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Computational Studies of CO₂ Activation via Photochemical Reactions with Reduced Sulfur Compounds

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Abstract

Reactions between CO₂ and reduced sulfur compounds (RSC) - H₂S and CH₃SH - were investigated using ground and excited state density functional theory (DFT) and coupled cluster (CC) methods to explore possible RSC oxidation mechanisms and CO₂ activation mechanisms in the atmospheric environment. Ground electronic state calculations at the CR-CC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) level show proton transfer as a limiting step in the reduction of CO₂ with activation energies of 49.64 and 47.70 kcal/mol, respectively, for H₂S and CH₃SH. On the first excited state surface, CR-EOMCC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculations reveal that energies of <250 nm are needed to form H₂S-CO₂ and CH₃SH-CO₂ complexes allowing facile hydrogen atom transfer. Once excited, all reaction intermediates and transition states are downhill energetically showing either C-H or C-S bond formation in the excited state whereas only C-S bond formation was found in the ground state. Environmental implications of these data are discussed with a focus on tropospheric reactions between CO₂ and RSC, as well as potential for carbon sequestration using photocatalysis.

Introduction

Carbon dioxide (CO₂) is a very stable trace atmospheric gas and a major contributor to anthropogenic climate change. As CO₂ has been associated with possible climate change, there is a need to better understand its possible chemical transformations in the atmosphere and pathways for its sequestration. The monthly mean concentration of CO₂ in the atmosphere increased to 393 ppm in January 2012¹ as a result of a steady rise over the latter part of the last century.² The major sources of CO₂, natural carbon cycle aside, are industrial, e.g. power generation and heat production via fossil fuel combustion.³ Reduction of emission or fixation of emitted CO₂ into organic compounds is thus an important and interesting challenge in atmospheric and energy sciences.³ Fossil fuels account for about 85% of the world's commercial energy needs.⁴ Sharp reduction of CO₂ emissions would necessitate a sudden decrease of fossil fuel use, hardly feasible in the foreseeable future, especially with the increased availability of relatively cheap natural gas resources and more efficient extraction technologies.⁵ Thus, if energy extraction from fossil fuels is to be a bridge to renewable energy,⁶ fixation of the resulting CO₂ will have to be addressed.

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Supporting Information.

The Supporting Information includes Cartesian coordinates, electronic energies, and enthalpy corrections for all species considered in this study. This information is available free of charge via the Internet at <http://pubs.acs.org>

Several routes of CO₂ transformations via reactive capturing exist.³ In general, high energy starting materials, such as hydrogen, or low energy synthetic targets need to be used to overcome unfavorable CO₂ chemical transformation energetics. Of particular interest to us are compounds in a reduced state that could act as electron donors to CO₂. Reduced sulphur compounds (RSC), such as H₂S, COS, CH₃SH, CH₃SCH₃ and CS₂ are generated via natural and anthropogenic processes, such as assimilatory and dissimilatory reduction of sulfate as well as volcanic activities, petroleum and biomass burning (see Nunes et al.⁷ and references therein) and direct emission into the atmosphere. Total estimates of atmospheric sulfur emissions were reported at ~147 million tons of S a year⁸ with tropospheric concentrations of H₂S ranging from 5 to 1000 pptv.⁹ While typical concentrations of RSCs are 0.5–1.0 ppbv, proximity of the petrochemical complexes can increase this concentration several times.⁷ Organic molecules in the troposphere react with strong oxidizers, such as ozone (O₃), hydroxyl (OH) and nitrate (NO₃) radicals with the latter two having appreciable reaction rates.¹⁰ Estimated lifetimes of RSCs from the perspective of the reactivity with free radicals in the troposphere range anywhere from 0.4 hours to 55 days with that for H₂S of 3–87 h.¹⁰ The question remains as to how the reduced sulfur compounds and their chemical transformations affect the composition of the atmosphere.¹¹ Further, understanding the reactive interactions between CO₂ and H₂S with and without energizing radiation present is important not only from the atmospheric chemistry perspective, but also in addressing industrial sulfur containing gas, such as flue gas or landfill gas, utilization concomitantly with a possible CO₂ fixation.

Previous studies have shown that reactive interactions between another sulfur containing compound, carbonyl sulfide (OCS), and atmospheric aerosol surfaces proceeded via interaction with surface hydroxyl groups to yield H₂S and CO₂ gaseous products,^{12–17} with hydrolysis of carbon disulfide, CS₂, as a most effective chemical transformation step.^{18,19} To our knowledge, there have been no experimental or computational mechanistic studies performed to investigate CO₂ and H₂S reactions under environmentally relevant conditions. In this work, our emphasis is on using solar light to possibly drive CO₂ activation via reactions with RSC. It can be proposed that reactions of a fully oxidized carbon species, such as CO₂, with a reduced sulfur species, such as H₂S or CH₃SH, under certain conditions of energizing solar radiation might result in formation of the reactive intermediates and stable final products. Photoreduction of CO₂ by metal sulfide semiconductor photocatalysts in the presence of H₂S has been observed previously.²⁰ The photocatalytic reduction of CO₂, including processes that generate formic acid, methanol and methane, has recently been reviewed.²¹ The major challenge lies in overcoming the inherent stability of CO₂ and its unfavorable reduction potential.

In this work we present combined DFT and coupled cluster studies where we investigate mechanistic transformations of CO₂ and RSC molecules under simulated atmospheric conditions of solar light. Our focus is on two reaction mechanisms: hydrogen abstraction by one oxygen atom of CO₂ followed by S-C bond formation and hydrogen abstraction by the carbon atom of CO₂ with the final product involving S-O bond formation. The latter process can be regarded as forming formic acid and sulfur atom, and would show CO₂ molecule activation.

Theoretical methods

The long range corrected CAM-B3LYP density functional²² combined with the 6-311+G(2df,2p) basis set and ultrafine integration grid was used for all ground (S0) and first excited (S1) state optimizations and frequency calculations. The CAM-B3LYP functional has been shown to provide good results for excited state energies and geometries for a variety of systems, with accuracy comparable to more sophisticated and expensive correlated molecular orbital methods.^{23–28} Accurate coupled cluster single point energies

were determined at the CR-CC(2,3)^{29,30} level of theory for the S0 states and the CR-EOMCC(2,3)^{11,13,14} level of theory for the S1 states, using the same basis set. The CR-CC(2,3) level is also known as the CR-CCSD(T)_L level (rigorously size-extensive, completely renormalized, coupled cluster theory), while CR-EOMCC(2,3) is synonymous with CR-EOMCCSD(T)_L (rigorously size-extensive, completely renormalized, equation-of-motion coupled cluster theory). Minima and transition states were confirmed by zero and one imaginary vibrational frequency, respectively. Enthalpy corrections to 298 K were obtained at the CAM-B3LYP/6-311+G(2df,2p) level. Intrinsic reaction coordinate (IRC) calculations were performed to verify every transition state geometry.³¹ All reaction energy diagrams are constructed using enthalpy-corrected CR-CC(2,3) or CR-EOMCC(2,3) energies.

All density functional calculations were performed using Gaussian'09³² whereas all coupled cluster calculation utilized the 11 August 2011 (R1) release of the GAMESS program suite³³.

Results and discussion

Structure and energetics of CO₂, H₂S and CH₃SH molecules in ground (S0) and first excited (S1) electronic states

CO₂—CAM-B3LYP/6-311+G(2df,2p) geometries of the CO₂ molecule optimized in the S0 and S1 electronic states are shown in Figure 1 together with the corresponding frontier orbitals. Electronic transitions involved in the vertical excitation of the S0 state and those of the optimized S1 state are tabulated in Table 1. Optimized in the S0 state (¹Σ_g), CO₂ is of linear geometry with C=O bonds of 1.15 Å while optimization in the S1 state breaks linearity and elongates the C=O bonds to 1.23 Å. This bent state can serve as a precursor to a thermodynamically metastable CO₂⁻ ion,³⁴ provided electron donation is possible from an external source. Vertical excitation of the CO₂ molecule requires as much as 141 nm, as calculated using CR-EOMCC(2,3) method, with zero oscillator strengths for all three lowest energy transitions. This agrees well with the experimentally observed absorption edge of 160–170 nm^{35,36} with peaks at ~150, 130 and 110 nm due to the ¹Δ_u, ¹Π_g and ¹Σ_u⁺ states, respectively.³⁷ Dominant vertical excitations involve transitions from the nonbonding lone pairs on the oxygen atoms (HOMO-1 and HOMO, MOs 10 and 11) to the spherically-symmetric LUMO (MO 12) localized on the carbon atom.

Upon optimization, molecule in the lowest S1 state becomes bent, and the SOMOs are MO 10 (p_z orbitals on the oxygen atoms) and MO 12 (nonbonding sp² orbital on the carbon atom). Notably, the electronic transitions from the S1 state are now shifted toward lower energies with the first transition at 363 nm due to n → σ* transition and the second excitation having a modest oscillator strength of 0.017. It can be inferred from these results that photo-excited CO₂ should react with single-electron donors readily at the carbon atom, due to significant single-electron density and greatly reduced steric hindrance relative to ground-state, linear CO₂.

H₂S—The CAM-B3LYP/6-311+G(2df,2p) optimized of the H₂S molecule in the S0 electronic state shows C_{2v} symmetry with S-H bonds of 1.34 Å while optimization to the S1 electronic state results in one S-H bond being effectively broken (1.94 Å) (Figure 2). This is due to the fact that the strongest excitation, at 205 nm, is from excitation of the sulfur p_z lone pair into the symmetric S-H σ* MO. These results are in good agreement with the reported absorption of hydrogen sulfide, which begins at 250 nm with a maximum at ~187 nm.^{38,39}

Upon optimization in the S1 electronic state, the C_{2v} symmetry of the ground state is broken, and the SOMOs are the p_z orbital on sulfur and the σ^* MO involving the longer S-H bond. This is in excellent agreement with the observation that absorption in the near UV by H_2S yields H atoms and SH radicals, as confirmed by early flash photolysis experiments.⁴⁰ As with CO_2 , the absorption spectrum of hydrogen sulfide in the S1 state shifts to lower energy and the HOMO-LUMO transition (434 nm) is well within the range of energies in the visible part of the solar spectrum. Importantly, while in the S1 state, H_2S can be regarded as a donor of hydrogen atoms, provided a suitable acceptor molecule is present.

CH₃SH—The electronic properties and structure of CAM-B3LYP/6-311+G(2df,2p) optimized CH₃SH shown in Figure 3 and tabulated in Table 1 follow similar behavior as those of H_2S . In both the S0 and S1 geometries, the HOMO/SOMO is mainly comprised of the p_z MO on the sulfur atom with some contributions from C-H bonds. A very different LUMO orbital configuration, mostly due to the population of the S-H σ^* MO makes CH₃SH a possible facile hydrogen atom donor in the excited state. Notably, vertical excitation from the S0 state of CH₃SH has appreciable oscillator strengths, but the lowest excitation energy of 231 nm is outside of the visible region of the spectrum. This is in agreement with experimental vacuum and near UV spectra that show an absorption edge around 290 nm and peaks at 200 and 250 nm.⁴¹

Reactions between CO₂ and H₂S

Ground Electronic State—The CR-CC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) relative enthalpies of CO₂ and H₂S in the ground state surface are shown in Figure 4 and tabulated in Table 2. On the ground state surface, the reaction between CO₂ and H₂S begins with formation of a non-covalent complex (**RCH-S0**) with C_s symmetry. The C-S distance is found to be 3.50 Å and the complex is essentially isoenergetic with infinitely separated reactants. These distances are comparable to those between CO₂ carbon atom and CH₂S or C₄H₄S calculated by de Lange *et al.*⁴² using explicitly correlated CCSD(T)-F12a/VDZ-F12 methods. The reaction then proceeds through **TS1H-S0** to generate carbiothioic *O,S*-acid (**INT1H-S0**) via simultaneous formation of the C-S and O-H bonds. The activation enthalpy for this step is found to be 49.64 kcal/mol, and the product lays 16.62 kcal/mol above separated reactants. TS1H-S0 is almost isostructural and isoenergetic with the analogous transition state investigated previously in the hydrolysis of linear CS₂ which lies 38.98 kcal/mol above the separated reactants, as estimated using GGA methods.¹⁹ The proton transfer barrier is also comparable with that in the CO₂-H₂O system of 51.40 kcal/mol at the RI-SCS-MP2/aug-cc-pVTZ//B3LYP/6-311++G(d,p) level of theory, as found during the hydration of CO₂ to form carbonic acid.⁴³ A proton shift through **TS2H-S0** (relative enthalpy 48.02 kcal/mol) leads to formation of carbiothioic *O,O*-acid (**PH-S0**), which lays 20.02 kcal/mol above separated reactants.

The initial activation enthalpy of 49.6 kcal/mol indicates that the ground state reaction is prohibitively slow at room temperature, and this process is unimportant for the chemistry of CO₂ and H₂S at moderate temperatures. Furthermore, based on the endothermicity alone, this reaction will favor reactants by more than 4×10^{14} to one should the activation barrier be achieved. The ground state electronic surface can be disregarded as playing any significant role in the reaction between CO₂ and H₂S.

First Excited Singlet State—The S1 state energy landscape for the reaction between carbon dioxide and hydrogen sulfide is shown in Figure 5 with CR-EOMCC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) relative enthalpies tabulated in Table 3. Vertical excitation of C_s -symmetric reactant complex **RCH-S0** yields an A' singlet excited state 169.44 kcal/mol above separated reactants (**RCH-vS1**), with modest oscillator strength

of 8.08×10^{-3} . This excited state is dominated by an $n \rightarrow \sigma^*$ transition on the H_2S as shown in Figure 6. Optimization of this excited state destroys the original symmetry of the reaction complex, resulting in a structure (**RCH-S1**) that has a relative enthalpy 123.72 kcal/mol. The optimized excited state complex is nearly perfectly planar, and has a partially broken S-H bond (1.92 Å) oriented toward the carbon atom of the CO_2 . The remaining, shorter S-H bond (1.34 Å) is oriented toward one of the CO_2 oxygen atoms. Attempts to locate the converse situation, with the short H-S bond complexed to the carbon and long S-H bond complexed to the oxygen, failed and any attempted optimization resulted in further dissociation of the complex, indicating a repulsive interaction between the two species in that orientation. Similarly, no stationary point could be found on the S1 surface for a $\text{CO}_2:\text{H}_2\text{S}$ complex in any other orientation. Thus, initial photoexcitation of the reactant complex between CO_2 and H_2S forms an attractive complex only when the reactive hydrogen is oriented toward the carbon of the CO_2 . This is an important finding as it can be regarded as an initial step in CO_2 activation via C-H bond formation under solar irradiation.

The reaction then proceeds via two possible transition states (TS), TS1Ha-S1 and TS1Ha-S1, very close in energy at 135.52 and 131.22 kcal/mol, respectively. The former TS results in hydrogen atom transfer from H_2S to the carbon atom of CO_2 along a very flat surface resulting in formation of formyl and thiyl radicals. The later TS is for concerted transfer of both hydrogen atoms from H_2S , one to the carbon atom of CO_2 and the second to one of the oxygen atoms, resulting in formation of formic acid and sulfur atom, which will presumably rapidly intersystem cross to its triplet ground state. While the first pathway is kinetically favored by a 4.30 kcal/mol, the second pathway is thermodynamically favored by more than 30 kcal/mol. However, both pathways are likely given that all transition states, intermediates, and products lie below the energy of the vertically photoexcited complex **RCH-vS1**. Thus, reduction of CO_2 by photoexcited H_2S is predicted to result from transfer of one or two hydrogen atoms in a spontaneous fashion once the photoexcited complex is formed. This is in contrast to the S0 mechanisms outlined in Figure 4 with the final PH-S0 lying 20.02 kcal/mol above the reactant complex RCH-S0.

Reactions between CO_2 and CH_3SH

Ground Electronic State—The CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df,2p) reaction energy diagram for the ground state reaction between CO_2 and CH_3SH is shown in Figure 7 and relative enthalpies are tabulated in Table 4. A similar situation is found for the ground state reaction of methanethiol with CO_2 as for reaction of CO_2 with H_2S . An analogous reaction complex (**RCM-S0**) is found to be slightly more stable than separated reactants, with a C-S bond distance of 3.46 Å. Concomitant C-S and O-H bond formation proceeds through **TS1M-S0** (47.70 kcal/mol) to *S*-methyl *O*-hydrogen carbonothioate (**INT1Ma-S0**, 11.11 kcal/mol above separated reactants). A methyl shift from this intermediate forms *O*-methyl *O*-hydrogen carbonothioate (**PM-S0**) through **TS2M-S0**. This second transition state is 77.82 kcal/mol above separated reactants, and the final product has a relative enthalpy of 24.99 kcal/mol. Alternatively, methyl group transfer from S to O atoms yields **INT1Mb-S0**. This is 22.61 kcal/mol higher than separated reactants, which after a proton transfer (**TS2Mb-S0**) with a barrier of 51.91 kcal/mol results in the same structure as in Path A, **PMa-S0**. Two alternative structural complexes are also presented in Figure 7 as Path C in green; **PMc1-S0** with O-S bond formation is at 36.97 kcal/mol whereas **PMc2-S0**, is located higher at 58.76 kcal/mol.

It is quite clear that this reaction is even less favorable than the parent ground state reaction when considering the second step as the rate-determining step. It is possible to imagine a single-step reaction that stops at ester **INT1M-S0**. However, even the barrier for this process is prohibitive at moderate temperatures. As with the parent system, it is evident that the

ground state chemistry is unimportant when considering the reaction of methanethiol with CO₂.

First Excited Singlet State—The S1 state energy landscape of CO₂ reacting with methane thiol was also explored with the CR-EOMCC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) data shown in Figure 8 and tabulated in Table 5. Vertical excitation of **RCM-S0** complex shown in Figure 8 results in **RCM-vS1**, located at 153.30 kcal/mol. This is lower in energy by ~10 kcal/mol than the corresponding CO₂+H₂S excitation. The MOs plotted in Figure 9 show this excitation being primarily due to the $n \rightarrow \sigma^*$ transition described previously for methane thiol. Optimization of the CO₂+CH₃SH complex on the S1 surface resulted in minimum **RCM-S1**, wherein the S-H bond is now pointed directly at the carbon atom of the CO₂ moiety, with a C-H distance of 1.42 Å. This complex has a relative enthalpy of 127.03 kcal/mol and the SOMOs are dominated by the p_z orbital on sulfur, the SH σ^* and the nonbonding sp² orbital on carbon (Figure 9). Hydrogen-atom transfer then proceeds through **TS1M-S1** at 137.42 kcal/mol. In contrast to the analogous **TS1Hb-S1**, **TS1M-S1** is non-planar due to steric interactions between the methyl group on the CO₂ moiety. A significant S-O interaction also develops in **INT1M-S1** (127.98 kcal/mol) that is not seen in the parent system. However, the final products, methane thiyl and formyl radicals, are directly analogous to those observed with single hydrogen-atom transfer from H₂S. Similarly to the CO₂+H₂S case, once vertically excited to the RCM-vS1 complex, the remainder of the mechanism is energetically favorable thus favoring final product formation.

Conclusions and implications

Results presented here show very different transformation mechanisms of CO₂ reduction by reduced sulfur compounds, such as H₂S and CH₃SH, with and without the presence of ionizing radiation. In the absence of ionizing radiation, CO₂ reduction and consecutive activation is disfavored both kinetically and thermodynamically due to the high proton transfer barrier. The identity of the RSC is largely immaterial, with the most favored pathways for both H₂S and CH₃SH having thermal barriers of approximately 50 kcal/mol and endothermicities in excess of 20 kcal/mol.

However, both H₂S and CH₃SH absorb radiation in the UV range (<250 nm) of the solar spectrum, which is found in the higher levels of the atmosphere. Since excitation of CO₂ alone requires much more energy (140 nm), it can be proposed that CO₂+H₂S and CO₂+CH₃SH complexes will undergo reactive interactions in the upper levels of the atmosphere, facilitated by the $n \rightarrow \sigma^*$ excitation of reduced sulfur compounds followed by hydrogen atom donation to the carbon atom of CO₂. Again, the exact identity of the RSC is unimportant. While methane thiol has a lower vertical transition energy than H₂S, the difference is small and both are expected to rapidly transfer a hydrogen atom to CO₂ with no additional barrier required. While tropospheric RSC can get oxidized via reactions with hydroxyl, nitrate, peroxy and hydroperoxy radicals, their lifetimes (up to several days)¹⁰ can warrant additional reactions with CO₂ not previously explored. In addition, both H₂S and methane thiol have been identified in the interstellar medium (ISM).^{44,45} Given the high flux of ionizing radiation in the ISM, it is reasonable to propose that these species could act as reducing agents in the ISM through delivery of hydrogen atoms on electronically-excited potential energy surfaces. In total, this could result in a change of greenhouse atmospheric gas balance.

The reaction mechanisms described here also have implications in applied CO₂ sequestration and activation as they can be regarded as natural processes of removing carbon from the atmosphere via C-H bond formation. Our data suggest that UV radiation (<250 nm)

can induce direct CO₂ and RSC reactions with potentially recoverable formate and elemental sulfur (Figure 5). We calculated photoreaction rate constant, J, using deMore *et al.*⁴⁶ solar actinic flux data for 50, 40, 30 and 20 km altitudes by assuming that primary reactive species involved in S1 excitation is H₂S due to the hydrogen atom release and thus using H₂S absorption crosssection from Wu *et al.*⁴⁷ in 160–260 nm region as well as quantum yield of 1 from Kamra *et al.*⁴⁸ The calculated J rate constants were 2.03×10^{-4} , 1.2×10^{-4} , 2.7×10^{-5} and $5.2 \times 10^{-7} \text{ s}^{-1}$ for 50, 40, 30 and 20 km altitudes, respectively, corresponding to atmospheric lifetimes of about 1.4, 2.3, 10.36 and 534 days. Atmospheric reactions with OH species in troposphere warrants anywhere from 1.5 to 24 days lifetime depending on season for H₂S and shorter 2.6 to 80 hours for CH₃SH while that for reaction with NO₃ species– 69 hours for H₂S and 1 h for CH₃SH over continent.¹⁰ Due to the relatively high excitation energies of H₂S-CO₂ and CH₃SH-CO₂ complexes calculated in our work (169 and 153 kcal corresponding to 170 and 185 nm) these reactions are likely to proceed at the altitudes 50-20 km, e.g. upper troposphere lower stratosphere. Thus in the lower to mid troposphere the estimated H₂S and CH₃SH lifetime is too long to compete with NO₃ and OH species removal pathways and this removal pathway is much more feasible in the lower stratosphere.

While UV radiation induced processes are hardly cost effective, mixed metal oxide or sulfide photocatalysts, such as TiO₂ or n-Bi₂S₃²⁰ can facilitate electron transfer to the reacting CO₂ and H₂S molecules indirectly via semiconductor bandgap related transitions. It has previously been shown that CO₂ adsorbs on metal sites via several coordination geometries, including a bent geometry reminiscent of the S1 optimized geometry for CO₂ reported here.^{34,49} Our work shows that initial high energy irradiation (<250 nm) is needed as the first step of CO₂ reactions with RSC (Figures 5 and 7). It can be proposed that adsorption on semiconductor photocatalyst in a bent configuration would result in charge redistribution of CO₂ followed by more facile reaction with RSC. This approach could substitute for the low efficiency photocatalytic CO₂ photoactivation to methane methods while using RSC, commonly found as waste in industrial processes.

Finally, a prototype reactive system based on the data reported in this work can be envisioned of CO₂ photoactivation into commodity hydrocarbons using H₂S as a source of hydrogen atoms. While thermal activation has been shown not to lead to the formation formic acid, photolysis would yield formic acid and elemental sulfur as final products. Phase separation of those between liquid and vapor phases could be ensured via certain conditions of temperature and pressure and will be investigated further using a combination of quantum chemical and molecular dynamic simulations.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. CAM-B3LYP/6-311+G(2df, 2p) S₀ (left) and S₁ state (right) optimized geometries of CO₂. Relevant SOMOs involved in the first excited state are shown at each geometry. Isosurface parameter is 0.03.

Figure 2. CAM-B3LYP/6-311+G(2df, 2p) S₀ (left) and S₁ state (right) optimized geometries of H₂S. Relevant SOMOs involved in the first excited state are shown at each geometry. Isosurface parameter is 0.03.

Figure 3. CAM-B3LYP/6-311+G(2df, 2p) S0 (left) and S1 state (right) optimized geometries of CH₃SH. Relevant SOMOs involved in the first excited state are shown at each geometry. Isosurface parameter is 0.03.

Figure 4. CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction energy diagram of CO_2 and H_2S reactions optimized on the S0 surface. All enthalpies are referenced to those of separated CO_2 and H_2S and are shown in Table 2.

Figure 5. CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction energy diagram of CO₂ and H₂S reactions optimized on the S1 surface. All enthalpies are referenced to those of separated CO₂ and H₂S optimized in the S0 state and are shown in Table 3. Reaction path A (C-S bond formation mechanism) shown in red, whereas path B – (H-S bond formation mechanism) in green.

Figure 6. CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) and CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) calculated frontier orbitals of $\text{CO}_2 + \text{H}_2\text{S}$ complex optimized in the S0 (RCH-S0) and S1 (RCH-S1) states, respectively. Isosurface parameter was 0.03.

Figure 7. CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction energy diagram of CO_2 and CH_3SH reactions optimized on the S_0 surface. All enthalpies are referenced to those of separated CO_2 and CH_3SH and are shown in Table 4.

Figure 8.

CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) reaction energy diagram of CO_2 and CH_3SH reactions optimized on the S1 surface. All energies are referenced to those of separated CO_2 and CH_3SH optimized in the S0 state and are shown in Table 5.

Figure 9. CR-CC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) and CR-EOMCC(2,3)/6-311+G(2df, 2p)//CAM-B3LYP/6-311+G(2df, 2p) calculated frontier orbitals of $\text{CO}_2+\text{CH}_3\text{SH}$ complex optimized in S0 (RCM-S0) and S1 (RCMa-S1 and RCMb-S1) geometry, respectively. Isosurface parameter was 0.03.

Table 1

CAM-B3LYP/6-311+G(2df,2p) calculated parameters of CO₂, H₂S and CH₃SH optimized in S0 and S1 states

Excited state	Transitions involved	Dominant contribution coefficients	Excitation energy, nm	Oscillator strength(mixed), arb units
CO ₂ S0 state geometry (MO 11: HOMO; MO 12: LUMO)				
1	10→12	0.41039	141	0.0000
	11→12	0.55473		
	11→18	−0.10925		
2	10→12	0.41039	141	0.0000
	11→12	0.55473		
	11→18	−0.10925		
3	10→14	−0.27891	140	0.0000
	10→16	0.10597		
	10→17	−0.40024		
	11→13	0.27890		
	11→16	0.40024		
	11→17	0.10597		
CO ₂ S1 state geometry (MO 11: HOMO; MO 12: LUMO)				
1	10→12	0.70467	363	0.000
2	10→13	−0.15713	330	0.017
	11→12	0.68625		
3	11→13	0.69754	185	0.000
	11→17	−0.10661		
H ₂ S S0 state geometry (MO 9: HOMO; MO 10: LUMO)				
1	9→11	0.7042	205	0.000
2	9→10	0.69655	200	0.0910
	9→15	0.11637		
3	9→12	0.70316	160	0.000
H ₂ S S1 state geometry (MO 9: HOMO; MO 10: LUMO)				
1	9→10	0.70526	434	0.0019
2	9→11	0.66725	197	0.0501
	9→13	0.13445		
	9→15	0.17562		
3	7→10	0.66820	183	0.0474
	8→10	−0.21853		
CH ₃ SH S0 state geometry (MO 13: HOMO; 14: LUMO)				

Excited state	Transitions involved	Dominant contribution coefficients	Excitation energy, nm	Oscillator strength(mixed), arb units
1	13→14	0.60714	231	0.0059
	13→16	−0.10293		
	13→18	−0.27926		
	13→21	0.16852		
2	13→15	0.67866	204	0.0461
	13→22	0.10767		
3	13→14	0.25290	179	0.0206
	13→15	−0.10114		
	13→16	0.57123		
	13→18	0.15499		
	13→21	−0.25622		
CH ₃ SH S1 state geometry (MO 13: HOMO; MO 14: LUMO)				
1	13→14	0.70322	453	0.0007
2	13→15	0.60695	203	0.0073
	13→16	−0.22735		
	13→17	−0.19443		
	13→22	−0.13543		
	13→23	0.14218		
3	11→14	0.43372	198	0.1177
	12→14	0.54523		

Table 2

CR-CC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated CO₂ and H₂S reaction S0 optimized energies.

Species	E _{CR-CC(2,3)} Hartree	Enthalpy Corr. (298 K) Hartree	E _{total} Hartree ^a	E _{relative} kcal/mol
CO ₂	-188.32959	0.01545	-188.314132	-
H ₂ S	-398.92561	0.01902	-398.906585	-
Separated reactants (RH-S0)			-587.220718	0.00
Reactant complex (RCH-S0)	-587.25653	0.03594	-587.220595	0.08
TS1H-S0	-587.17412	0.03252	-587.141604	49.64
Carbothiolic O,S-acid(INT1H-S0)	-587.23336	0.03913	-587.194234	16.62
TS2H-S0	-587.18053	0.03634	-587.144190	48.02
Carbothiolic O,O-acid (PH-S0)	-587.23147	0.04265	-587.188817	20.02

^aCR-CC(2,3)/6-311+G(2df,2p) energy plus CAM-B3LYP/6-311+G(2df,2p) enthalpy correction to 298 K.

Table 3

CR-EOMCC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated CO₂ and H₂S reaction S1 optimized energies

Reaction coordinate	E _{CR-EOMCC(2,3)} Hartree	Enthalpy Corr. (298 K) Hartree	E _{total} , Hartree ^a	E _{relative} , kcal/mol
Reactant complex, vertical (RCH-vS1)	-586.98663	0.035939	-586.950692	169.44
Reactant complex, optimized (RCH-S1)	-587.05455	0.030984	-587.023565	123.72
Path A				
TS1Ha-S1	-587.04161	0.030984	-587.011602	131.22
INT1Ha-S1	-587.04152	0.031886	-587.009633	132.46
Formyl + thiyl radicals (PHa-S1)	-587.059380 ^b	0.032409	-587.059380	101.24
Path B				
TS1Hb-S1	-587.03488	0.030129	-587.00475	135.52
Formic acid + sulfur (S1) (PHb-S1)	-587.098586 ^b	0.040567	-587.058019	102.10
Formic acid + sulfur (T) (PHb-T)	-587.148263 ^b	0.040567	-587.107696	70.92

^a CR-EOMCC(2,3)/6-311+G(2df,2p) energy plus CAM-B3LYP/6-311+G(2df,2p) enthalpy correction to 298 K

^b CR-CC(2,3)/6-311+G(2df,2p) energy

Table 4

CR-CC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated CO₂ and CH₃SH reaction S0 optimized energies

Species	E _{CR-CC(2,3)} Hartree	Enthalpy Corr. (298 K) Hartree	E _{total} , Hartree ^a	E _{relative} , kcal/mol
Path A				
CO ₂	-188.329585	0.015453	-188.314132	-
CH ₃ SH	-438.15709	0.050921	-438.106169	-
Separated Reactants (RM-S0)			-626.4203015	0.00
Reactant Complex (RCM-S0)	-626.488019	0.067829	-626.420190	0.07
TS1M-S0	-626.408565	0.064276	-626.344289	47.70
INT1Ma-S0	-626.473125	0.070523	-626.402602	11.11
TS2Ma-S0	-626.364865	0.068578	-626.296287	77.82
PMa-S0	-626.452731	0.072254	-626.380477	24.99
Path B				
INT1Mb-S0	-626.453271	0.069000	-626.384271	22.61
TS2Mb-S0	-626.403665	0.066087	-626.337578	51.91
Path C				
PMc1-S0	-626.430688	0.069303	-626.361385	36.97
PMc2-S0	-626.394280	0.067623	-626.326657	58.76

^a CR-CC(2,3)/6-311+G(2df,2p) energy plus CAM-B3LYP/6-311+G(2df,2p) enthalpy correction to 298 K

Table 5

CR-EOMCC(2,3)/6-311+G(2df,2p)//CAM-B3LYP/6-311+G(2df,2p) calculated CO₂ and CH₃SH reaction S1 optimized energies

Reaction coordinate	$E_{\text{CR-EOM}(2,3)}$ Hartree	Enthalpy Corr. (298 K) Hartree	E_{total} Hartree ^a	E_{relative} kcal/mol
Reactant Complex, vertical (RCM-vS1)	-626.243822	0.067829	-626.175993	153.30
Reactant Complex, optimized (RCM-S1)	-626.280955	0.063084	-626.217871	127.03
TS1M-S1	-626.264063	0.062752	-626.201311	137.42
INT1M-S1	-626.284303	0.067950	-626.216353	127.98
Formyl + methanethiyl radicals (PMA-S1)	-626.328638	0.062931	-626.265707	97.01

^aCR-EOMCC(2,3)/6-311+G(2df,2p) energy plus CAM-B3LYP/6-311+G(2df,2p) enthalpy correction to 298 K