

Reactions of HSCH₂ Radical with O₂, NO, and NO₂: Ab Initio Calculations of Enthalpies of Reaction

Carl Trindle* and Kristin Romberg

Chemistry Department, University of Virginia, Charlottesville, Virginia 22903

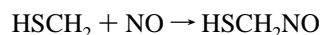
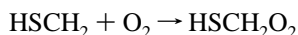
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For reactions of the HSCH₂ radical with atmospheric gases O₂, NO, and NO₂, we describe the thermochemistry by HF, MP2, and density functional computational methods, by Petersson's complete basis set extrapolation (CBS-4 and CBS-Q), and, in part, by Pople's G2MP2 model chemistry method. We offer recommendations of values of heats of formation for the participants in these reactions, which differ in some cases from the estimates based on the group additivity principle. The least expensive post-Hartree–Fock methods provide a coherent account of the thermochemistry, but are not superior to group additivity estimation.

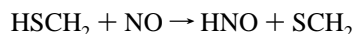
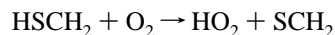
Introduction

Anastasi et al. (ABNP)¹ studied the kinetics of the reactions of HSCH₂ with atmospheric gases O₂, NO, and NO₂. They considered the following reactions:

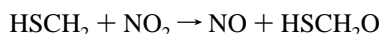
addition



hydrogen transfer



and for NO₂, oxygen transfer



Faced with the need to estimate thermochemical properties for these reactions, involving molecules so large that computational methods are demanding and their performance not well determined, ABNP modeled the thermochemistry of the system by group additivity methods, using Benson's well-tested methods² and extensions by Finlayson-Pitts and Pitts.³ Their estimates provided a convincing confirmation of their conjecture that addition reactions were most important in the degradation of the thiomethyl radical HSCH₂.

Accurate computational estimates of thermochemical parameters would provide an independent description of the thermochemistry of these reactions and could serve as a check on the empirical estimates. All our calculations were conducted with the Gaussian 94W⁴ suite. Our investigations quickly convinced us that Hartree–Fock methods were of no quantitative value in the description of these reactions. This was to be expected in systems containing both open shell and closed shell molecules and especially molecules with low-lying excited states and polarizable lone pairs. We hoped that the least demanding

CHART 1: Model Chemistry Techniques

Model	CBS-4	CBS-Q	G2MP2
Step			
1	3-21G* (U)HF Geometry	6-31G* (U)HF geometry	6-31G* geometry
2	3-21G* (U)HF Frequency and ZPE	6-31G* (U)HF frequency and ZPE	6-31G* (U)HF frequency and ZPE
3		6-31G* (U)MP2 geometry	6-31G* (U)MP2 geometry
4	HF 6-311+G(3d2f,2df,p) energy	HF 6-311+G(3d2f,2df,2p) energy	MP2 6-311+G(d,p) energy
5	MP2 6-31G* energy	MP2 6-311+G(3d2f,2df,2p) energy	MP2 6-311+G(3d2f,2df,2p) energy
6	MP4(SDQ) 6-31G	MP4(SDQ) 6-31+G(d,p) energy	
7		QCISD(T) 6-31+G* energy	QCISD(T) 6-31G(d,p)
8	Empirical terms	Empirical terms	Empirical terms

Sequence:

Steps 1-3	Find initial Geometry and frequencies (to be scaled for thermal correction), then refine geometry by MP2.
Steps 4-5	Evaluate increments in energy from diffuse functions and polarization functions.
Steps 6-7	Evaluate increments due to triple excitations and high order corrections
Step 8	Add empirical corrections and (CBS) extrapolation terms

methods that contain some account of electron correlation would be a substantial improvement over HF methods and of accuracy adequate to judge the validity of empirical estimates. Some reference values would be necessary, since experimental values are, as always, lacking.

Pople et al. developed the Gaussian-1 and Gaussian-2⁵ methods to compute accurate thermochemical parameters for small molecules, including radicals and ions. The great demands of these methods encouraged simplification, i.e. G2(MP2)⁶ and alternatives, such as the complete basis set (CBS) techniques.⁷ The sequence of calculations in the CBS-4, CBS-Q, and GZMPZ models are listed in Chart 1. The reach of the most approximate of these computational methods has been extended to systems with as many as 10 non-hydrogen atoms. Ochterski, Petersson, and Wiberg⁸ (OPW) have extended the G2 test set of molecules considerably, in their systematic comparison of the G2, G2(MP2), CBS-4, and CBS-Q methods. One may reasonably expect these methods to provide estimates with accuracy on the order of 1–2 kcal/mol (4–8 kJ/mol) in a wide variety of heats of formation and reaction.

In this report we make application of the G2(MP2) and CBS methods to treat the reactions studied by ABNP. This represents

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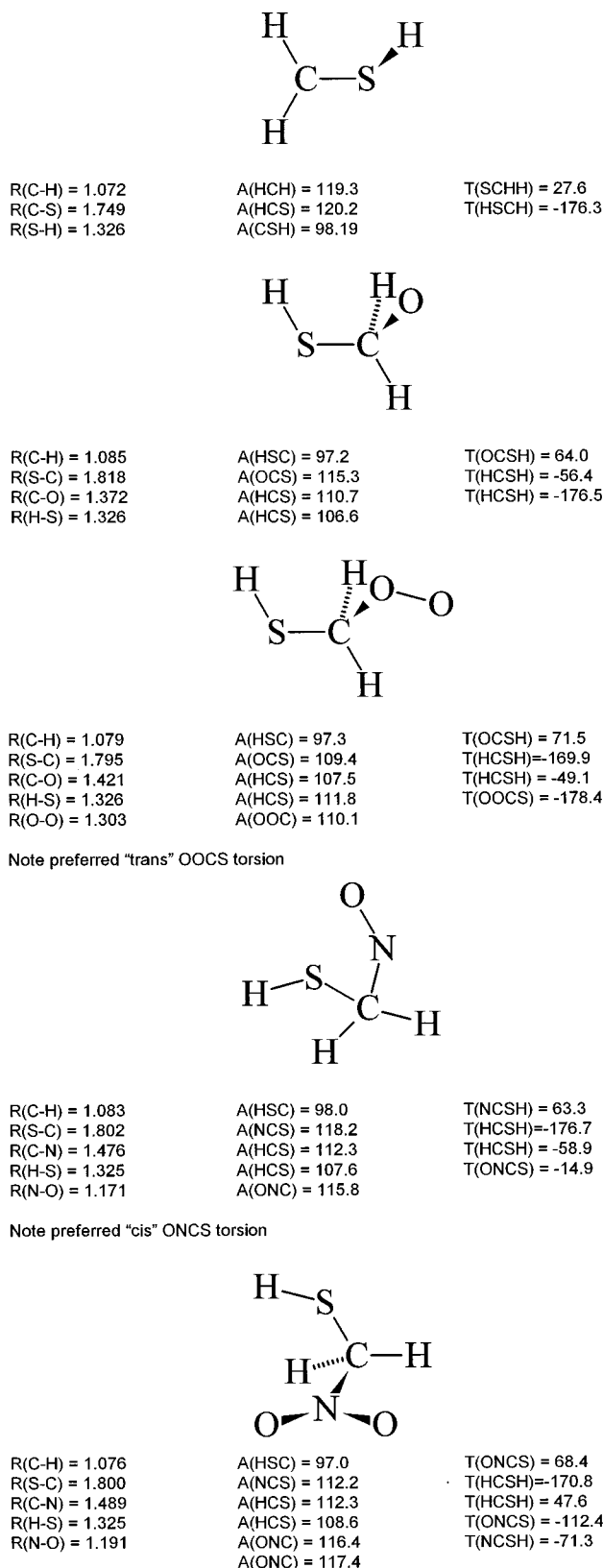


Figure 1. Structures of species: R = distances, A = angle, T = torsion computed by the best methods of Table 1.

an extension of the quantum mechanical methods to systems outside the collection of molecules in the G2 test set and the set studied by OPW. Because density functional methods promise computational efficiency and accuracy comparable to the best ab initio methods, we also report B3LYP results for comparison and judgment.

The G2MP2 and CBS modules in the Gaussian-94 suite report electronic energy at 0 K and add statistical mechanical terms to define increments of energy for the thermodynamic quantities enthalpy, internal energy, and free energy at 298 K. To report heats of formation for molecular species, we require experimental values of the heats of formation of atoms. OPW report these at 0 K; we have reproduced their reported values for the computed electronic energy of atoms taking part in this reaction scheme. We only added the translational correction $1.5RT$ of atoms to correct values to 298, neglecting electronic effects.

Table 1 summarizes our computed heats of formation. Structures of species are detailed in Figure 1.

We can obtain a preliminary judgment of the accuracy of computational methods by comparing calculated values to well-established experimental quantities. The G2(MP2) and CBS-Q methods do keep their promises of accuracy of 1–2 kcal/mol (<10 kJ/mol), with a mean absolute deviation (MAD) in this small set of 1.5 kcal/mol or 6 kJ/mol. Inexpensive methods DFT and CBS-4 fare less well.

It is harder to draw definite conclusions on the accuracy of computations and estimates when experimental data are lacking. The best calculation schemes produce very consistent values; the MAD between G2(MP2) and CBS-Q results is only 2 kJ/mol. If one takes G2(MP2) or CBS-Q as the reference, we see that the empirical methods are far superior to inexpensive calculations. Density functional calculations in the modest 6-31G* basis do not appear to fare well.

The OPW molecule set includes two very important members of the reaction scheme, HSCH₂ and SCH₂. OPW located an experimental estimate of the heat of formation of 152 kJ/mol for HSCH₂, which is interesting in several ways. The experimental value lies below the ABNP estimate by 16 kJ/mol, but the error range is given as ± 8 kJ/mol. The least demanding computational method, CBS-4, places the heat of formation 27 kJ/mol below the experimental value. In contrast, the best methods employed here, G2(MP2) and CBS-Q, provide heats of formation which lie 11 and 15 kJ/mol above the experimental value, very close to the empirical estimate. We consider that the empirical and superior computational estimates may be more credible than the experimental value.

The results in Table 1 allow a speculation that the heat of formation of S=CH₂ should be taken as closer to 115 kJ/mol, rather than the estimated 140 kJ/mol. All computational methods are consistent in this closed shell system, which should be susceptible to accurate description. Then the estimates of enthalpies of reaction for the hydrogen-transfer reactions become -32, -43, and -164 kJ/mol, not so far away from the average of the best calculated enthalpies of reaction, -39, -30, and -158 kJ/mol.

Similar arguments yield the set of recommended computationally based estimates of enthalpies of formation collected in Table 2. These values are obtained from differences in computed enthalpies at 298 K, except for the DFT results that are for 0 K.

Table 3 contains computed enthalpies of reaction. Conventional wisdom holds that heats of reaction should be computed more accurately than heats of atomization or formation. There is an opportunity for errors to cancel. These are not isodesmic reactions, however, in which that cancellation is most fortunate. Still we tend to place confidence in results that are consistent for several kinds of calculation. This is the case for the O₂ and NO addition reactions and to a degree for the NO₂ addition reactions. It is definitely not the case for the oxygen transfer.

TABLE 1: Estimates of Enthalpy of Formation (kJ/mol)

species	heat of formation (kJ/mol) at 298 K					
	ABNP estimate	ABNP exp ^{298 K}	CBS-4	CBS-Q	G2(MP2)	DFT ^{0 K} 6-31+G*
HSCH ₂	168	152 ± 8	119	157	161	112
SCH ₂	140		114	115	115	88
HSCH ₂ O	34		57	56(47) ^a	57(48) ^a	-5
HSCH ₂ O ₂	48		78	56(39) ^b	37	-11
HSCH ₂ NO	87		107	106	98	64
HSCH ₂ NO _{2-12,6}	-56		-40	In ^c	In ^c	-75
MAD ^d -G2MP2	12		23	2		47
MAD ^d -Est			27	15	12	47
NO		91	99.5	89.5	85.4	112.2
NO ₂		33	14.2	25.5	26.9	29.6
HNO		100	102.6	107.9	100.7	96.1
HONO		-78	-90.6	-81.2	-89.9	-65.5
HO ₂		2 ^e	43.2	12.2	8.7	-8.6
MAD ^d -exptl			16.7	6.1	6.2	15.7

^a Convergence of the CISD(T) step required imposing *C_s* symmetry. According to the UHF and UMP2 stages of calculation which were completed, the gauche conformer is more stable by 8 (UHF) or 10(MP2) kJ/mol, which appears in the table as a correction of 9 ± 1 kJ/mol for G2MP2. Similar behavior produces an adjustment of 9 ± 1 kJ/mol for CBS-Q from the *C_s* symmetric conformer. ^b Convergence of the CBS-PNO extrapolation step required imposing *C_s* symmetry. According to the UHF and UMP2 stages of calculation which were completed, the gauche conformer is more stable by 16 (UHF) or 18(MP2) kJ/mol which appears in the table as a correction of 17 ± 1 kJ/mol. ^c In = inadequate computer resources. ^d MAD = mean absolute deviation from experimental values; MAD-G2MP2 takes that method as the reference; MAD-est takes empirical estimates as the reference point. ^e The value +21 kJ/mol used by ABNP agrees with values in Karapetyants and Karapetyants,⁹ which were drawn from JANAF Tables of 1963¹⁰ among other sources. A more recent value based on more recent measurements quoted in JANAF Thermochemical Tables, 3rd ed. (1985¹¹) is 2 kJ/mol.

TABLE 2: Recommended Values of Heats of Formation at 298 K (kJ/mol)

species	EST	recommended
HSCH ₂	168	165 ± 5
SCH ₂	140	115 ± 5
HSCH ₂ O	34	47 ± 5
HSCH ₂ O ₂	48	38 ± 5
HSCH ₂ NO	87	100 ± 5
HSCH ₂ NO ₂	-56	-40 ± 15

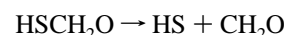
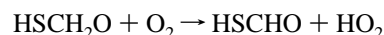
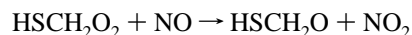
Apparently the energy value of HSCH₂O is very hard to capture. The best calculations agree that the estimated 34 kJ/mol is too low by 20 kJ/mol.

The hydrogen-transfer results seem to be a severe test of the computational thermochemistry. The best computations are not in excellent agreement with one another, disagreeing by as much as 20 kJ/mol for the O₂ reaction. This may be a particularly difficult system, containing triplet and doublet open shell reactants and two doublet radical products.

Returning to our question, is there hope for inexpensive methods, DFT and MP2? They seemed very poor performers when compared with the empirical estimates of heats of reaction and formation. However we should compare their performance against our recommended thermochemical values (see Table 4). In this test, they do not look so bad. Their mean absolute

deviations from recommended values are mutually comparable and about the same as the MAD for the empirical estimates. Although all approximate methods are inaccurate in detail, it is worth noting that the broad predictions of exothermicity are consistent across all modeling schemes.

ABNP conjecture that the fate of the HSCH₂O₂ is likely to follow the reactions



Our CBS-Q calculations of free energy changes -70, -175, and -65 kJ/mol, respectively, for these processes suggest that these reactions are all spontaneous at standard states. Tables 5 and 6 contain our estimates for enthalpies for these reactions and enthalpies of formation for the participants.

We conclude that there is no reason to prefer inexpensive post-HF methods to empirical group-additivity modeling! But there is good reason to work toward extending the clearly superior G2 and CBS model chemistries to systems of experimental importance.

TABLE 3: Estimates of Enthalpies of Reaction (kJ/mol)

reaction	source				
	ABNP estimate	G2(MP2) H-298	CBS-4 H-298	CBS-Q H-298	DFT E-el
HSCH ₂ + O ₂ → HSCH ₂ O ₂	-120	-131.3	-76.2	-100(-117) ^b	-120.7
HSCH ₂ + NO → HSCH ₂ NO	-172	-146.8	-155.2	-139	-160.0
HSCH ₂ + NO ₂ → HSCH ₂ NO ₂	-257	-246 ^a	-221.7	-249 ^b	-216.2
HSCH ₂ + O ₂ → SCH ₂ + HO ₂	-7	-48.0	+3.9	-29.4	-29.6
HSCH ₂ + NO → SCH ₂ + HNO	-18	-34.4	-34.9	-26.1	-39.5
HSCH ₂ + NO ₂ → SCH ₂ + HONO	-139	-165.9	-141.9	-151.2	-118.4
HSCH ₂ + NO ₂ → NO + HSCH ₂ O	-76	-44.3(-53) ^a	-13.1	-36.0(-45)	-34.2
MAD-G2MP2	24		28	12	19
MAD-est		24	27	18	22

^a This heat of reaction estimated by differences in electronic energy at QCISD(T)/6311G(d,p). Thermal correction estimated from CBS-4 as +5 kJ/mol. ^b This heat of reaction estimated by differences in electronic energy at QCISD(T)/631+G(d). Thermal correction estimated from CBS-4 as +5 kJ/mol.

TABLE 4: Performance of DFT and MP2 Calculations in $\Delta H_{\text{RX}-298}$ (kJ/mol)

reaction	ABNP estimate	recommended	DFT	MP2
HSCH ₂ + O ₂ → HSCH ₂ O ₂	-120	-115	-121	-74
HSCH ₂ + NO → HSCH ₂ NO	-172	-141	-160	-167
HSCH ₂ + NO ₂ → HSCH ₂ NO ₂	-257	-248	-216	-248
HSCH ₂ + O ₂ → SCH ₂ + HO ₂	-7	-29	-29	+10
HSCH ₂ + NO → SCH ₂ + HNO	-18	-41	-39	-20
HSCH ₂ + NO ₂ → SCH ₂ + HONO	-139	-161	-118	-144
HSCH ₂ + NO ₂ → NO + HSCH ₂ O	-76	-49	-34	-30
MAD-rec	20		17	23

TABLE 5: Calculated Enthalpies for Proposed Reactions of HSCH₂O₂ (kJ/mol)

reaction	ABNP estimate	using recommended values of $\Delta H_{\text{formation}}$	G2MP2	CBS-Q	B3LYP
HSCH ₂ O ₂ + NO → HSCH ₂ O + NO ₂	-72	-50 ± 10	-40.8	-64.1	-76.2
HSCH ₂ O + O ₂ → HSCHO + HO ₂		-174 ± 10	-193.8	-173.7	-152.8
HSCH ₂ O → HS + CH ₂ O		-20 ± 10	-33.9	-27.4	-15.8
MAD-rec			16	8	16

TABLE 6: Calculated Enthalpies of Formation for Species Produced by Reactions of HSCH₂O₂ (kJ/mol)

formation of	exptl data	recommended value of $\Delta H_{\text{formation}}$	G2MP2	CBS-Q	B3LYP
H ₂ CO	-115.9 ± 0.1 ¹²		-105.7	-108.7	-157
HS	143 ± 3		142.6	141.6	136
HSCHO		-129 ± 5	-131.7	-126.1	-151

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