

Extraordinary Difference in Reactivity of Ozone (OOO) and Sulfur Dioxide (OSO): A Theoretical Study

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ABSTRACT: Ozone and sulfur dioxide are valence isoelectronic yet show very different reactivity. While ozone is one of the most reactive 1,3-dipoles, SO₂ does not react in this way at all. The activation energies of dipolar cycloadditions of sulfur dioxide with either ethylene or acetylene are predicted here by B3LYP, M06-2X, CBS-QB3, and CCSD(T) to be much higher than reactions of ozone. The dipolar cycloaddition of ozone is very exothermic, while that of sulfur dioxide is endothermic. The prohibitive barriers in the case of SO₂ arise from large distortion energies as well as unfavorable interaction energies in the transition states. This arises in part from the HOMO–LUMO gap of sulfur dioxide, which is larger than that of ozone. Valence bond calculations also show that while ozone has a high degree of diradical character, SO₂ does not, and is better characterized as a ditterion.

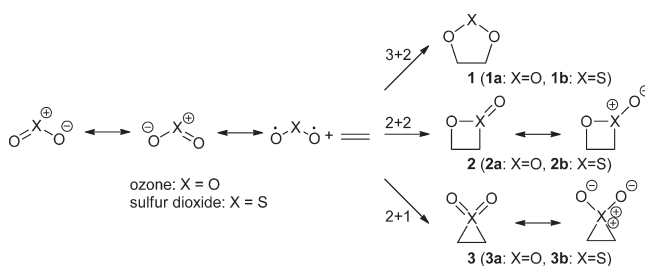
INTRODUCTION

We have recently computed activation barriers and reaction energies for 1,3-dipolar cycloaddition reactions (3 + 2 cycloadditions) of 48 1,3-dipoles¹ as part of a general investigation of the factors that control reactivities in 1,3-dipolar cycloadditions. We were struck by the very great difference between the reactivity of ozone, O₃, which reacts with virtually all CC multiple bonds, and SO₂, which is so unreactive that it is not even considered a 1,3-dipole. This prompted a more detailed investigation of the various cycloadditions, such as those outlined in Scheme 1, that these species can undergo, as well as an exploration of the differences in reactivity.

The 1,3-dipolar cycloaddition² is a powerful synthetic tool used in materials chemistry,³ drug discovery,⁴ and chemical biology.⁵ Quantum chemistry calculations⁶ and molecular dynamics investigations⁷ have shown that the 3 + 2 cycloaddition of 1,3-dipoles to C–C multiple bonds occurs via a concerted transition state, as proposed by Huisgen.⁸

The factors controlling reactivity in 1,3-dipolar cycloadditions have recently been elucidated.^{9,12} Frontier molecular orbital (FMO) theory¹⁰ is a successful qualitative reactivity model for 1,3-dipolar cycloadditions. This model commonly involves the use of approximate quantum mechanical methods and the calculation of electronic properties of isolated reactants. To evaluate the cycloaddition reactivity, conceptual density functional theory and configuration mixing also have been employed.¹¹ We have found that most of the activation energy of a 1,3-dipolar cycloaddition is due to the distortion of the reactants.¹¹ Interaction energies, such as FMO effects, slightly reduce these barriers. The distortion energies of 1,3-dipolar cycloadditions of ethylene and acetylene and for substituted alkenes and alkynes correlate rather quantitatively with activation energies.¹² Recently, Hiberty demonstrated that the diradical character of 1,3-dipoles is related to computed activation barriers,¹³ with lower barriers correlated with more substantial diradical character, but the correlation is not quantitative.

Scheme 1. Possible Cycloaddition Reactions of Ozone or Sulfur Dioxide with Ethylene



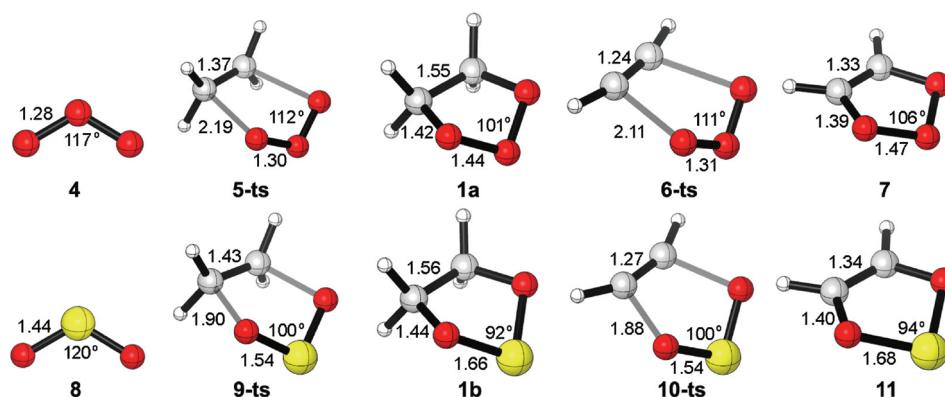
Ozone (O₃), which like all 1,3-dipoles is represented in an all-octet valence bond structure as a zwitterionic (dipolar) species,¹⁴ readily reacts with alkenes and alkynes.¹⁵ This reaction is used for the synthesis of ketones, aldehydes, and epoxides or derivatives.¹⁶ Early work employing natural orbital occupation and generalized valence bond computations showed the significant diradical character of ozone,¹⁷ and ab initio studies have shown that the 1,3-dipolar cycloaddition of ozone occurs via a concerted transition state.¹⁸ Barriers for these reactions are difficult to compute using standard computational approaches, leading to predicted activation enthalpies for the cycloaddition of O₃ with ethylene and acetylene ranging from 2 to 18 kcal/mol and 5 to 23 kcal/mol, respectively.¹⁹ Recent high-accuracy focal point extrapolations yielded activation enthalpies for the cycloadditions with ethylene and acetylene of 5.3 and 9.4 kcal/mol, respectively.²⁰

Sulfur dioxide (SO₂), in which the central oxygen atom of ozone is replaced by sulfur, has the same Lewis structures as ozone.²¹ The geometries of SO₂ and O₃ are similar, with bond angles of 120° for SO₂ and 117° for O₃. The bond length of SO₂ (1.43 Å) is longer than the bond length of O₃ (1.27 Å).²²

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Scheme 2. Geometries of Ozone, Sulfur Dioxide, and the Transition States and Cycloadducts of 1,3-Dipolar Cycloadditions with Ethylene and Acetylene Calculated by the CCSD(T)/cc-pV(T+d)Z Method



Although many $3 + 2$ cycloadditions of ozone are known, there is no experimental report of a $3 + 2$ cycloaddition of sulfur dioxide (SO_2), and when sulfur dioxide and an alkene or alkyne are mixed, no dioxathiolane is formed.²³

As shown in Scheme 1, there are three possible cycloaddition pathways for the reaction between SO_2 and ethylene. The $3 + 2$ cycloaddition generates the 1,3,2-dioxathiolane **1b**. A previous theoretical investigation²⁴ showed that this $3 + 2$ cycloaddition can proceed on a graphite surface at 900 °C. Although the reaction energy, ring strain of products,²⁵ and reactivity toward carbon surfaces²⁶ of SO_2 have been studied, the activation energy of the $3 + 2$ cycloaddition of SO_2 with simple alkenes or alkynes has not been reported. The endothermic $2 + 2$ cycloaddition generates 1,2-oxathietene 2-oxide (**2b**).^{24,27} The reverse reaction of the thermal extrusion of SO_2 from **2b** is used to generate a double bond via a proposed concerted pathway.²⁸ The generation of $2 + 1$ cycloaddition product thiirane 1,1-dioxide (**3b**) is also endothermic.²⁷ Oxidation of thiirane by oxone gives **3b**, which is a general method to prepare thiirane 1,1-dioxide.²⁹ The thermal extrusion of SO_2 from **3b** gives the alkene.³⁰ The methanolysis of complex **3b** is used to generate methyl 2-methoxyethanesulfinate.³¹ In the present work, we focus on the different reactivities of ozone and sulfur dioxide in $3 + 2$ cycloadditions.

COMPUTATIONAL METHODS

Optimized geometries, reaction barriers, and reaction energies were computed at the B3LYP/6-311+G(d), M06-2X/6-311+G(d), CBS-QB3, and CCSD(T)/cc-pV(T+d)Z levels of theory. B3LYP³² is the most widely used hybrid generalized gradient approximation (GGA) functional.³³ M06-2X is a recently developed hybrid meta GGA functional parametrized for nonmetal atoms.³⁴ It has been benchmarked against a number of main-group energetic databases and is suitable for main-group thermochemistry and kinetics,³⁵ provided that adequate integration grids are used.^{35c} The complete basis set (CBS) methods³⁶ strive to eliminate errors that arise from basis set truncation in quantum mechanical calculations by extrapolating to the CBS limit by exploiting the N^{1-} asymptotic convergence of MP2 pair energies calculated from pair natural orbital expansions. In particular, CBS-QB3 uses B3LYP/6-311G(2d,d,p) geometries and frequencies³⁷ followed by CCSD(T), MP4(SDQ), and MP2 single-point calculations and a CBS

extrapolation.³⁶ While ordinarily reliable, CBS-QB3 has previously been shown to predict anomalous activation energies in some cases,³⁸ including for 1,3-dipolar cycloadditions of ozone to ethylene and acetylene.²⁰ These errors have been shown²⁰ to arise from the exclusive reliance on MP2 to recover basis set effects. Consequently, in this work, geometries and energies were also computed using CCSD(T)³⁹ paired with the cc-pV(T+d)Z basis set.^{40a} At this level of theory, benchmark values²⁰ for the reaction barriers of $\text{O}_3 + \text{C}_2\text{H}_2$ and C_2H_4 are reproduced within 0.5 kcal/mol, and the corresponding reaction energies are within 1.0 kcal/mol. Use of this modified form of the standard cc-pVTZ basis set of Dunning^{40b} has been shown to be necessary to achieve qualitatively correct geometries and energies for some sulfur-containing molecules.^{40c} All B3LYP, M06-2X, and CBS-QB3 calculations were performed here using the Gaussian 09 package,⁴¹ while the CCSD(T) calculations were performed using CFOUR.⁴²

Reported molecular orbital energies were evaluated at the RHF/6-311++G(2d,p) level of theory to avoid the poor estimates for ionization potentials of small molecules provided by Kohn–Sham orbitals. The large basis set also can give better estimates of unoccupied orbital eigenvalues.⁴³

Finally, the diradical character of various species was quantified using valence bond (VB) theory,⁴⁴ a powerful tool to calculate the weights of VB structures for 1,3-dipoles.^{13,45} Here the D-BOVB⁴⁶ approach was used to calculate the weights of VB structures for ozone and sulfur dioxide. The VB calculations were carried out with the Xiamen VB (XMVB) package.⁴⁷

RESULTS AND DISCUSSION

1. Competition of the Dipolar Cycloaddition Reactivity between Ozone and Sulfur Dioxide. The geometries of the transition states and products for the dipolar cycloaddition of ozone and sulfur dioxide with ethylene and acetylene are shown in Scheme 2. Ozone (**4**) reacts with ethylene to form the primary ozonide **1a** via transition state **5-ts**. In this transition state, the O–O bond length increases by 0.02 Å, and the O–O–O bond angle is reduced about 5°, compared to isolated O_3 . The forming C–O bond is 2.19 Å. In product **1a**, the O–O bond is increased to 1.44 Å, and the bond angle is reduced to 101°. The activation energy for the dipolar cycloaddition of ozone and ethylene is known to be only 3.4 kcal/mol,²⁰ and as seen in Table 1, all but the CCSD(T) method underestimate this value. The reaction is

Table 1. Activation Energies and Reaction Energies for the 1,3-Dipolar Cycloaddition of Ozone and Sulfur Dioxide to Ethylene and Acetylene

	B3LYP	CBS-QB3	M06-2X	CCSD(T)
5-ts	−1.5	0.3	−1.3	3.6
1a	−57.7	−55.1	−74.9	−57.3
6-ts	2.7	4.7	2.9	8.0
7	−65.6	−60.9	−79.2	−64.1
9-ts	39.9	49.4	39.3	51.0
1b	2.0	17.1	−12.2	13.7
10-ts	43.2	52.6	43.6	54.7
11	−10.0	8.6	−20.7	4.1

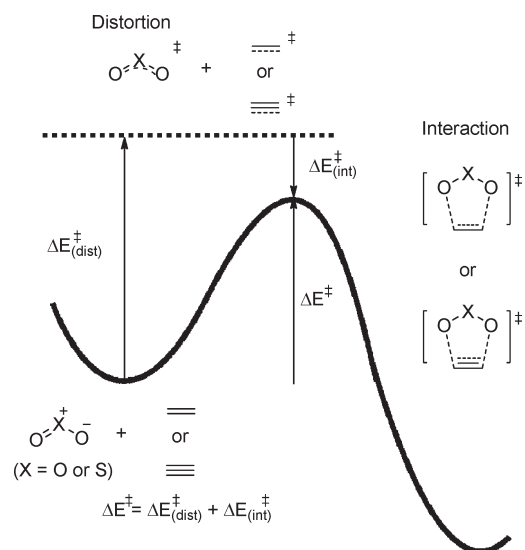
highly exothermic ($\Delta E = -56.4$ kcal/mol),²⁰ and CBS-QB3 and CCSD(T) predict values in qualitative agreement with this benchmark result. B3LYP yields a similar prediction (−57.7 kcal/mol), while the M06-2X reaction energy is about 20 kcal/mol too exothermic.

Sulfur dioxide reacts with ethylene to form cycloadduct **1b** via transition state **9-ts**. The O–S bond length increases 0.10 Å in the transition state, and the O–S–O angle is reduced by 20°. The forming C–O bond is 1.90 Å. These geometric differences demonstrate that the transition state **9-ts** is significantly later than **5-ts**. B3LYP and M06-2X predict an activation energy of 40 kcal/mol, and the CBS-QB3 and CCSD(T) data are higher still by about 10 kcal/mol. In the geometry of dipolar cycloaddition product **1b**, the O–S bond length increased to 1.66 Å, and the O–S–O bond angle is reduced to 92°. These geometric distortions going from reactant to product are more severe than for ozone. CBS-QB3 and CCSD(T) predict that the dipolar cycloaddition of sulfur dioxide with ethylene is endothermic by 17.1 and 13.7 kcal/mol, respectively. The endothermicity of this reaction is consistent with the late transition state. M06-2X, on the other hand, predicts that this reaction is exothermic by 12.2 kcal/mol.

The dipolar cycloadditions of ozone and sulfur dioxide with acetylene follow the same trends as ethylene. Transition state **10-ts** is significantly later than **6-ts**, and the activation energy of the dipolar cycloaddition between sulfur dioxide and acetylene is about 41–48 kcal/mol higher than between ozone and acetylene. The predicted reaction energy for the dipolar cycloaddition of O₃ to acetylene is 56–70 kcal/mol more exothermic than for SO₂.

2. Distortion and Interaction of the Dipolar Cycloaddition Reactivity between Ozone and Sulfur Dioxide. For bimolecular reactions, distortion–interaction energy analysis is a powerful tool to explain reactivity trends.^{12,48} In this analysis, the total activation energy (ΔE^\ddagger) is decomposed into the sum of distortion energy ($\Delta E_{\text{dist}}^\ddagger$) and interaction energy ($\Delta E_{\text{int}}^\ddagger$) between distorted reactants (see Figure 1).

Table 2 shows the distortion energies and interaction energies of the transition states (**5-ts**, **6-ts**, **9-ts**, and **10-ts**). The CCSD(T) calculations show that for the dipolar cycloaddition of ozone with ethylene (**5-ts**), the distortion energy is 4.0 kcal/mol and the interaction energy is −0.3 kcal/mol. For the dipolar cycloaddition between sulfur dioxide and ethylene (**9-ts**), the distortion energy is 30 kcal/mol larger and the interaction energy is repulsive by 16.5 kcal/mol. The results for the cycloaddition to acetylene follow the same trend; both the distortion and interaction energies of the dipolar cycloaddition between sulfur dioxide and acetylene are larger than between ozone and acetylene. Although

**Figure 1.** The relationship between activation, distortion, and interaction energies.**Table 2.** Distortion Energies and Interaction Energies of the Transition States **5-ts**, **6-ts**, **9-ts**, and **10-ts**

	B3LYP		CBS-QB3		M06-2X		CCSD(T)	
	E_{dist}	E_{int}	E_{dist}	E_{int}	E_{dist}	E_{int}	E_{dist}	E_{int}
5-ts	3.6	−5.1	1.4	−1.1	3.7	−5.0	4.0	−0.3
6-ts	6.6	−3.8	3.5	1.2	5.9	−3.0	6.3	1.7
9-ts	33.0	6.9	36.1	13.3	29.8	9.5	34.5	16.5
10-ts	33.2	10.0	35.2	17.4	32.1	11.5	35.7	19.1

the other theoretical methods (B3LYP, M06-2X, and CBS-QB3) give somewhat different distortion and interaction energies, the overall trends hold across each of these levels of theories.

To shed further light on the disparate behavior of O₃ and SO₂ in dipolar cycloadditions, the distortion and interaction energies have been computed along the reaction pathway at the B3LYP level of theory, using the forming C–O bond distances as a reaction coordinate (see Figure 2). As shown in Figure 2, as long as the forming C–O bonds are longer than 2.0 Å, the distortion energies for O₃ and SO₂ are essentially the same. As the C–O bond decreases below 2.0 Å, the distortion energy of the reaction of sulfur dioxide climbs higher than for ozone. In contrast to SO₂, the interaction energy for the reaction of ozone is negative throughout the reaction pathway and drops off rapidly as the C–O bond shortens. The transition state, which occurs when $d(\Delta E_{\text{dist}})/dr + d(\Delta E_{\text{int}})/dr = 0$, occurs at a C–O bond length of 2.30 Å. The interaction between sulfur dioxide and ethylene is unfavorable at long range. As the C–O distance decreases, the repulsion between sulfur dioxide and ethylene increases, until the forming C–O bond reaches 2.15 Å. The maximum of the interaction energy is about 23 kcal/mol at the B3LYP level, and this value is expected to be larger at the CCSD(T) level of theory. The transition state occurs at a C–O distance of 1.94 Å, at which point the interaction energy is still highly unfavorable. This positive interaction energy, along with the large distortion energy associated with a late transition state, leads to the prohibitive reaction barrier for the dipolar cycloaddition of SO₂ to ethylene.

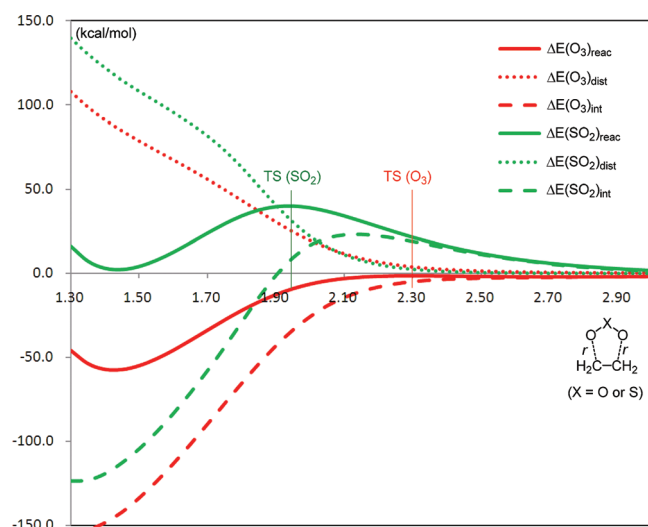


Figure 2. Distortion, interaction, and total energies along the reaction pathways of the dipolar cycloadditions between ozone or sulfur dioxide and ethylene. The solid lines are the reaction energies. The dotted lines are the distortion energies. The dashed lines are the interaction energies.

3. Molecular Orbital Analysis of Ozone and Sulfur Dioxide.

There is no simple way to explain the distortion–interaction energies and the reactivity in dipolar cycloadditions, but molecular orbital theory provides some insight.^{12a} The molecular orbitals and orbital energies of ozone and sulfur dioxide are shown in Figure 3. The gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for the ground state of ozone is 13.8 eV at the RHF/6-311++G(2d,p) level. The HOMO of ground state SO₂ is 1.0 eV lower than ozone and the LUMO is 0.8 eV higher, leading to a HOMO–LUMO gap for SO₂ that is 1.8 eV larger than that of ozone. These differences in HOMO–LUMO gaps help explain the differences in interaction energies displayed in Figure 2 and Table 2. The high energy level of the HOMO is responsible for the pseudodiradical character of ozone and increases the reactivity. As shown below, both distortion and interaction energies are influenced by the HOMO–LUMO gaps of reactants.

As shown in Figure 4, a schematic diagram of the molecular orbital of ozone and sulfur dioxide explains why the LUMO of ozone is lower than that of sulfur dioxide, and the HOMO of ozone is higher than that of sulfur dioxide. For both ozone and sulfur dioxide, the delocalized π bond can be separated into two parts: the p orbitals of the two terminal oxygen atoms (Figure 4, column c) and the p orbital of the center oxygen (Figure 4, column a) or sulfur (Figure 4, column e) atom. The p orbital of the two terminal oxygen atoms can combine into symmetric or antisymmetric combination to form orbital π_{O-O} and π^*_{O-O} . In ozone, the p orbital of the center oxygen atom has the same symmetry and similar energy as the π_{O-O} orbital, and thus it forms the π_{1a} and π_{3a} orbital with the π_{O-O} orbital in ozone (Figure 4, column b), and the π^*_{O-O} orbital forms the π_{2a} orbital. For sulfur dioxide, the energy level of the 3p orbital of sulfur atom is higher than the 2p orbital of the oxygen atom. The combination of p_S orbital and π_{O-O} orbital forms the π_{1b} and π_{3b} orbitals (Figure 4, column d). The energy level of π_{3b} is higher than that of π_{3a} because the p_S orbital is higher than the p_O orbital. In Figure 3, it can be seen that the weight of the sulfur

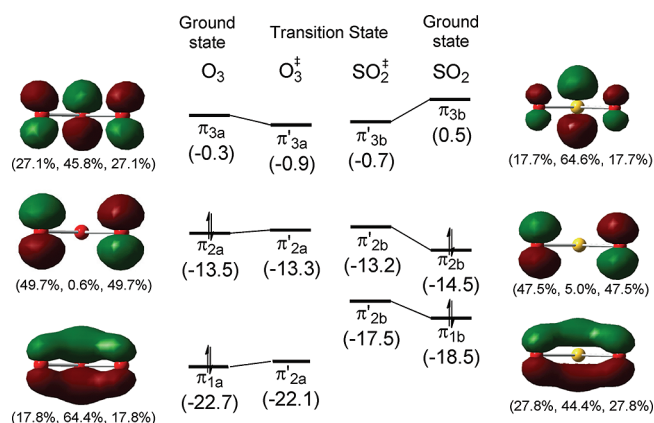


Figure 3. The molecular orbitals of ozone and sulfur dioxide at the reactant and transition state geometries. The values in parentheses are the orbital levels in eV. The percentages are the weight of the atomic orbitals in the ground state molecular orbitals.

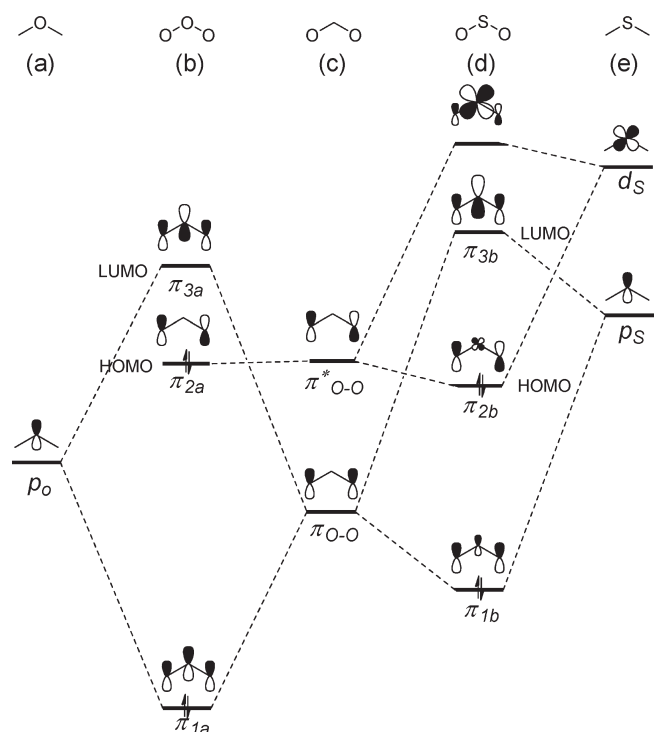


Figure 4. Schematic diagram of the molecular orbital of ozone and sulfur dioxide.

orbital (64.6%) in the π_{3b} orbital is higher than the weight of the oxygen orbital (45.8%) in π_{3a} , and the weight of the sulfur orbital (44.4%) in the π_{1b} orbital is lower than the weight of the oxygen orbital (64.4%) in π_{1a} . Atomic sulfur has an unoccupied d orbital, although the energy level of it is high.⁴⁹ The symmetry of one d orbital of sulfur atom is the same as the π^*_{O-O} orbital, and they form the π_{2b} orbital. Consequently, the energy level of the π_{2b} orbital is lower than that of π_{2a} orbital. In molecular orbital π_{2b} , the weight of the d orbital of sulfur is 5.0%.

4. The Singlet–Triplet Gap of Ozone and Sulfur Dioxide.

Previous theoretical investigations of 1,3-dipolar cycloadditions showed that the activation energy is determined by the avoided crossing of the singlet ground state of the 1,3-dipole and

Table 3. Optimized (ΔE_o) and Vertical (ΔE_v) Singlet–Triplet Gap of O_3 and SO_2 ^a

	B3LYP	CBS-QB3	M06-2X	CCSD(T)
$\Delta E_o(O_3)$	21.6	30.9	24.2	34.3
$\Delta E_v(O_3)$	28.6	41.5	32.4	40.3
$\Delta E_o(SO_2)$	61.0	70.6	66.3	73.2
$\Delta E_v(SO_2)$	67.6	76.6	73.4	79.0

^a The values of the O–O and O–S bond lengths in the ground state and excited state are also given in Å.

Table 4. Hydrogenation Energies of Ozone and Sulfur Dioxide

$ \begin{array}{c} \text{O}_3 \xrightarrow[\Delta E_1(O_3)]{H_2} \text{H-O-O-H} \xrightarrow[\Delta E_2(O_3)]{H_2} \text{H}_2\text{O} + \text{H}_2\text{O} \\ \text{SO}_2 \xrightarrow[\Delta E_1(SO_2)]{H_2} \text{H-S-O-H} \xrightarrow[\Delta E_2(SO_2)]{H_2} \text{H}_2\text{S} + \text{H}_2\text{O} \end{array} $				
	B3LYP	CBS-QB3	M06-2X	CCSD(T)
$\Delta E_1(O_3)$	−61.5	−56.3	−74.3	−63.6
$\Delta E_2(O_3)$	−63.4	−66.6	−66.3	−70.3
$\Delta E_1(SO_2)$	−12.7	4.6	−21.1	−4.0
$\Delta E_2(SO_2)$	−18.6	−17.2	−18.7	−20.2

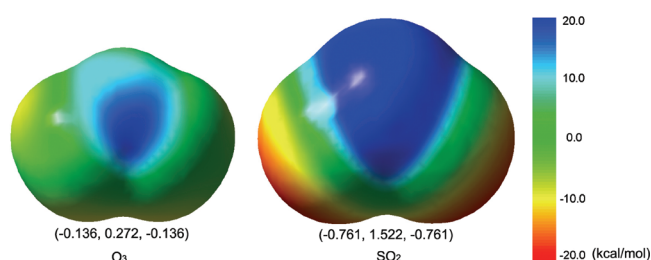
dipolarophile leading to the triplet excited state of the cycloadduct and the excited state triplet of the reactants leading to the ground state singlet of the product.^{5c,5d} For the dipolar cycloaddition with simple dipolarophiles, the transition state is typically correlated with the singlet–triplet energy gap of the 1,3-dipole. Lower singlet–triplet energy gaps for the 1,3-dipole correlates with an earlier transition state, lower activation energy, and a more exothermic reaction energy.⁵⁰

Optimized (ΔE_o) and vertical (ΔE_v) singlet–triplet gaps for O_3 and SO_2 are given in Table 3. Although the different theoretical methods give different values, the relative singlet–triplet energy gap of ozone and sulfur dioxide is almost the same across all four levels of theory considered. ΔE_o for ozone is 34.3 kcal/mol at the CCSD(T) level of theory. ΔE_o for sulfur dioxide is 38.9 kcal/mol higher, explaining the earlier transition state, lower activation energy, and greater exothermicity for cycloadditions of ozone versus SO_2 .

5. The Hydrogenation Energy of Ozone and Sulfur Dioxide. To investigate the strength of the π -bonds in ozone and SO_2 , hydrogenation energies were computed. As shown in Table 4, the first hydrogenation (ΔE_1) yields H–O–X–O–H (X = O or S), which no longer has a delocalized π bond. ΔE_1 for ozone is about 50 kcal/mol more exothermic than for sulfur dioxide. The hydrogenation of H–O–X–O–H (ΔE_2) breaks one of the O–X (X = O or S) bonds. ΔE_2 for ozone is again about 50 kcal/mol more exothermic than for sulfur dioxide. The hydrogenation energies show that both the delocalized π bond and O–X σ bond of sulfur dioxide is significantly stronger than those of ozone. This enhanced stability of sulfur dioxide contributes to its reduced reactivity compared to ozone.

6. The Diradical Character of Ozone and Sulfur Dioxide. In the VB theory study of Hiberty, the reactivity of 1,3-dipoles in dipolar cycloaddition was qualitatively related to the diradical character of the 1,3-dipoles.¹³ The six VB structures of ozone and sulfur dioxide are shown in Figure 5. For ozone, the dominant VB

$\ddot{O}-\dot{O}-\ddot{O}$ 4a 49.5%	$\dot{O}=\ddot{O}-\ddot{O}$ 4b 22.1%	$\ddot{O}=\dot{O}-\ddot{O}$ 4c 22.1%	$\dot{O}-\ddot{O}-\ddot{O}$ 4d 2.6%	$\ddot{O}-\ddot{O}-\dot{O}$ 4e 2.6%	$\ddot{O}-\ddot{O}-\ddot{O}^{++}$ 4f 1.1%
$\ddot{O}-\dot{S}-\ddot{O}$ 8a 2.4%	$\dot{O}=\ddot{S}-\ddot{O}$ 8b 18.0%	$\ddot{O}=\dot{S}-\ddot{O}$ 8c 18.0%	$\dot{O}-\ddot{S}-\ddot{O}$ 8d 0.9%	$\ddot{O}-\ddot{S}-\dot{O}$ 8e 0.9%	$\ddot{O}-\ddot{S}-\ddot{O}^{++}$ 8f 59.8%

Figure 5. Weight of VB structures for ozone and sulfur dioxide.**Figure 6.** Electrostatic potential of ozone and sulfur dioxide. The natural population analysis (NPA) charges are given in parentheses.**Table 5.** Reaction Energies (kcal/mol) for 3 + 2 (1), 2 + 2 (2), and 2 + 1 (3) Cycloadditions of Ozone (a) and Sulfur Dioxide (b) to Ethylene

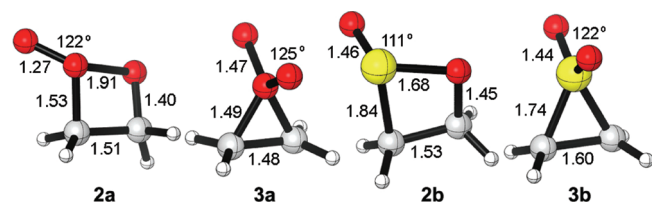
	B3LYP	CBS-QB3	M06-2X	CCSD(T)
1a	−57.7	−55.1	−74.9	−57.3
2a	−17.3	−19.1	−19.4	—
3a	67.3	72.5	52.1	54.8
1b	2.0	17.1	−12.2	13.7
2b	5.0	10.6	−4.2	9.1
3b	30.1	21.3	19.4	21.0

structure is the diradical structure **4a**, and ozone shows 49.5% diradical character. The weight of the sum of the traditional all-octet dipolar VB structures **4b** and **4c** is 44.2%. In other words, ozone has about half diradical and half zwitterionic character. For sulfur dioxide, the weight of the diradical VB structure **8a** is only 2.4%. The weight of the sum of the traditional all-octet dipolar VB structures **8b** and **8c** is 36.0%. The weight of dicationic sulfur VB structure **8f** is largest. Thus, although sulfur dioxide has both zwitterionic and dicationic character, the diradical character of sulfur dioxide is very weak, providing further explanation for the reduced reactivity of sulfur dioxide compared to ozone.

The characterization of SO_2 as dominated by a VB structure with a central dication is corroborated by NPA calculations (see Figure 6). In particular, the NPA charge on sulfur is 1.522, with the two terminal oxygen atoms carrying charges of −0.761. This accumulation of negative charge on the oxygen atoms, which is significantly reduced in O_3 , is one source of the repulsive electrostatic interaction between SO_2 and an approaching dipolarophile.

7. The Stability of 2 + 2 and 2 + 1 Cycloaddition Products. Finally, to assess the thermodynamic viability of other cycloadditions of ozone and SO_2 to ethylene and acetylene, the 2 + 2 and 2 + 1 cycloaddition products have been predicted (see Table 5). The 2 + 2 cycloaddition between ozone and ethylene forms complex **13**. At the CCSD(T)/cc-pV(T+d)Z level of theory, a

Scheme 3. Geometries of 3 + 2, 2 + 1, and 2 + 2 Cycloadducts of Ozone and SO₂ with Ethylene Calculated at the CCSD(T)/cc-pV(T+d)Z Level of Theory^a



^a For **2a**, the B3LYP/6-311+G(d) geometry is given; see the text.

stationary point corresponding to this cycloadduct could not be located, and all optimizations gave a ring-opened diradical species. This structure is a minimum on the B3LYP and M06-2X potential energy surfaces, and the B3LYP geometry is presented in Scheme 3. At all levels of theory considered, these 2 + 1 and 2 + 2 cycloadducts are less favorable energetically than the corresponding 3 + 2 cycloadditions, except for the 2 + 2 cycloaddition of SO₂ to ethylene. When the center atom of the 1,3-dipole is an oxygen atom, the 2 + 2 and 2 + 1 cycloaddition species (**2a** and **3a**) are 35 and 112 kcal/mol less stable than the 3 + 2 cycloaddition product **1a**. When the center atom of the 1,3-dipole is a sulfur atom, the 2 + 2 cycloaddition species **2b** is 4.6 kcal/mol more stable than 3 + 2 cycloaddition product **1b**, and the 2 + 1 cycloaddition species **3b** is only 7.3 kcal/mol less stable than **1b**. Therefore, on thermodynamic grounds, adduct **2b** is the expected intermediate in cycloadditions of sulfur dioxide and ethylene; indeed, such species have been established as intermediates in reactions of SO₂ with dienes by Vogel and co-workers.²⁷

CONCLUSIONS

Ozone and sulfur dioxide show very different reactivities in 1,3-dipolar cycloadditions. In particular, while O₃ undergoes facile addition to ethylene and acetylene, the barriers for the corresponding reactions of SO₂ are 40 kcal/mol larger. Moreover, the highly exothermic nature of the cycloaddition of ozone to C–C multiple bonds is not mimicked by SO₂, for which accurate CCSD(T) calculations predict reactions with ethylene and acetylene that are uphill by 14 and 4 kcal/mol, respectively. These stark differences in reactivity can be understood from a number of perspectives. In particular, we have shown that unfavorable interaction energies between SO₂ and an approaching dipolarophile, which emanate in part from the large charge separation in SO₂, paired with large distortion energies in the cycloaddition transition state lead to the large predicted reaction barriers. Alternatively, these differences in reactivity can be understood in terms of the enhanced stability of both the π - and σ -bonds of SO₂ compared to O₃, the reduced diradical character of SO₂ compared to O₃, or the increased HOMO–LUMO gap in SO₂ compared to O₃. At the CBS-QB3 and CCSD(T)/cc-pV(T+d)Z levels of theory, the 2 + 2 cycloadduct of SO₂ with ethylene (**3b**) is thermodynamically favored over the 1,3-dipolar cycloaddition product and is the expected intermediate in cycloadditions of SO₂ with ethylene.

ASSOCIATED CONTENT

Supporting Information. Cartesian coordinates and energies of all reported structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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