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Article

Probing the Chemistry of Sulfurous Pollutants: Accurate Thermochemistry Determination of Extensive Sulfur-Containing Species

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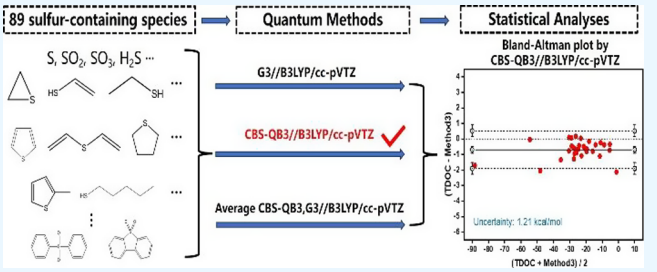
ABSTRACT: Sulfur-containing fuels, such as petroleum fuels, natural gas, and biofuels, produce SO_2, SO_3, and other highly toxic gases upon combustion, which are harmful to human health and the environment, making it essential to understand their thermochemical properties. This study used high-level quantum chemistry calculations to determine thermodynamic parameters, including entropy, enthalpy, and specific heat capacity for an extensive set of sulfur-containing species. The B3LYP/cc-pVTZ level of theory was used for geometry optimization, vibration frequency, and dihedral scan calculations. To determine an appropriate ab initio method for energy calculation, the Bland−Altman diagram, a statistical analysis method, was employed to visualize the 298 K enthalpy value between experimental data and three sets of ab initio methods: G3, CBS-QB3, and the average of G3 plus CBS-QB3. The CBS-QB3 method exhibited the highest accuracy and was eventually selected for the energy calculation in this study. Thermochemical property parameters were then calculated with the MultiWell program suite for all these sulfur-containing species, and the results were in good agreement with the thermochemical data of organic compounds and the National Institute of Standards and Technology Chemistry WebBook databases. The thermochemical property database established in this study is essential to studying sulfur-containing species in desulfurization.



1. INTRODUCTION

Determining the accurate thermochemical properties of species related to combustion is vital to developing chemical kinetic models. In a chemical kinetic model, the rate constants of elementary reactions are typically included in only one direction; the rate constant in the opposite direction is calculated by the equilibrium constant determined from the thermodynamic properties of the reactants and products in the reaction.[1]

In the past two decades, the progress of sulfur chemistry in synthesis and reaction mechanisms has significantly promoted the application of new knowledge in industrial applications, such as pharmaceuticals, polymers, antioxidants, and fuels.[2] Sulfur, an element commonly found in crude oil (up to 1.3% by weight), is considered an undesirable pollutant, generating sulfur oxides upon combustion. Crude oil is a complex liquid mixture containing several hydrocarbons and small portions of sulfur, nitrogen, oxygen, and metals (such as iron, nickel, copper, and vanadium), as shown in Table 1.[3] The sulfur content in crude or heavy oil is generally below 0.05 wt % to about 10 wt %, but mostly between 1 and 4 wt %. Crude oil contains elemental sulfur, dissolved H_2S, COS, and sulfur-bonded hydrocarbons such as mercaptans, sulfides, disulfides, and S-PAHs (sulfur polycyclic aromatic hydrocarbons, thiophenes). Mercaptans, sulfides, and disulfides can be cyclic and aromatic and are found primarily in lighter fractions. In comparison, thiophenes are present in the heavier fractions. When combusted, sulfur-rich oil leads to the emission of sulfur dioxide, and SO_2 forms tiny particles in the air, affecting the respiratory system and inducing asthma when exposed continuously.[3]

Table 1. Typical Elemental Composition of Crude Oil[3]

element	concentration (wt %)
carbon	83−87
hydrogen	10−14
sulfur	0.05−6
nitrogen	0.1−0.2
oxygen	0.05−2
nickel	<120 ppm
vanadium	<1200 ppm

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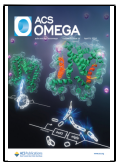

Table 2. Thermochemistry Studies of Sulfur-Containing Species from the Previous Literature

no.	class of species	references
1	oxygen-protonated sulfur dioxide isomers	Puzzarini[6]
2	divalent to hexavalent sulfur and the oxidation of sulfur-containing molecule	Benson[7]
3	thirty-five selected sulfur compounds	Denis[8]
4	HSO, HOS, $HOSO_2$, HSNO, SH, CH_2SO, CH_2SH, S_2COH, and SCSOH	Nagy et al.[9]
5	HSO and SOH	Denis and Ventura[10]
6	CH_3SO and CH_3SO_2	Resende and Ornellas[11]
7	methyl ethyl sulfide alcohols and corresponding radicals	Song and Bozzelli[12]
8	sulfones relevant to oxidative desulfurization	Weh and de Klerk[13]

Affected by traditional energy prices, environmental protection, and global climate change, countries worldwide have given increasing attention to the development of biofuels since the 1970s. However, biofuels also contain many sulfur elements, and the combustion of these biofuels also produces sulfur-containing pollutants. Natural gas also contains many sulfur-containing species. Although the main component of raw natural gas is methane (60−90%), it also contains a certain amount of hydrogen sulfide (0−5%). After the gas is desulfurized, acid gas (H_2S and CO_2 mixture) is generated, which is also harmful to human health and the environment after being discharged into the atmosphere.[3,4] Refinery fuel gas, particularly other refinery hydrocarbon streams, contains higher quantities of hydrogen sulfide—the distillation products or management of the distillation cuts in hydro-treaters and other treatment units.[5]

When these sulfur-containing fuels combust, they produce SO_2, SO_3, H_2SO_4, SO, COS, CS_2, and other highly toxic and environmentally malignant products.[5] Sulfur and sulfur-containing species also harm human and animal biological systems, and many catalysts are used in the petroleum refining process. Therefore, understanding such sulfur species' chemical properties is essential for energy use and environmental protection.

Thermochemistry is an essential physical and chemical property for the essential chemical transformation of species such as combustion, pyrolysis, and catalysis. Previous studies[6−13] have reported the enthalpies of formation at 298 K for some sulfur-related compounds, as shown in Table 2. Nagy et al.[9] also calculated the entropy values of HSO, HOS, $HOSO_2$, HSNO, SH, CH_2SO, CH_2SH, S_2COH, and SCSOH. Weh and de Klerk[13] studied the thermochemistry, melting point temperature, fusion enthalpy, and vapor pressure of selected noncycloaliphatic (dimethyl sulfone and dibutyl sulfone), cycloaliphatic (tetrahydrothiophene 1,1-dioxide and 2,5-dihydrothiophene 1,1-dioxide), noncyclic aromatic (diphenyl sulfone), and aromatic (thiophene 1,1-dioxide and dibenzothiophene 5,5-dioxide) sulfones. However, there is still a lack of thermochemical properties of sulfur-containing species at various temperatures.

This research reports the temperature-dependent thermochemical properties (enthalpy of formation, entropy, and heat capacity) of an extensive set of sulfur-containing species (89 species containing C/H/O/S atoms) by performing high-level quantum chemistry calculations. The chemical formulas, InChI, SMILES, and molecular structures of all selected species are summarized in Table 3, with the classification of the species into "C/H/S, C/H/S2, C/H/O/S, and others" groups, representing the atoms of these species.

2. METHOD AND THEORY

2.1. Ab Initio Method. The Gaussian 16 software package was used for all density functional theory (DFT)[14,15] and composite compound method calculations. Although accurate and widely used for the thermochemistry computation of organic compounds, M06-2*X*/6-311++G (d,p) failed to converge for some large sulfur-containing species. Therefore, the B3LYP method, with the cc-pVTZ basis set,[16,17] was used for geometry optimizations, vibrational frequency calculations, and dihedral angle scans for the lower-frequency modes, in which the internal rotations corresponding to low-frequency torsional modes were scanned in 10 degrees increments as a function of dihedral angle. All vibrational frequencies were scaled by 0.983 and 0.9698, respectively.

For Zero Kelvin energies (ZKEs), the combination of CBS-QB3[18] and G3[19] yielded results within *chemical accuracy* (arbitrarily, ∼4 kJ mol^{-1} or 1 kcal mol^{-1}), when benchmarked against enthalpy of formation values in the active thermochemical tables (ATcT).[20−22] Some previous studies[23,24] aimed at the thermochemistry of sulfur-containing species used CBS-QB3 and achieved excellent performance.[23,24] Hence, both methods were employed to generate the ZKE data, and the resulting enthalpies were compared with the experimental values.

2.2. Atomization Method. The atomization method was used to derive the species' enthalpies of formation at 0 K ($\Delta_f H_0$). In the atomization method, a molecule or radical is formed from its component atoms via eq 1:

$$C_aH_bO_cS_d \rightarrow a^3C + b^2H + c^3O + d^3S \quad (1)$$

The theoretical atomization energy at 0 K (TAE_0) can be obtained with eq 2:

$$TAE_0 = aH_0(^3C) + bH_0(^2H) + cH_0(^3O) + dH_0(^3S) - H_0(C_aH_bO_cS_d) \quad (2)$$

where H_0 is ZKE for each atom and species.

Enthalpy of formation at 0 K can then be calculated using eq 3:

$$\Delta_f H_0(C_aH_bO_cS_d) = a\Delta_f H_0(^3C) + b\Delta_f H_0(^2H) + c\Delta_f H_0(^3O) + d\Delta_f H_0(^3S) - TAE_0 \quad (3)$$

where $\Delta_f H_0$ is the enthalpy of formation at 0 K for each atom in its gaseous state from the ATcT, computed H_0 and experimental $\Delta_f H_0$ for each atom are shown in Table 4.

The MultiWell program suite, based on statistical thermodynamics,[25] was then used to obtain thermochemical parameters. The Lamm module of MultiWell calculated both external rotational constants and the reduced moment of inertia for hindered internal rotations.[26] Thermochemical parameters were

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Table 3. Glossary of Species in This Study

Formula	Name	InChI	Structure
C/H/S			
C5H6S_2	Thiophene, 3-methyl-	InChI=1S/C5H6S/c1-5-2-3-6-4-5/h2-4H,1H3	
C5H10S_1	2H-Thiopyran, tetrahydro-	InChI=1S/C5H10S/c1-2-4-6-5-3-1/h1-5H2	
C5H10S_2	Cyclopentanethiol	InChI=1S/C5H10S/c6-5-3-1-2-4-5/h5-6H,1-4H2	
C5H10S_3	Thiophene, tetrahydro-2-methyl-	InChI=1S/C5H10S/c1-5-3-2-4-6-5/h5H,2-4H2,1H3	
C5H10S_4	Thiophene, tetrahydro-3-methyl-	InChI=1S/C5H10S/c1-5-2-3-6-4-5/h5H,2-4H2,1H3	
C5H10S_5	3-Ethylthio-1-propene	InChI=1S/C5H10S/c1-3-5-6-4-2/h3H,1,4-5H2,2H3	
C5H12S_1	1-Pentanethiol	InChI=1S/C5H12S/c1-2-3-4-5-6/h6H,2-5H2,1H3	
C5H12S_2	2-Methyl-2-butanethiol	InChI=1S/C5H12S/c1-4-5(2,3)6/h6H,4H2,1-3H3	
C5H12S_3	Butyl methyl sulfide	InChI=1S/C5H12S/c1-3-4-5-6-2/h3-5H2,1-2H3	
C5H12S_4	Ethyl propyl sulfide	InChI=1S/C5H12S/c1-3-5-6-4-2/h3-5H2,1-2H3	
C5H12S_5	Ethyl isopropyl sulfide	InChI=1S/C5H12S/c1-4-6-5(2)3/h5H,4H2,1-3H3	
C5H12S_6	Tert-Butyl methyl sulfide	InChI=1S/C5H12S/c1-5(2,3)6-4/h1-4H3	
C5H12S_7	Isoamyl mercaptan	InChI=1S/C5H12S/c1-5(2)3-4-6/h5-6H,3-4H2,1-2H3	
C5H12S_8	3-Methyl-2-butanethiol	InChI=1S/C5H12S/c1-4(2)5(3)6/h4-6H,1-3H3	
C5H12S_9	Neopentyl mercaptan	InChI=1S/C5H12S/c1-5(2,3)4-6/h6H,4H2,1-3H3	
C5H12S_10	2-Methyl-1-butanethiol	InChI=1S/C5H12S/c1-3-5(2)4-6/h5-6H,3-4H2,1-2H3	
C6H5SH	Benzenethiol	InChI=1S/C6H6S/c7-6-4-2-1-3-5-6/h1-5,7H	
C/H/S2			
C2H6S2_1	1,2-Ethanedithiol	InChI=1S/C2H6S2/c3-1-2-4/h3-4H,1-2H2	
C2H6S2_2	Dimethyl disulfide	InChI=1S/C2H6S2/c1-3-4-2/h1-2H3	
C3H8S2	1,3-Propanedithiol	InChI=1S/C3H8S2/c4-2-1-3-5/h4-5H,1-3H2	
C4H10S2	1,4-Butanedithiol	InChI=1S/C4H10S2/c5-3-1-2-4-6/h5-6H,1-4H2	
C/H/S3			
C3H4S3	1,3-Dithiolane-2-thione	InChI=1S/C3H4S3/c4-3-5-1-2-6-3/h1-2H2	
C2H6S3	Dimethyl trisulfide	InChI=1S/C2H6S3/c1-3-5-4-2/h1-2H3	
C3H6S3_1	1,3,5-Trithiane	InChI=1S/C3H6S3/c1-4-2-6-3-5-1/h1-3H2	
C3H6S3_2	Carbonotrithioic acid, dimethyl ester	InChI=1S/C3H6S3/c1-5-3(4)6-2/h1-2H3	

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Table 3. continued

Formula	Name	InChI	Structure
C/H/S			
H2CS	Methanethione	InChI=1S/CH2S/c1-2/h1H2	
C2H4S_1	Thiirane	InChI=1S/C2H4S/c1-2-3-1/h1-2H2	
C2H4S_2	Ethenethiol	InChI=1S/C2H4S/c1-2-3/h2-3H,1H2	
C2H4S_3	Ethanethial	InChI=1S/C2H4S/c1-2-3/h2H,1H3	
CH3SH	Methanethiol	InChI=1S/CH4S/c1-2/h2H,1H3	
C2H6S_1	Ethanethiol	InChI=1S/C2H6S/c1-2-3/h3H,2H2,1H3	
C2H6S_2	Dimethyl sulfide	InChI=1S/C2H6S/c1-3-2/h1-2H3	
C3H6S_1	Thietane	InChI=1S/C3H6S/c1-2-4-3-1/h1-3H2	
C3H6S_2	Thiirane, methyl-	InChI=1S/C3H6S/c1-3-2-4-3/h3H,2H2,1H3	
C3H6S_3	Thioacetone	InChI=1S/C3H6S/c1-3(2)4/h1-2H3	
C3H8S_1	1-Propanethiol	InChI=1S/C3H8S/c1-2-3-4/h4H,2-3H2,1H3	
C3H8S_2	2-Propanethiol	InChI=1S/C3H8S/c1-3(2)4/h3-4H,1-2H3	
C3H8S_3	Ethyl methyl sulfide	InChI=1S/C3H8S/c1-3-4-2/h3H2,1-2H3	
C4H4S	Thiophene	InChI=1S/C4H4S/c1-2-4-5-3-1/h1-4H	
C4H6S_1	Divinyl sulfide	InChI=1S/C4H6S/c1-3-5-4-2/h3-4H,1-2H2	
C4H6S_2	Thiophene, 2,3-dihydro-	InChI=1S/C4H6S/c1-2-4-5-3-1/h1,3H,2,4H2	
C4H6S_3	Thiophene, 2,5-dihydro-	InChI=1S/C4H6S/c1-2-4-5-3-1/h1-2H,3-4H2	
C4H8S	Thiophene, tetrahydro-	InChI=1S/C4H8S/c1-2-4-5-3-1/h1-4H2	
C4H10S_1	1-Butanethiol	InChI=1S/C4H10S/c1-2-3-4-5/h5H,2-4H2,1H3	
C4H10S_2	2-Butanethiol	InChI=1S/C4H10S/c1-3-4(2)5/h4-5H,3H2,1-2H3	
C4H10S_3	2-Methyl-1-propanethiol	InChI=1S/C4H10S/c1-4(2)3-5/h4-5H,3H2,1-2H3	
C4H10S_4	2-Methyl-2-propanethiol	InChI=1S/C4H10S/c1-4(2,3)5/h5H,1-3H3	
C4H10S_5	Methyl propyl sulfide	InChI=1S/C4H10S/c1-3-4-5-2/h3-4H2,1-2H3	
C4H10S_6	Diethyl sulfide	InChI=1S/C4H10S/c1-3-5-4-2/h3-4H2,1-2H3	
C4H10S_7	Isopropyl methyl sulfide	InChI=1S/C4H10S/c1-4(2)5-3/h4H,1-3H3	
C5H6S_1	Thiophene, 2-methyl-	InChI=1S/C5H6S/c1-5-3-2-4-6-5/h2-4H,1H3	

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Table 3. continued

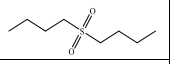
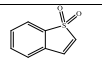
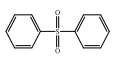
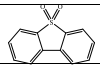
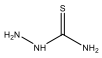
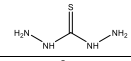
Formula	Name	InChI	Structure
C/H/O/S			
C2H6OS	Dimethyl sulfoxide	InChI=1S/C2H6OS/c1-4(2)3/h1-2H3	
C4H8OS	S-Ethyl thioacetate	InChI=1S/C4H8OS/c1-3-6-4(2)5/h3H2,1-2H3	
C4H10OS	Diethyl sulfoxide	InChI=1S/C4H10OS/c1-3-6(5)4-2/h3-4H2,1-2H3	
C2H6O2S	Dimethyl sulfone	InChI=1S/C2H6O2S/c1-5(2,3)4/h1-2H3	
C3H4O2S	2H-Thiete-1,1-dioxide	InChI=1S/C3H4O2S/c4-6(5)2-1-3-6/h1-2H,3H2	
C4H6OS_1	Dihydro-3-(2H)-thiophenone	InChI=1S/C4H6OS/c5-4-1-2-6-3-4/h1-3H2	
C4H6OS_2	Dihydro-2-(3H)-thiophenone	InChI=1S/C4H6OS/c5-4-2-1-3-6-4/h1-3H2	
C4H6OS_3	Vinyl sulfoxide	InChI=1S/C4H6OS/c1-3-6(5)4-2/h3-4H,1-2H2	
C4H6OS_4	4,5-dihydrothiophene-3-ol	InChI=1S/C4H6OS/c5-4-1-2-6-3-4/h3,5H,1-2H2	
C4H6OS_5	2,5-dihydrothiophene-3-ol	InChI=1S/C4H6OS/c5-4-1-2-6-3-4/h1,5H,2-3H2	
C4H6OS_6	4,5-dihydrothiophene-2-ol	InChI=1S/C4H6OS/c5-4-2-1-3-6-4/h2,5H,1,3H2	
C4H6OS_7	2,3-dihydrothiophene-2-ol	InChI=1S/C4H6OS/c5-4-2-1-3-6-4/h1,3-5H,2H2/t4-/m1/s1	
C2H6O3S	Sulfurous acid, dimethyl ester	InChI=1S/C2H6O3S/c1-4-6(3)5-2/h1-2H3	
C3H8O2S	(Methylsulfonyl)ethane	InChI=1S/C3H8O2S/c1-3-6(2,4)5/h3H2,1-2H3	
C8H18O2S	Di-n-butyl sulfone	InChI=1S/C8H18O2S/c1-3-5-7-11(9,10)8-6-4-2/h3-8H2,1-2H3	
C4H8O2S	Tetrahydrothiophene 1,1-dioxide	InChI=1S/C4H8O2S/c5-7(6)3-1-2-4-7/h1-4H2	
C4H6O2S	2,5-dihydrothiophene 1,1-dioxide	InChI=1S/C4H6O2S/c5-7(6)3-1-2-4-7/h1-2H,3-4H2	
C12H10O2S	Diphenyl sulfone	InChI=1S/C12H10O2S/c13-15(14,11-7-3-1-4-8-11)12-9-5-2-6-10-12/h1-10H	
C8H6O2S	Thianaphthene 1,1-dioxide	InChI=1S/C8H6O2S/c9-11(10)6-5-7-3-1-2-4-8(7)11/h1-6H	
C12H8O2S	Dibenzothiophene 5,5-dioxide	InChI=1S/C12H8O2S/c13-15(14)11-7-3-1-5-9(11)10-6-2-4-8-12(10)15/h1-8H	
Others			
CH5N3S	Hydrazinecarbothioamide	InChI=1S/CH5N3S/c2-1(5)4-3/h3H2,(H3,2,4,5)	
C4H5NS	4-Methylthiazole	InChI=1S/C4H5NS/c1-4-2-6-3-5-4/h2-3H,1H3	
CH6N4S	Carbonothioic dihydrazide	InChI=1S/CH6N4S/c2-4-1(6)5-3/h2-3H2,(H2,4,5,6)	
C2H4N2S2	Ethanedithioamide	InChI=1S/C2H4N2S2/c3-1(5)2(4)6/h(H2,3,5)(H2,4,6)	
CH3SO2NH2	Methanesulfonamide	InChI=1S/CH5NO2S/c1-5(2,3)4/h1H3,(H2,2,3,4)	
CS	Methanidylidynesulfanium	InChI=1S/CS/c1-2	

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Table 4. Atomic ZKEs Calculated by Each Method (a.u.) and Gaseous Formation Enthalpies at 0 K from ATcT (kcal mol^{-1})

parameter	method/source	C (^{3}P)	H ($^2S_{1/2}$)	O (^{3}P)	S (^{3}P)
H_0	CBS-QB3	−37.785376	−0.499818	−74.987619	−397.657353
	G3	−37.827717	−0.501003	−75.030991	−397.961110
$\Delta_f H_0$	ATcT	170.03	51.63	59.00	66.18

calculated using the "Thermo" module of MultiWell. Eventually, the best combination of methods for ZKE was identified, and the temperature-dependent enthalpies of formation, entropies, and heat capacities of all species were calculated based on the statistical thermodynamics theory using the MultiWell solver.

Enthalpies of formation at 298 K derived from the G3, CBS-QB3, and G3/CBS-QB3 combination were further benchmarked by evaluating the root mean squared error (RMSE)[27] between the calculation results and some available databases:

a) Experimental data: thermochemical data of organic compounds (TDOC)[28]
b) Literature review: National Institute of Standards and Technology (NIST) Chemistry WebBook (NCWB)[29]

3. RESULTS AND DISCUSSION

3.1. Comparison between Computational Methods for ZKE. To benchmark the computational method, the Bland−Altman plot was employed to compare enthalpies of formation calculated by G3 only, CBS-QB3 only, and the G3/CBS-QB3 combination with values taken from the TDOC. The results of the comparison can be seen in Figures 1−3. All calculated

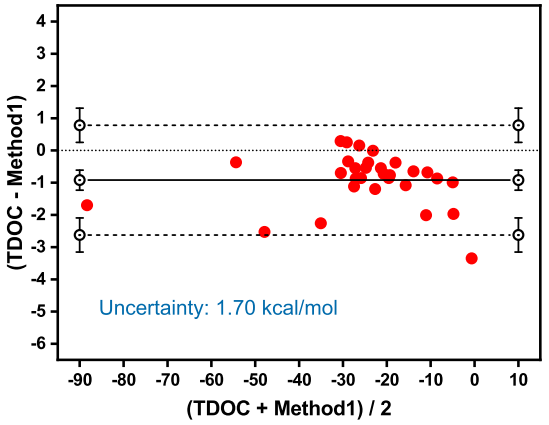

Figure 1. Comparison of 298 K enthalpies of formation (kcal mol^{-1}) with ZKE calculated by the G3 methods with values from TDOC.

enthalpies of formation for 30 species were in good agreement with values in TDOC, where most were within the 95% limit of agreement. The RMSE for results of the three methods calculated based on the 95% limit of agreement are labeled in Figures 1−3. Their biases were all below 1 kcal mol^{-1}, confirming the excellent accuracy of these quantum calculations.

Comparing the results from the above three methods, both CBS-QB3 and the combination of G3/CBS-QB3 outperformed the G3. The accuracy of the other two methods was comparable to that in the figures. The combination of G3/CBS-QB3 yielded better results for species containing oxygen, while CBS-QB3 was better for species consisting of only C, H, and S. Since the oxygen-containing species in the data set were few, the CBS-QB3 method achieved lower bias and similar standard deviation with the combination of G3 and CBS-QB3. Therefore, the CBS-QB3 method was chosen to perform all of the calculations in this study.

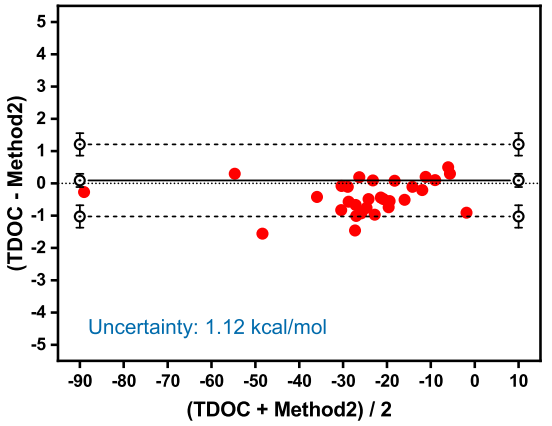

Figure 2. Comparison of 298 K enthalpies of formation (kcal mol^{-1}) with ZKE calculated by CBS-QB3 methods with values from TDOC.

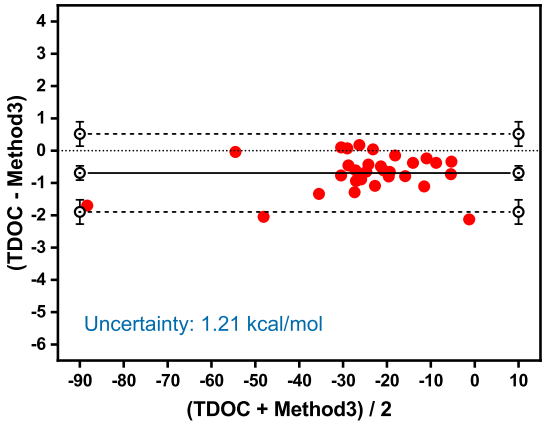

Figure 3. Comparison of 298 K enthalpies of formation (kcal mol^{-1}) with ZKE calculated by combining G3 and CBS-QB3 with values from TDOC.

3.2. Validation of Enthalpies of Formation. The calculated thermochemical parameters of all 89 sulfur-containing species are listed in Tables 5−7. Notably, given many species, they were classified as S1−S3, C1−C3, and C4−C12 groups listed in each table. These results are of significant importance to the study of kinetic models. Several different comparisons were subsequently performed to verify the validity of the results.

There is considerable experimental or theoretical data on the enthalpy of the formation of sulfur-containing species in the literature. However, they are rarely reported, because temperature-related entropy and heat capacity parameters are relatively difficult to measure. It was noted that the accuracy of the predicted entropy and heat capacity could be reflected by comparing the enthalpy of formation due to the main uncertainty factors in calculating thermochemical parameters being electronic energy. This work compared the enthalpy of

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Table 5. Thermochemistry for S1−S3 Sulfur-Containing Species Calculated in This Study[a]

	Δ_fH	S	C_p						
species	298.15 K	298.15 K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
S1 species									
H2S	−4.82	49.16	8.17	8.50	8.88	9.29	10.11	10.86	12.12
SO	1.41	53.06	7.22	7.54	7.84	8.07	8.38	8.56	8.76
HOSH	−26.74	58.32	10.64	11.94	12.97	13.78	14.99	15.91	17.43
SO2	−69.20	59.41	9.58	10.42	11.15	11.72	12.48	12.92	13.44
SO3	−92.09	61.59	12.38	14.01	15.29	16.26	17.52	18.25	19.10
H2SO3	−121.82	70.20	18.67	20.86	22.38	23.47	24.94	25.97	27.72
H2SO4	−170.39	71.55	20.29	23.63	26.06	27.84	30.21	31.75	34.08
S2 species									
S2	31.35	54.57	7.80	8.16	8.39	8.54	8.70	8.78	8.87
SSO	−10.61	63.95	10.63	11.48	12.08	12.51	13.03	13.32	13.63
S3 species									
S3	41.55	63.11	11.77	12.56	13.00	13.26	13.53	13.66	13.80

[a]Units: kcal mol^{-1} for $\Delta_fH^{\ominus}$, cal K^{-1} mol^{-1} for $S^{\ominus}$ and C_p.

Table 6. Thermochemistry for C1−C3 Sulfur-Containing Species Calculated in This Study[a]

	$\Delta_fH^{\ominus}$	$S^{\ominus}$	C_p						
species	298.15 K	298.15 K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
C1 species									
CS	66.60	50.29	7.12	7.38	7.67	7.91	8.26	8.46	8.71
CH2S	27.75	55.15	9.12	10.39	11.56	12.56	14.13	15.30	17.18
COS	−35.56	55.35	9.97	10.97	11.67	12.21	12.98	13.49	14.17
CS2	25.51	56.84	10.90	11.83	12.49	12.98	13.63	14.01	14.47
CH4S	−5.37	61.07	12.03	14.02	15.87	17.51	20.24	22.37	25.84
CH5N3S	33.65	77.72	23.53	28.01	31.65	34.57	38.94	42.12	47.31
CH5NO2S	−83.84	76.28	23.76	28.29	31.9	34.77	39.07	42.20	47.19
CH6N4S	65.25	85.29	27.83	33.27	37.8	41.48	47.01	51.03	57.49
C2 species									
C2H4S_1	18.98	61.03	12.85	16.41	19.41	21.82	25.41	28.00	32.03
C2H4S_2	19.34	67.30	15.50	18.48	20.89	22.83	25.83	28.07	31.64
C2H4S_3	17.06	65.49	14.00	16.66	19.13	21.27	24.68	27.23	31.21
C2H4N2S2	22.27	80.54	25.42	30.37	34.16	37.07	41.24	44.14	48.68
C2H6S_1	−10.83	70.92	17.68	21.17	24.30	27.00	31.37	34.72	40.09
C2H6S_2	−8.58	68.82	17.76	20.96	23.93	26.55	30.87	34.26	39.75
C2H6OS	−34.82	74.55	21.98	26.00	29.39	32.21	36.7	40.13	45.66
C2H6O2S	−87.47	76.59	24.55	29.17	33.09	36.35	41.43	45.21	51.16
C2H6O3S	−112.78	88.51	25.37	30.91	36.34	41.7	51.38	57.02	59.74
C2H6S2_1	−0.19	81.12	23.05	26.72	30.00	32.81	37.34	40.77	46.16
C2H6S2_2	−5.05	78.89	22.31	25.89	29.14	31.95	36.49	39.97	45.58
C2H6S3	−3.33	87.49	27.64	31.51	34.89	37.77	42.36	45.88	51.51
C3 species									
C3H4O2S	−27.78	74.76	22.28	27.88	32.37	35.85	40.82	44.19	49.11
C3H4S3	26.74	80.99	24.26	29.52	33.7	36.95	41.61	44.81	49.48
C3H6S_1	15.69	67.17	17.02	22.34	26.97	30.78	36.53	40.68	46.99
C3H6S_2	10.54	71.40	18.92	23.78	27.92	31.31	36.5	40.31	46.26
C3H6S_3	6.61	73.09	18.99	22.94	26.68	29.94	35.16	39.07	45.18
C3H6S3_1	17.19	80.46	27.34	33.75	38.83	42.82	48.65	52.78	59.02
C3H6S3_2	13.76	89.78	29.52	34.38	38.53	41.95	47.2	51.07	57.09
C3H8O2S	−93.13	88.00	29.9	35.91	41.12	45.48	52.31	57.38	65.33
C3H8S_1	−15.96	77.48	22.41	27.45	32.07	36.06	42.48	47.33	54.96
C3H8S_2	−18.52	77.85	23.4	28.57	33.07	36.85	42.82	47.33	54.48
C3H8S_3	−14.45	80.48	22.87	27.58	31.93	35.7	41.8	46.48	53.95
C3H8S2	−6.41	88.17	27.43	32.78	37.67	41.85	48.47	53.42	61.07

[a]Units: kcal mol^{-1} for $\Delta_fH^{\ominus}$, cal K^{-1} mol^{-1} for $S^{\ominus}$ and C_p.

formation of 298 K with the values obtained from the NIST Chemistry WebBook database and the experimental data from TDOC, shown in Table 8.

Table 8 shows that the 298 K enthalpies calculated in this study agreed well with the experimental data in TDOC and those in the NIST database; the differences are all within 1 kcal

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Table 7. Thermochemistry for C4−C12 Sulfur-Containing Species Calculated in This Study[a]

	$\Delta_fH^\ominus$	$S^\ominus$	C_p						
species	298.15 K	298.15 K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
C4 species									
C4H4S	28.00	66.60	17.50	22.94	27.25	30.58	35.28	38.48	43.21
C4H5NS	26.47	76.06	21.96	27.78	32.68	36.63	42.46	46.53	52.55
C4H6S_1	40.70	82.44	23.77	29.07	33.35	36.74	41.79	45.47	51.26
C4H6S_2	20.44	71.47	19.88	26.01	31.18	35.35	41.57	45.97	52.60
C4H6S_3	21.07	70.80	19.85	25.97	31.14	35.32	41.56	45.98	52.62
C4H6OS_1	−32.28	78.34	23.49	30.02	35.52	39.98	46.63	51.32	58.28
C4H6OS_2	−41.06	76.43	23.07	29.54	35.05	39.56	46.32	51.09	58.18
C4H6OS_3	18.65	85.36	29.19	35.19	39.94	43.54	48.6	52.11	57.57
C4H6OS_4	−19.47	77.50	25.94	32.18	37.14	41.07	46.9	51.06	57.46
C4H6OS_5	−21.67	76.64	25.2	31.58	36.75	40.85	46.87	51.11	57.54
C4H6OS_6	−20.02	77.51	24.63	31.00	36.22	40.37	46.51	50.83	57.39
C4H6OS_7	−21.15	78.52	24.41	31.05	36.48	40.75	46.9	51.16	57.56
C4H6O2S	−53.43	82.65	26.59	33.98	40.08	44.92	51.98	56.85	64.01
C4H8S	−7.13	73.48	21.34	28.43	34.66	39.82	47.67	53.32	61.89
C4H8OS	−54.50	86.58	28.36	34.72	40.28	44.94	52.22	57.6	65.94
C4H8O2S	−82.71	82.84	28.11	36.47	43.62	49.44	58.09	64.19	73.27
C4H10S_1	−21.44	84.20	27.29	33.97	40.10	45.39	53.81	60.12	69.93
C4H10S_2	−24.04	85.39	28.29	34.92	40.82	45.85	53.84	59.85	69.30
C4H10S_3	−23.05	84.01	28.38	34.98	40.87	45.88	53.84	59.84	69.28
C4H10S_4	−27.05	81.74	29.75	36.54	42.36	47.17	54.63	60.20	69.00
C4H10S_5	−19.99	86.40	27.64	34.05	39.92	44.99	53.1	59.24	68.90
C4H10S_6	−20.12	88.48	27.79	34.14	39.92	44.88	52.77	58.75	68.19
C4H10S_7	−21.99	86.88	29.12	35.4	40.98	45.73	53.31	59.08	68.31
C4H10OS	−48.17	85.83	32.02	39.48	45.89	51.24	59.61	65.86	75.66
C4H10S2	−12.04	94.89	32.14	39.18	45.61	51.1	59.75	66.16	76.01
C5 species									
C5H6S_1	20.14	76.91	22.84	29.31	34.75	39.15	45.69	50.30	57.20
C5H6S_2	20.14	76.78	22.98	29.45	34.89	39.27	45.77	50.35	57.22
C5H10S_1	−14.42	77.59	26.06	34.78	42.52	48.99	58.91	66.07	76.87
C5H10S_2	−11.01	83.11	26.74	35.17	42.7	49	58.66	65.64	76.20
C5H10S_3	−14.83	80.04	27.33	35.86	43.3	49.47	58.9	65.74	76.17
C5H10S_4	−14.09	80.37	27.24	35.75	43.17	49.32	58.76	65.61	76.09
C5H10S_5	7.63	94.92	33.40	40.48	46.25	51.03	58.66	64.53	73.95
C5H12S_1	−26.62	90.97	32.26	40.54	48.16	54.72	65.14	72.90	84.90
C5H12S_2	−31.26	93.93	34.65	42.88	50.1	56.13	65.48	72.41	83.22
C5H12S_3	−25.17	93.15	32.57	40.59	47.96	54.31	64.43	72.02	83.88
C5H12S_4	−25.49	95.64	32.52	40.53	47.83	54.09	64.01	71.46	83.12
C5H12S_5	−26.72	91.82	34.13	42.27	49.42	55.45	64.95	72.09	83.39
C5H12S_6	−29.88	91.47	34.80	42.95	50.00	55.87	65.02	71.89	82.79
C5H12S_7	−26.85	89.84	33.07	41.35	48.78	55.1	65.09	72.57	84.21
C5H12S_8	−29.48	92.39	34.25	42.29	49.37	55.38	64.93	72.13	83.47
C5H12S_9	−30.9	90.14	34.26	42.61	49.89	55.98	65.49	72.6	83.74
C5H12S_10	−27.61	92.32	32.95	41.07	48.44	54.77	64.83	72.37	84.11
C6 species									
C6H6S	27.23	80.28	25.49	32.69	38.74	43.60	50.75	55.70	62.95
C8 species									
C8H6O2S	−14.33	90.99	36.40	46.79	55.20	61.79	71.14	77.34	86.12
C8H18O2S	−118.41	119.09	54.66	68.84	81.59	92.38	109.17	121.46	140.27
C12 species									
C12H8O2S	−9.24	102.85	47.89	62.23	74.03	83.34	96.57	105.33	117.61
C12H10O2S	−19.41	113.70	51.64	66.73	79.07	88.78	102.65	112.01	125.46

[a]Units: kcal mol^{-1} for $\Delta_fH^\ominus$, cal K^{-1} mol^{-1} for $S^\ominus$ and C_p.

mol^{-1}; the average error was only 0.44 and 0.42 kcal mol^{-1}, respectively, indicating that the calculation methods used here were accurate and reliable.

3.3. Comparison with NIST Chemistry WebBook. Since species with relatively complex structures rarely have corresponding specific heat capacity at various temperatures, 10 sulfur-containing species with simple structures in the NIST Chemistry WebBook database were selected, and corresponding thermodynamic data were compared with those in the NIST Chemistry WebBook database, as shown in Table 9. Results

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Table 8. Comparison of 298 K Enthalpy of Formation for 10 Sulfur-Containing Species Calculated in This Study (kcal mol^{-1})

Species	Structure	Current study	TDOC	NIST
C2H6S_1		-10.83	-11.07	-11.03
C2H6S_2		-8.58	-8.96	-8.96
C3H8S_1		-15.96	-16.23	-16.39
C3H8S_2		-18.52	-18.21	-18.39
C3H8S_3		-14.45	-14.24	-14.41
C4H10S_2		-24.04	-23.16	-22.97
C4H10S_3		-23.05	-23.26	-23.06
C4H10S_4		-27.05	-26.20	-25.98
C5H12S_1		-26.62	-26.31	-26.48
C5H12S_3		-25.17	-24.43	-24.43

Table 9. Comparison of Thermochemistry for 10 Sulfur-Containing Species against NIST[a]

		$\Delta_fH^\ominus$	$S^\ominus$	C_p						
species	source	298.15 K	298.15K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CS	NIST	67.00	50.32	7.13	7.40	7.69	7.94	8.30	8.51	8.78
	current study	66.60	50.29	7.12	7.38	7.67	7.91	8.26	8.46	8.71
COS	NIST	−33.08	55.35	9.94	10.96	11.68	12.25	13.07	13.62	14.40
	current study	−35.56	55.35	9.97	10.97	11.67	12.21	12.98	13.49	14.17
CS2	NIST	27.95	56.88	10.93	11.87	12.55	13.05	13.74	14.17	14.72
	current study	25.51	56.84	10.90	11.83	12.49	12.98	13.63	14.01	14.47
H2S	NIST	−4.92	49.18	8.18	8.49	8.89	9.31	10.16	10.93	12.30
	current study	−4.82	49.16	8.17	8.50	8.88	9.29	10.11	10.86	12.12
SO	NIST	1.20	53.04	7.22	7.55	7.84	8.08	8.42	8.62	8.95
	current study	1.41	53.06	7.22	7.54	7.84	8.07	8.38	8.56	8.76
SO2	NIST	−70.94	59.32	9.55	10.40	11.13	11.72	12.54	13.02	13.63
	current study	−69.20	59.41	9.58	10.42	11.15	11.72	12.48	12.92	13.44
SO3	NIST	−94.59	61.37	12.14	13.79	15.07	16.07	17.40	18.15	19.05
	current study	−92.09	61.59	12.38	14.01	15.29	16.26	17.52	18.25	19.10
H2SO4	NIST	−175.70	71.41	20.08	23.40	25.79	27.63	30.14	31.69	34.15
	current study	−170.39	71.55	20.29	23.63	26.06	27.84	30.21	31.75	34.08
S2	NIST	29.12	54.53	7.79	8.14	8.35	8.51	8.75	8.94	9.31
	current study	31.35	54.57	7.8	8.16	8.39	8.54	8.7	8.78	8.87
S3	NIST		64.42	11.44	12.30	12.75	13.05	13.44	13.74	14.35
	current study	41.55	63.11	11.77	12.56	13.00	13.26	13.53	13.66	13.80

[a]Units: kcal mol^{-1} for $\Delta_fH^\ominus$, cal K^{-1} mol^{-1} for $S^\ominus$ and C_p.

showed that the 298 K entropies of about half of the species were in good agreement with the data in NIST. In contrast, the others show about a 2 kcal mol^{-1} difference with NIST data. Considering that much of the data in NIST comes from studies conducted in the last century, the methods used for that time may not have the high accuracy of existing methods nowadays. The 298 K enthalpy of formation for all overlapping species between our study and the references[7,8] was also compared, as shown in Tables 10 and 11. The results show that the current calculations are in better agreement with the reference data than with the NIST database and that the differences are within 1 kcal mol^{-1}. In terms of entropy and heat capacity, the 298 K entropy and heat capacity at the temperature range from 300 to 1500 K calculated in this study agreed well with the results of the NIST database. All values were within the difference of 1 cal K^{-1} mol^{-1}.

Table 10. Comparison with Reference 7 and NIST Data on 298 K Enthalpy of Formation (kcal mol^{-1})

	$\Delta_fH^\ominus$		
species	current study	reference	NIST
S2	31.35	30.70	29.12
H2S	−4.82	−4.90	−4.92
SO	1.41	1.20	1.20
CH3SH	−5.37	−5.40	
C2H6S_1	−10.83	−11.00	−11.07
C2H6S_2	−8.58	−8.90	−8.96
C6H6S	27.23	26.70	
C2H4S_1	18.98	19.70	
C2H4S_2	19.34	21.0 ± 2	
C2H6S2_2	−5.05	−5.80	

4. CONCLUSIONS

This study calculated thermochemical parameters using a high-level DFT method, including the enthalpy of formation, entropy, and specific heat capacity for extensive sulfur-containing species. The consistent ab initio method (CBS-QB3/G3//B3LYP/cc-pVTZ) was utilized for geometry optimization, frequency

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Table 11. Comparison with Reference 8 and NIST Data on 298 K Enthalpy of Formation (kcal mol^{-1})

	$\Delta_fH^{\ominus}$		
species	current study	reference	NIST
S2	31.35	30.1 ± 0.6	29.12
CS	66.6	66.9 ± 0.5	67.00
H2S	−4.82	−5.35	−4.92
SO	1.41	1.2 ± 0.3	1.20
SO2	−68.59	−70.2	−70.94
SSO	−10.61	−12.0	
CH2S	27.75	27.6 ± 1	

calculation, and dihedral scanning. The atomization reaction method was used to calculate the 0 K enthalpy of formation; statistical thermodynamics was applied to calculate temperature-related thermochemical parameters. The theoretical calculation results agreed with the experimental data in the TDOC and NIST databases. Using the Bland−Altman diagram, the statistical analysis found that the CBS-QB3 method produced the most reliable results for predicting the 298 K enthalpy of the formation of sulfur-containing species. Therefore, it is recommended for future thermochemistry calculations of other sulfur-containing compounds.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c00477.

T1 diagnostic and energy; thermochemistry in NASA polynomial format; and all input and output files for MultiWell solver (ZIP)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Li, Y.; Curran, H. J. Extensive Theoretical Study of the Thermochemical Properties of Unsaturated Hydrocarbons and Allylic and Super-Allylic Radicals: The Development and Optimization of Group Additivity Values. *journal of physical chemistry. A* **2018**, *122* (20), 4736−4749.

(2) Martin, G. *Pyrolysis of Organosulfur Compounds.* **1993**, 395−437.

(3) Raj, A.; Ibrahim, S.; Jagannath, A. Combustion kinetics of H2S and other sulfurous species with relevance to industrial processes. *Prog. Energy Combust. Sci.* **2020**, *80*, No. 100848.

(4) Ibrahim, S.; Al Shoaibi, A.; Gupta, A. K. Xylene addition effects to H2S combustion under Claus condition. *Fuel* **2015**, *150*, 1−7.

(5) Gargurevich, I. A. Hydrogen Sulfide Combustion: Relevant Issues under Claus Furnace Conditions. *Ind. Eng. Chem. Res.* **2005**, *44* (20), 7706−7729.

(6) Puzzarini, C. Accurate thermochemistry and spectroscopy of the oxygen-protonated sulfur dioxide isomers. *Phys. Chem. Chem. Phys.* **2011**, *13* (48), 21319−21327.

(7) Benson, S. W. Thermochemistry and kinetics of sulfur-containing molecules and radicals. *Chem. Rev.* **1978**, *78* (1), 23−35.

(8) Denis, P. A. Thermochemistry of 35 selected sulfur compounds, a comparison between experiment and theory. *Journal of Sulfur Chemistry* **2008**, *29* (3−4), 327−352.

(9) Nagy, B.; Szakács, P.; Csontos, J.; Rolik, Z.; Tasi, G.; Kállay, M. High-Accuracy Theoretical Thermochemistry of Atmospherically Important Sulfur-Containing Molecules. *J. Phys. Chem. A* **2011**, *115* (26), 7823−7833.

(10) Denis, P. A.; Ventura, O. N. Density Functional Investigation of Atmospheric Sulfur Chemistry. I. Enthalpy of Formation of HSO and Related Molecules. *Int. J. Quantum Chem.* **2000**, *80*, 439−453.

(11) Resende, S. M.; Ornellas, F. R. Enthalpy of Formation of CH3SO and CH3SO2: A Difficult Case in Quantum Chemistry. *J. Braz. Chem. Soc.* **2002**, *13*, 565.

(12) Song, G.; Bozzelli, J. W. Structural and thermochemical properties of methyl ethyl sulfide alcohols: HOCH2SCH2CH3, CH3SCH(OH)CH3, CH3SCH2CH2OH, and radicals corresponding to loss of H atom. *J. Phys. Org. Chem.* **2018**, *31* (7), No. e3836.

(13) Weh, R.; de Klerk, A. Thermochemistry of Sulfones Relevant to Oxidative Desulfurization. *Energy Fuels* **2017**, *31* (6), 6607−6614.

(14) Marrazzini, G.; Giovannini, T.; Scavino, M.; Egidi, F.; Cappelli, C.; Koch, H. Multilevel Density Functional Theory. *J. Chem. Theory Comput.* **2021**, *17*, 791−803.
(15) Liu, S.; Zhang, X. Chemical Concepts from Density Functional Theory. *Acta Phys. -Chim. Sin.* **2018**, *34* (6), 563−566.
(16) Türker, L. Trans-dinitroglycoluril isomers-A DFT treatment. *Defence Technology* **2017**, *13* (1), 6−15.
(17) Khaikin, L. S.; Ageev, G. G.; Grikina, O. E.; Shishkov, I. F.; Kuznetsov, V. V.; Makhova, N. N. Intramolecular Motions in 1,2,3-Triethyldiaziridine: A Quantum Chemistry Study. *Russian Journal of Physical Chemistry A* **2020**, *94* (9), 1836−1842.
(18) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. A complete basis set model chemistry. VII. Use of the minimum population localization method. *J. Chem. Phys.* **2000**, *112* (15), 6532−6542.
(19) Curtiss, L. A.; Raghavach Ari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. Gaussian-3 (G3) theory for molecules containing first and second-row atoms. *J. Chem. Phys.* **1998**, *109* (18), 7764−7776.
(20) Ruscic, B.; Pinzon, R. E.; Morton, M. L.; von Laszevski, G.; Bittner, S. J.; Nijsure, S. G.; Amin, K. A.; Minkoff, M.; Wagner, A. F. Introduction to Active Thermochemical Tables: Several "Key" Enthalpies of Formation Revisited. *J. Phys. Chem. A* **2004**, *108* (45), 9979−9997.
(21) Ruscic, B.; Pinzon, R. E.; von Laszevski, G.; Kodeboyina, D.; Burcat, A.; Leahy, D.; Montoy, D.; Wagner, A. F. Active Thermochemical Tables: thermochemistry for the 21st century. *J. Phys.: Conf. Ser.* **2005**, *16* (1), 561.
(22) Ruscic, B.; Bross, D. H. *Active Thermochemical Tables (ATcT) values based on ver. 1.130 of the Thermochemical Network*; Argonne National Laboratory: Lemont, IL, 2022; available at ATcT.anl.gov.
(23) Paraskevas, P. D.; Sabbe, M. K.; Reyniers, M.-F.; Papayannakos, N.; Marin, G. B. Group Additive Values for the Gas-Phase Standard Enthalpy of Formation, Entropy and Heat Capacity of Oxygenates. *Chem. − A Eur. J.* **2013**, *19* (48), 16431−16452.
(24) Vandeputte, A. G.; Sabbe, M. K.; Reyniers, M.-F.; Marin, G. B. Modeling the Gas-Phase Thermochemistry of Organosulfur Compounds. *Chem. − A Eur. J.* **2011**, *17* (27), 7656−7673.
(25) Li, Y.; Sarathy, S. M. Probing hydrogen−nitrogen chemistry: A theoretical study of important reactions in NxHy, HCN and HNCO oxidation. *Int. J. Hydrogen. Energy* **2020**, *45* (43), 23624−23637.
(26) Li, Y.; Klippenstein, S. J.; Zhou, C.-W.; Curran, H. J. Theoretical Kinetics Analysis for Ḣ Atom Addition to 1,3-Butadiene and Related Reactions on the Ċ4H7 Potential Energy Surface. *J. Phys. Chem. A* **2017**, *121* (40), 7433−7445.
(27) Ćalasan, M.; Abdel Aleem, S. H. E.; Zobaa, A. F. On the root mean square error (RMSE) calculation for parameter estimation of photovoltaic models: A novel exact analytical solution based on Lambert W function. *Energy Conversion and Management* **2020**, *210*, No. 112716.
(28) Cox, J. D.; Pilcher, G. *Thermochemistry of organic and organometallic compounds*, 1970.
(29) Linstrom, P. NIST Chemistry WebBook, NIST Standard Reference Database 69; National Institute of Standards and Technology, 1997.

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