

Paradigms and Paradoxes: Systematics and Surprises in the Study of the Simplest Sulfenic Acids and Sulfoxides, and a comparison between sulfur–oxygen and nitrogen–oxygen bonds.

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Abstract

Some particularities in the bonding of simple sulfenic acids and their sulfoxide isomers are explored using accurate theoretical methods. Some unexpected results are described using thermochemical results on diverse nitrogen– and/or oxygen–containing functionalities such as amino, nitro, nitroso and nitrite derivatives.

Keywords

Sulfenic acids, sulfoxides, nitro derivatives, bonding patterns, thermochemistry, composite methods.

Introduction

Sulfur-containing organic compounds exhibit a wide variety of structural features in which the formal oxidation state of sulfur ranges from -2 to $+6$. In many of these species, the sulfur is bonded to both carbon and oxygen, resulting again in a wide diversity of bonding patterns and structural features. In this study, the discussion is limited to two of these many classes of species. The first class is sulfenic acids [1–4], which can be represented by the simple $R-S-O-H$ bonding pattern, and their related $R-S-O-R'$ sulfenate esters [5–7]. The second class of species are sulfoxides [8–10], normally represented as $R-S(O)-R'$. Inseparable from both classes are the compounds where $R'=H$, i.e. $R-S(O)-H$, which generally have not been observed experimentally [11–15]. These are simultaneously tautomers of sulfenic acids, wherein the H has migrated from the oxygen atom to the sulfur atom, and sulfoxides derived from alkyl and aryl mercaptans instead of alkyl and aryl sulfides. Indeed, the simplest isomeric structures, $H-S-O-H$ and $H-S(O)-H$, have never been isolated as pure, condensed phase, bulk samples [11–15]. With their dicoordinated sulfur and oxygen, and tricoordinated sulfur and unicoordinate oxygen, they can be considered as the parent compounds of sulfenic acids and sulfoxides respectively.

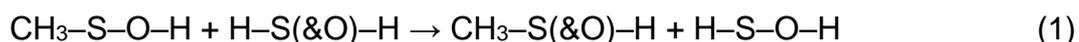
For the purpose of the ensuing analysis, we note that sulfenic acids and their sulfenate esters may simply be described as having three defining single bonds, $R-S$, $S-O$ and $O-H$ (or $O-R'$). By contrast, the much better known sulfoxides have two defining single bonds, $R-S$ and $R'S$, accompanied by a sulfur–oxygen bond that has been represented variously as $-SO-$ and $-S(O)-$ (with no bond description conveyed or even intended), the hypervalent $-S(=O)-$, the zwitterion $-S^+(-O^-)-$, or an explicit resonance hybrid of the last two structures, the polarized $-S^{\delta+}(-O^{\delta-})-$, and also as $-S(\rightarrow O)-$. In the current study, we will use $-S(\&O)-$ to denote the sulfur–oxygen bond in sulfoxides since $-SO-$ invites confusion with sulfenic acids/sulfenate esters. Additionally, we do not wish to enter the foray of the qualitative and quantitative controversy implicit in the key vocabulary words, bonding, backbonding, *d* orbitals, *d* polarization functions, covalent, ionic, partial charges, etc., but to obtain bonding information from the thermochemistry of some of their reactions.

We will discuss in the following some energy-related aspects of the simple methanesulfenic acid and its tautomer, $CH_3-S-O-H$ and $CH_3-S(\&O)-H$ respectively,

and the even simpler H–S–O–H and H–S(&O)–H, where we fully acknowledge that the last two species are not sulfur-containing organic compounds because they altogether lack carbons. Nonetheless, we consider them relevant to the current discussion much as “C₁ and C₂ organic species” such as formaldehyde, methanol, methyl mercaptan, and acetaldehyde, ethanol and ethyl mercaptan, accompany inorganic substances in the aging, but venerable compendium of experimental thermochemical data by Wagman et al. [16].

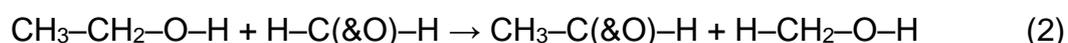
Results & Discussion

Let us start our discussion with the enthalpy of formation difference for the tautomers H–S–O–H and H–S(&O)–H. Ventura et al. [17] recent study of the subject using high-accuracy theoretical methods showed that the former species is more stable than the latter by 16.2 ± 1.2 kcal mol⁻¹. Likewise, the enthalpy of formation difference for the methylated tautomers CH₃–S–O–H and CH₃–S(&O)–H was shown [17] to be 11.6 ± 0.4 kcal mol⁻¹. A question that poses itself then is: are these results reasonable? The structural difference between H–S–O–H and H–S(&O)–H is the same as between CH₃–S–O–H and CH₃–S(&O)–H. In other words, the difference of the enthalpies of formation of H–S–O–H and H–S(&O)–H is expected to be very similar to that of CH₃–S–O–H and CH₃–S(&O)–H. Said differently, consider the isodesmotic reaction (1)



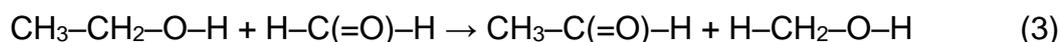
in that the number and type of C–H, O–H, S–H, S–O and S(&O) bonds are the same for the two sets of reactants and products. Simple bond additivity logic would suggest that this reaction is thermoneutral. From the aforementioned numbers, our calculations result in a gas phase reaction exothermicity of 4.9 ± 1.3 kcal mol⁻¹. Qualitatively and quantitatively, we may ask whether this depart of thermoneutrality is reasonable.

Regardless of the choice of electronegativity scale, the values of carbon and sulfur are numerically close. Consider thus now the reaction (2), i.e. the all-carbon analog of reaction (1), where we temporarily wrote >C(&O) for the carbon–oxygen double bond as found in aldehydes, ketones and other carbonyl-containing species.



(We know enough to avoid using the hydroxycarbenes $\text{CH}_3\text{-C-O-H}$ and H-C-O-H , i.e. C replacing S instead of CH_2 because whether they be singlet or triplet, they are electron deficient, and we are relatively knowledge deficient as to their energetics. This is even more problematic should we decide to discuss other sulfenic acid/sulfenate esters and the corresponding sulfoxides.)

Since sulfur–oxygen bonds in H-C(&O)-H and $\text{CH}_3\text{-C(&O)-H}$ are normally represented as double bonds, reaction (2) is usually written as reaction (3) or even (4), where all specific bonding specifications have been obliterated.



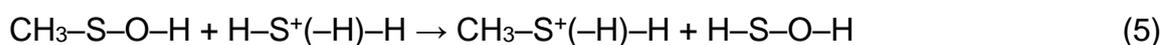
There are many thermochemical archives from which one may obtain the enthalpies of formation of the four species in reaction (4), ethanol, formaldehyde, acetaldehyde, and methanol respectively. For example, Wagman's compendium [16] qualifies. However, we chose to use those given by Pedley [18] because this source gives us the majority of the desired values for other alcohols and aldehydes of interest, should we wish to later discuss other sulfenic acids, sulfenate esters and the tautomericly related sulfoxides. Similarly, there are many theoretical composite methods that can provide chemical ($< 1 \text{ kcal mol}^{-1}$) or benchmark ($< 1 \text{ kJ mol}^{-1}$) accuracy for the energies of so small species [17–22]. In the spirit of these works, we choose the W1BD method [23–25] to perform the theoretical calculations not contained in our previous work [17]. The results obtained for atomization energies (from which enthalpies of reaction and formation are derived) are more accurate than 1 kcal mol^{-1} on average when applied to an extensive database of many chemical species.

Using Pedley's archive of experimentally measured values [18], we deduce that reaction (4) is exothermic by $5.7 \pm 0.2 \text{ kcal mol}^{-1}$, while the calculation at the chemically accurate W1BD composite method affords a value of $7.9 \pm 2.0 \text{ kcal mol}^{-1}$. Although the upper and lower error limits of both values are close, the averages are more different than what one usually observes for calculations on isodesmic reactions. In this respect, da Silva et al. published a study [26] challenging the values of the experimental enthalpies of formation used in equation (4) to determine the exothermicity.

In the case of formaldehyde, the most commonly cited value of $\Delta_f H_{298}^0$ is that included in Pedley's work [18], -25.95 ± 0.12 kcal mol⁻¹. However, the reanalysis of this data by Chase [27] included in the NIST Thermochemical Data Tables, proposed a $\Delta_f H_{298}^0$ value of -27.72 ± 1.5 kcal mol⁻¹. Using reaction (4) to determine the enthalpy of formation of formaldehyde, da Silva et al. [26] propose a theoretical value of -26.21 ± 0.58 kcal mol⁻¹, overlapping in part the value of Chase [27]. Our own value calculated at the accurate W1BD level gives -26.13 kcal mol⁻¹, very similar to that of da Silva et al. [26], Chase [27], and the value given in the Active Thermochemical Tables [28–30], -26.12 ± 0.02 kcal mol⁻¹. Similarly, two different values are available for the enthalpy of formation of acetaldehyde, another one of the species employed in reaction (4). While Wiberg et al. [31] report -40.80 ± 0.58 kcal mol⁻¹ for the heat of formation of acetaldehyde, the ATcT tables [28–30] list a value of -39.58 ± 0.06 kcal mol⁻¹, again non-overlapping intervals. Our own accurate value for the enthalpy of formation of acetaldehyde was obtained as -38.95 kcal mol⁻¹, again closer to the ATcT value. Given these considerations, one could say that the W1BD exothermicity value of 7.9 ± 2.0 kcal mol⁻¹ for reaction (4) is reasonably in agreement with the experimental value. Therefore, we can conclude that both reactions (1) and (4) have similar experimental and theoretical exothermicities.

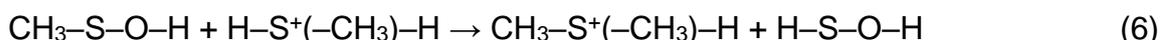
Taking into account the significant understanding of the thermochemistry of alcohols and carbonyl compounds, sulfoxides are to be understood as sulfur-analogs of carbonyl compounds, i.e., representing definitely the SO bond as >S=O. As such, we seemingly understand sulfenic acids (and their sulfenate esters) and sulfoxides better than we thought.

Let us return to reaction (1) where we now assume S(&O) is a single, however polarized, bond. More precisely, let us replace the >S(&O) bond by >S⁺(-H) with its unequivocally single bond containing a positive sulfur. As such, let us now consider the energetics of reaction (5) for which the enthalpies of formation of both sulfenic acids are taken from reference [17], and that of H-S⁺(-H)-H derived from the enthalpy of formation and the proton affinity of H₂S taken from Wagman et al. [16] and Hunter and Lias [32] respectively, and the enthalpy of formation and proton affinity of CH₃SH from Pedley [18] and Hunter and Lias [32] respectively.



Using the references above, reaction (5) is found to be exothermic by 9.6 kcal mol⁻¹ with a plausible uncertainty of 1–2 kcal mol⁻¹. Our calculation at the W1BD level affords a similar value of 10.1 ± 1.0 kcal mol⁻¹. In other words, reaction (5) is between 2 and 4 kcal mol⁻¹ more exothermic than reaction (1). Remembering our earlier near equality of the enthalpies of reactions (1) and (4), suggests that the double bond description for sulfoxides, >S=O, is to be preferred over the polar >S⁺–O⁻, should we wish to have a unique bonding picture.

Alternatively, let us now discuss the energetics of reaction (6) instead of (5)



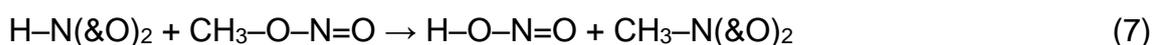
Here, the “third” group attached to sulfur mimicking that of sulfoxides is –CH₃ which we recognized as isoelectronic, and comparatively isosteric, with –O⁻. Let us thus parallel our discussion of eq. (5); taking the enthalpies of formation of both sulfenic acids from reference [17], those of H–S⁺(–CH₃)–H and CH₃–S⁺(–CH₃)–H using the enthalpy of formation and the proton affinity values of both CH₃SH and (CH₃)₂S from Pedley [18] and Hunter and Lias [32], respectively. In so doing, we found the exothermicity of reaction (6) to be 10.0 kcal mol⁻¹ according to the experimental references and 9.8 kcal mol⁻¹ as calculated at the W1BD level, almost the same as for reaction (5). Once again, we would prefer the description of sulfoxides as >S=O instead of >S⁺–O⁻, should we want to give a unique bonding picture.

We stated earlier that H–S–O–H is more stable than H–S(&O)–H. Our recent study [17] showed the former species to be more stable than the latter by 16.2 ± 1.2 kcal mol⁻¹, and that CH₃–S–O–H is more stable than CH₃–S(&O)–H by a smaller value, 11.6 ± 0.4 kcal mol⁻¹. In other words, the CH₃ group stabilizes sulfoxides more than it does to sulfenic acids, likely because of the hyperconjugative effect of that group.

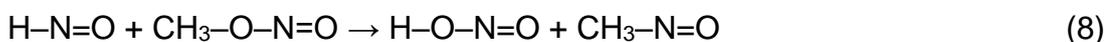
The enhanced stabilization of H–S(&O)–H over H–S–O–H by the methyl group is unequivocal regardless of how the sulfur–oxygen bonds are described. Then, let’s now consider briefly some nominally related species with nitrogen–oxygen bonds instead of sulfur–oxygen, again disregarding any detailed description of the nitrogen–oxygen bonds [33]. For example, for nitro compounds we could choose to write –NO₂ and –N(O)₂ (with no bond description conveyed or even intended), the hypervalent formula –N(=O)₂, either one of the pair of zwitterions –N⁺(=O)(O⁻) and –N⁺(O⁻)(=O), an explicit

resonance hybrid of the last two structures, the polarized $-N^{\delta+}(-O^{\delta-})_2$ bond, the dative $-N(=O)(\rightarrow O)-$ and/or $-N(\rightarrow O)(=O)-$ forms, or the biradical $-N(-O\bullet)_2$ formulation. The nitrogen–oxygen bonds in nitrites seem simpler and are usually described as $-O-N=O$. Yet, the related nitroso compounds, RNO , are seemingly not so simple to describe. Many of these species are green or blue, and readily dimerize to form (E)– and/or (Z)– $N(O)=N(O)-$ species, with structural and electronic complications not unlike nitro compounds. Additionally, these dimers have adjacent (partial) positive charges and are customarily drawn as $-N(\rightarrow O)=N(\rightarrow O)-$ [33–35].

From the experimental data, we found that the enthalpy of formation of $H-O-N=O$ is more negative than $CH_3-O-N=O$ by ca. 3 kcal mol⁻¹, with a small uncertainty derived from choosing the enthalpies of formation for only the most stable rotamer, or that of the equilibrium mixture. From the accurate theoretical calculations, we obtain a value of 3.2 kcal mol⁻¹, in good agreement with the previously mentioned. By analogy to our earlier discussion, the enthalpy of formation of the experimentally not yet characterized tautomer $H-N(\&O)_2$ should be more positive than that of $CH_3-N(\&O)_2$ by 7.4 kcal mol⁻¹. Indeed, we found at the W1BD level that $H-O-N=O$, nitrous acid, is more stable than $H-N(\&O)_2$, nitryl hydride, by 8.4 kcal mol⁻¹. On the contrary, in the methyl substituted species, $CH_3-O-N=O$, methyl nitrite, is less stable than $CH_3-N(\&O)_2$, nitromethane, by ca. 2 kcal mol⁻¹ (2.5 kcal mol⁻¹ at the W1BD level). Equivalently, reaction (7) is exothermic by ca. 10.3 kcal mol⁻¹ using the experimental data, and 11.0 kcal mol⁻¹ using the W1BD values.



The related nitroso reaction (8) involves nitrosyl hydride and nitrosomethane



We found reaction (8) to be exothermic by 11.4 and 11.5 kcal mol⁻¹ at the experimental and theoretical levels respectively. This result is surprisingly similar to that we obtained for reaction (7). It is unexpected that the CH_3 groups stabilize very similarly nitro compounds as nitrous acid esters. CH_3 groups likewise also stabilize N^+ when found in ammonium ions. From Wagman et al. [16] and Pedley [18] respectively, we find the enthalpies of formation of NH_3 and CH_3NH_2 to be -11.0 and -5.5 kcal mol⁻¹. From Hunter and Lias [32] we find that the proton affinity of NH_3 is smaller than that of CH_3NH_2 by 10.9 kcal mol⁻¹. Accordingly, using this data, the enthalpy of formation of

(CH₃NH₃)⁺ is more negative than that of (NH₄)⁺ by ca. 5.4 kcal mol⁻¹. Encouragingly, the difference obtained from the heats of formation of both species obtained theoretically by W1BD, affords a value of 5.8 kcal mol⁻¹.

Summary

We analyzed in this report the characteristics of the SO bonds in sulfenic acids, as well as CO and NO bonds in inorganic and a few-carbon nitro and nitroso compounds, investigating whether the bonds are better represented by polarized (or dative) bonds or by a double bond. Some unexpected results are described. We performed this analysis purely on the basis of enthalpies of formation and reaction, and compared the effect caused by methyl substituents on the parent compounds. The results show that the SO bond behaves in a similar way than analogous CO and NO bonds in the other species, and documents the ability of high level theoretical composite methods to describe accurately the isomerizations and other reactions of the species considered.

Declarations

Ethical Approval We did not perform any experiments when preparing this article, so neither ethics review nor informed consent was necessary.

Competing interests All authors declare that they have no conflicts of interest.

Authors' contributions All authors have contributed equally to writing and reviewing the manuscript.

Consent to participate All authors agreed with participation in research and publication of the results.

Consent to publish All authors have approved the manuscript before submission, including the names and order of authors.

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Availability of data and materials Not applicable.

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