<sup>8</sup> are excellent examples showing this difficulty.

The enthalpy of formation of  $\text{CH}_3\text{SO}$  was estimated by Benson as being  $-16 \text{ kcal mol}^{-1}$ ,<sup>9</sup> and a G2(MP2) calculation by Turecek produced a value of  $-18.5 \text{ kcal mol}^{-1}$ .<sup>10</sup> More recently, a calculation at the CCSD(T)/cc-pVTZ level conducted by Resende and De Almeida led to a lower value of  $-11.9 \text{ kcal mol}^{-1}$ .<sup>11</sup> To the best of our knowledge, no experimental determination has been reported in the

\* e-mail: frornell@iq.usp.br

literature. For  $\text{CH}_3\text{SO}_2$ , there are a number of theoretical investigations. Benson's estimate is  $-55 \text{ kcal mol}^{-1}$ ,<sup>9</sup> a calculation at the HF/STO-3G level has produced a value of  $-62.7 \text{ kcal mol}^{-1}$ ,<sup>12</sup> while more recent determinations using the G2 and G2(MP2) methodologies have led to values of  $-47.6$  and  $-50.4 \pm 1 \text{ kcal mol}^{-1}$ , respectively.<sup>13,14</sup> Resende and De Almeida have obtained  $-38.9 \text{ kcal mol}^{-1}$ ,<sup>11</sup> and the most recent value, reported by Denis and Ventura,<sup>15</sup> using the DFT/6-311+G(3df,2p) level of calculation, is  $-56.3 \pm 2 \text{ kcal mol}^{-1}$ . On the experimental side, the only determination reported gives a value of  $-61.8 \pm 1.8 \text{ kcal mol}^{-1}$ .<sup>16</sup> This variety of results clearly show that the values of the heats of formation for these two sulfur compounds differ considerably depending on the methodology used. Considering the possibility of carrying out calculations at a very high level of description of electronic correlation and the extrapolation of results to the basis set limit, we have reexamined the determination of the heat of formation of these two molecules hoping to unambiguously set a very accurate and definite value, and thus contribute with reliable results for scientists involved with the atmospheric chemistry of sulfur compounds.

The reactions used by Resende and De Almeida<sup>11</sup> for the determination of the enthalpies of formation of  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ , shown below, were investigated in their own contexts of atmospheric chemistry, and the enthalpies of formation were obtained as an additional information among other thermodynamic data.



These reactions are not isodesmic, but are isogyric, which means that the number of unpaired spins is conserved.<sup>6</sup> This property raised the expectation that it would lead to reasonable values of the enthalpies of formation, however, a comparison of the results obtained in that study with the ones more recently reported shows a significant difference. An analysis of the possible sources of this difference raises two possibilities: one is the level of the calculation, and the other is the choice of the reactions used. Pushing the calculation to a very high level of theory is the alternative to identify the sources of inaccuracies in the first calculation and, therefore, to provide more accurate values for the enthalpies of formation of  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ . Since the rationale behind the use of isodesmic reactions is the cancelation of computational errors between the two sides of a reaction, the minimization of these errors by means of a choice of a theoretical method where the complete basis set limit is

reached and where a high level of electronic correlation is included in the calculation of the energies of the species involved can bypass the need of using this type of reactions. Under this circumstance, reactions 1 and 2 can be used to obtain accurate values for the enthalpies of formation of  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ .

## Calculations

All calculations were carried out using the Gaussian package of programs.<sup>17</sup> The MP2/cc-pVTZ level of theory was used for the optimizations of the five species involved in reactions 1 and 2. Harmonical frequencies were also determined at this level. The complete basis set limit was reached through the procedure developed and tested by Dunning and co-workers<sup>18</sup> using single point calculations at the MP2/cc-pVDZ and MP2/cc-pVQZ levels of theory. This approach states that the dependence on basis set of several molecular properties, as the stabilization energy, is well represented by a simple exponential function of the form

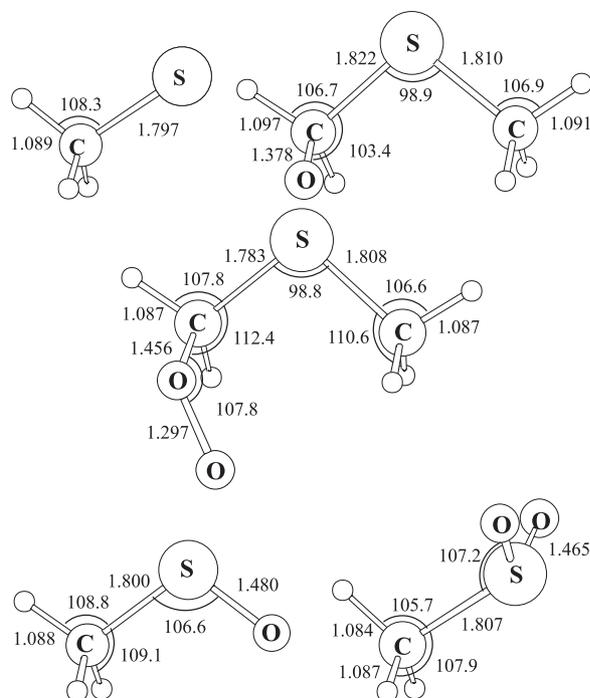
$$F(n) = A_\infty - B e^{-cn} \quad (3)$$

where  $n$  is the index of the basis set, and  $B$ ,  $c$ , and  $A_\infty$  are adjustable parameters, with  $A_\infty$  being the asymptotic limit for the function. The limiting value of this function provides an estimate of the complete basis set (CBS) limit. In our calculation,  $n$  ranged from 2 to 4, and the function extrapolated was the energy for every stationary point at the MP2 level. Since all species are radicals, and spin contamination could be relevant in these systems, the respective projected values were used. Single point calculations also were conducted at the CCSD(T)/cc-pVTZ level of theory, aiming to include electronic correlation effects in a more accurate form. Recourse to the additivity approximation<sup>2,19</sup> also made possible the prediction of more accurate values for the energies through the relation:

$$E_{\text{CCSD(T)/CBS}} = E_{\text{CCSD(T)/cc-pVTZ}} + (E_{\text{MP2/CBS}} - E_{\text{MP2/cc-pVTZ}}) \quad (4)$$

## Results and Discussion

The calculated energy values are given in Table 1. Figure 1 displays the geometrical parameters of the molecules considered in this work. It is interesting to note that the species  $\text{CH}_3\text{SO}_2$  has the two oxygen atoms staggered with one hydrogen of  $\text{CH}_3$ , which is in agreement with the findings of Davis,<sup>20</sup> and Frank and Turecek,<sup>14</sup> but different from the result reported by McKee.<sup>21</sup> From the reaction energies listed also in Table 1, one can notice the significant variation in these values as one goes from the



**Figure 1.** Geometrical representation of the molecules involved in reactions 1 and 2. The optimizations were done at the MP2/cc-pVTZ level of theory. Distances are given in Å and angles in degrees.

**Table 1.** Energy values (in Hartree) for the molecules involved in reactions 1 and 2. The optimizations were done at the MP2/cc-pVTZ level of theory. Energies for reactions 1 and 2 are given in kcal mol<sup>-1</sup>. (1 cal = 4.18 J)

	PMP2/ cc-pVDZ	PMP2/ cc-pVTZ	PMP2/ cc-pVQZ	PMP2/ CBS	CCSD/ cc-pVTZ	CCSD(T)/ cc-pVTZ	CCSD(T)/ CBS
$\text{CH}_3\text{S}$	-437.37919	-437.47971	-437.51102	-437.52518	-437.51182	-437.52576	-437.57123
$\text{CH}_3\text{SCH}_2\text{O}_2$	-626.53762	-626.83140	-626.92564	-626.97015	-626.87600	-626.91922	-627.05796
$\text{CH}_3\text{SO}$	-512.40168	-512.60148	-512.66393	-512.69232	-512.62615	-512.65176	-512.74260
$\text{CH}_3\text{SCH}_2\text{O}$	-551.55509	-551.77538	-551.84575	-551.87877	-551.82242	-551.85429	-551.95769
$\text{CH}_3\text{SO}_2$	-587.41162	-587.71030	-587.80409	-587.84704	-587.71972	-587.75866	-587.89540
reaction 1	-25.08	-41.26	-45.82	-47.54	-38.13	-38.33	-44.61
reaction 2	-17.20	-33.13	-37.82	-39.75	-25.10	-26.34	-32.96

**Table 2.** Standard enthalpy of formation at 298.15 K ( $\Delta H_{298}^0$ , in kcal mol<sup>-1</sup>) for  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ . (1 cal = 4.18 J)

	$\Delta H_{298}^0$	Method	Reaction used	Reference
$\text{CH}_3\text{SO}$	-16 ± 4	group additivity	-	[9]
	-18.5	G2 (MP2)	$\text{CH}_3\text{SOH} + \text{OH} \rightarrow \text{CH}_3\text{SO} + \text{H}_2\text{O}$	[10]
	-11.9	CCSD(T)/cc-pVTZ	reaction 1	[11]
	-16.7	CCSD(T)/CBS	reaction 1	This Work
$\text{CH}_3\text{SO}_2$	-61.8 ± 1.8	calorimetric data	-	[16]
	-55	group additivity	-	[9]
	-62.7	HF/STO-3G	-	[12]
	-47.6	G2	$\text{CH}_3\text{SO}_2 + \text{H} \rightarrow \text{CH}_3 + \text{HSO}_2$	[13]
	-38.9	CCSD(T)/cc-pVTZ	reaction 2	[11]
	-50 ± 1	G2 (MP2)	$\text{CH}_3\text{SO}_2 \rightarrow \text{C}(\text{P}) + 3\text{H}(\text{S}) + \text{S}(\text{P}) + \text{O}(\text{P})$	[14]
			$\text{CH}_3\text{SO}_2 \rightarrow \text{CH}_3 + \text{SO}$	
			$\text{CH}_3\text{SO}_2 + \text{S}(\text{P}) \rightarrow \text{CH}_3\text{S} + \text{SO}_2$	
			$\text{CH}_3\text{SO}_2 + \text{HS} \rightarrow \text{CH}_3\text{SH} + \text{SO}_2$	
			$\text{CH}_3\text{SO}_2 + \text{CH}_3\text{S} \rightarrow \text{CH}_3\text{SCH}_3 + \text{SO}_2$	
-56.3	B3LYP/6-311+G(3df,2p) and B3PW91/6-311+G(3df,2p)	$\text{CH}_3\text{SO}_2 + \text{CH}_3\text{S} \rightarrow \text{CH}_3\text{SCH}_3 + \text{SO}_2$	[15]	
-53.1	CCSD(T)/CBS	reaction 2	This Work	

double-zeta to the complete basis set limit. At the MP2 level, it amounts to  $-22.5$  kcal mol<sup>-1</sup>, and shows the influence of the basis set size on this property. On the other hand, electronic correlation turns out to be more important for reaction 2 than for reaction 1. The variation in energy from PMP2 to CCSD(T) is  $2.9$  kcal mol<sup>-1</sup> for reaction 1 and  $6.8$  kcal mol<sup>-1</sup> for reaction 2. The influence of the triples contributions on the CCSD values is also slightly greater for reaction 2 than for reaction 1.

The nuclear contributions to the enthalpy are  $0.18$  and  $-0.11$  kcal mol<sup>-1</sup>, respectively, for reactions 1 and 2, leading therefore to a theoretical reaction enthalpy of  $-44.43$  kcal mol<sup>-1</sup> for reaction 1, and  $-33.07$  kcal mol<sup>-1</sup> for reaction 2, at the CCSD(T)/CBS level of theory. With the values of  $9.8$  and  $6.51$  kcal mol<sup>-1</sup> for the standard heat of formation of  $\text{CH}_3\text{SCH}_2\text{O}$  and  $\text{CH}_3\text{CH}_2\text{O}_2$ , determined previously by Resende and De Almeida,<sup>11,23</sup> and the most recent value for  $\text{CH}_3\text{S}$  reported in the literature,  $31.04 \pm 0.42$  kcal mol<sup>-1</sup>, determined by photodissociation spectroscopy,<sup>22</sup> the enthalpy of formation of  $\text{CH}_3\text{SO}$  can be calculated as  $-16.7$  kcal mol<sup>-1</sup>, using reaction 1. From this value and reaction 2, the  $\text{CH}_3\text{SO}_2$  enthalpy of formation will be  $-53.1$  kcal mol<sup>-1</sup>. These results are shown in Table 2, together

with existing experimental and theoretical values.

The value calculated in this work for the enthalpy of formation of  $\text{CH}_3\text{SO}$  is in excellent agreement with Benson's estimate, being both about  $2 \text{ kcal mol}^{-1}$  smaller than the theoretical estimate of Turecek.<sup>10</sup> As discussed above, basis set size effects are quite significant for this system, and in the G2 (MP2) methodology used in Turecek's work it corresponds to the 6-311+G(3df,2p) basis set. From Table 1, the variation in energy for reaction 1 is about  $6 \text{ kcal mol}^{-1}$ , as one moves from the cc-pVTZ basis set to the complete basis set limit. This difference should be smaller for the reaction used by Turecek, since it is isodesmic, but it can explain the observed differences. In the case of Resende and De Almeida's value, the difference is clearly due to the size of the basis set. In that work, optimizations were done at the MP2/6-31G(d) level of theory, and the CCSD(T)/cc-pVTZ level was reached through the additivity approximation. The PMP2/cc-pVTZ//PMP2/6-31G(d) value from the previous work compares very well (less than  $0.5 \text{ kcal mol}^{-1}$ ) with the PMP2/cc-pVTZ result of this calculation, indicating that the convergence in geometry is reached with a double zeta quality basis set. Electronic correlation was equally included, but reaching the basis set limit makes a significant contribution, explaining the difference between these two values.

The theoretical determination of the enthalpy of formation of  $\text{CH}_3\text{SO}_2$  was investigated by various groups, but the calculated values present a high dispersion. Interestingly, as indicated in Table 2, only for the simplest *ab initio* calculation (HF/STO-3G) there has been a very good (incidental) agreement theory and experiment. Also worth noting in Table 2 is the close agreement between Benson's value ( $-55 \text{ kcal mol}^{-1}$ ) and the one calculated in this work ( $-53.1 \text{ kcal mol}^{-1}$ ). The most recent *ab initio* results employed triple-zeta quality basis sets, which we have shown not adequate to describe this system accurately. Similar methodologies such as G2 and G2(MP2) have produced different values, but the reactions used were not the same. The reaction employed by Laakso *et al.*<sup>13</sup> is not isodesmic, and, besides, the value used for  $\Delta H_f^0$  of  $\text{HSO}_2$  ( $-33.8 \text{ kcal mol}^{-1}$ ) has a large uncertainty in its determination.<sup>12,15</sup> On the other hand, Frank and Turecek's<sup>14</sup> value represents an average value of results from five different reactions: atomization, dissociation and three other reactions that they consider as being isodesmic. The determination of the enthalpy of formation of  $\text{CH}_3\text{SO}_2$  in Resende and De Almeida's work used the enthalpy of formation of  $\text{CH}_3\text{SO}$  calculated at that time, and the error in its determination certainly reflects the error in their value. The reaction used by Denis and Ventura<sup>15</sup> is one of those used by Frank and Turecek. The  $\Delta H_f(\text{CH}_3\text{SO}_2)$  obtained in Ref. 14 using this reaction is  $-50.0$

$\text{kcal mol}^{-1}$ , which does not compare very well with the DFT result. Since it is known that DFT approaches can not completely account for electronic correlation effects, the difference of about  $6 \text{ kcal mol}^{-1}$  found in these studies can only be explained by the level of theory employed. A further point we consider worth being addressed in more detail is the concept of isodesmic reaction. Formally, a reaction is isodesmic when the number of bonds of each type is conserved. It ensures that the errors arising from basis sets deficiencies and inadequacies in the treatment of electronic energy will tend to cancel. So, a reaction where the number of unpaired electrons is different in the two sides of the reaction equation should not be considered isodesmic, because electronic correlation will be different in the two cases. From this point of view, therefore, none of the reactions used by Frank and Turecek are isodesmic. In fact, the results in Table 2 show that the most important rule in an accurate determination of enthalpy of formation is the level of calculation. Consequently, our present results for the heats of formation are expected to be the most reliable and accurate values available to date, since reaching the complete basis set limit at a high level of correlation treatment overcomes the need of using an isodesmic reaction.

## Conclusions

In this work, we have calculated the enthalpies of formation of  $\text{CH}_3\text{SO}$  and  $\text{CH}_3\text{SO}_2$ . Their determination used a high level of electronic correlation treatment and approached the complete basis set limit, which overcomes the need of using isodesmic reactions. These values are expected to represent the most accurate results reported for this property. The importance of using a large basis set is stressed, and an analysis of results previously reported in the literature showed that the existing discrepancies can be traced to differences in the level of calculation used, which was not adequate for treating these systems correctly. The high quality of the present results also suggests that an experimental reinvestigation of these enthalpies of formation is certainly warranted.

## Acknowledgements

The authors are grateful to Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the academic support (Grants No. 99/02962-5 and 01/05986-4), and to Laboratório de Computação Científica Avançada (LCCA-USP) for partial use of their computational resources. Helpful discussions with Dr. Josefredo R. Pliego Jr. are also acknowledged. FRO also thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq).

## References

1. Benson, S.W.; *J. Phys. Chem. A* **1999**, *103*, 11481.
2. Curtiss, L.A.; Raghavachari, K.; Trucks, G.W.; Pople J.A.; *J. Chem. Phys.* **1991**, *94*, 7221.
3. Curtiss, L.A.; Raghavachari, K.; Pople, J.A.; *J. Chem. Phys.* **1993**, *98*, 1293.
4. Curtiss, L.A.; Redfern, P.C.; Rassolov, V.; Pople, J.A.; *J. Chem. Phys.* **1998**, *109*, 7764.
5. Petersson, G.A.; Frisch, M.J.; *J. Phys. Chem. A* **2000**, *104*, 2138.
6. Yarkony, D.R., ed. *Modern Electronic Structure Theory - Part I*, World Scientific: Singapore, 1995; p 315.
7. Martin, J.M.L.; *J. Chem. Phys.* **1998**, *108*, 2791.
8. Saltzman, E. S.; Cooper, W. J., eds.; *Biogenic Sulfur in the Environment*, American Chemical Society: Washington, DC, 1989.
9. Benson, S.W.; *Chem. Rev.* **1978**, *78*, 23.
10. Turecek, F.; *J. Phys. Chem.* **1994**, *98*, 3701.
11. Resende, S.M.; De Almeida, W.B.; *Phys. Chem. Chem. Phys.* **1999**, *1*, 2953.
12. Boyd, R.J.; Gupta, A.; Langler, R.F.; Lownie, S.P.; Pincock, J.A.; *Can. J. Chem.* **1980**, *58*, 331.
13. Laakso, D.; Smith, C.E.; Goumri, A.; Rocha, J.R.; Marshall, P.; *Chem. Phys. Lett.* **1994**, *227*, 77.
14. Frank, A.J.; Turecek, F.; *J. Phys. Chem. A* **1999**, *103*, 5348.
15. Denis, P.A.; Ventura, O.N.; *Chem. Phys. Lett.* **2001**, *344*, 221.
16. Busfield, W.K.; Ivin, K.J.; Mackle, H.; O'Hare, R.A.G.; *Trans. Faraday Soc.* **1961**, *57*, 1064.
17. Gaussian 98 (Revision A.9), Frisch M.J. et al., Gaussian Inc.: Pittsburgh PA, 1998.
18. Woon, D.E.; Dunning Jr., T.H.; *J. Chem. Phys.* **1993**, *99*, 1914.
19. Nobes, R.H.; Bouma, W.J.; Radom, L.; *Chem. Phys. Lett.* **1982**, *89*, 497.
20. Davis, S.R.; *J. Phys. Chem.* **1993**, *97*, 7535.
21. McKee, M.L.; *Chem. Phys. Lett.* **1993**, *211*, 643.
22. Bise, R.T.; Choi, H.; Pedersen, H.B.; Mordaunt, D.H.; Neumark, D.M.; *J. Chem. Phys.* **1999**, *110*, 805.
23. Resende, S.M.; De Almeida, W.B.; *J. Phys. Chem. A* **1999**, *103*, 4191.

Received: February 5, 2002

Published on the web: June 14, 2002

**FAPESP helped in meeting the publication costs of this article.**