

Organocatalysis

Hydrogen Sulfide Induced Carbon Dioxide Activation by Metal-Free Dual Catalysis

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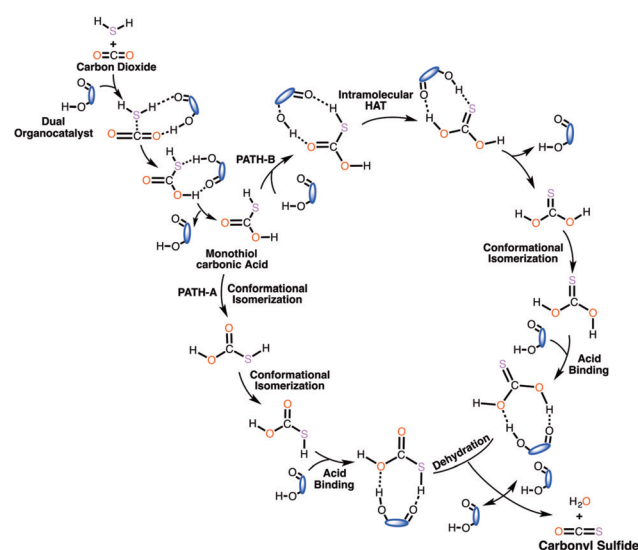
Abstract: The role of metal free dual catalysis in the hydrogen sulfide (H₂S)-induced activation of carbon dioxide (CO₂) and subsequent decomposition of resulting monothiolcarbonic acid in the gas phase has been explored. The results suggest that substituted amines and monocarboxylic type organic or inorganic acids via dual activation mechanisms promote both activation and decomposition reactions, implying that the judicious selection of a dual catalyst is crucial to the efficient C–S bond formation via CO₂ activation. Considering that our results also suggest a new mechanism for the formation of carbonyl sulfide from CO₂ and H₂S, these new insights may help in better understanding the coupling between the carbon and sulfur cycles in the atmospheres of Earth and Venus.

Carbon dioxide (CO₂) emissions into the atmosphere are increasing at an alarming rate with every passing year.^[1] According to a recent report,^[2] CO₂ levels in the atmosphere have already crossed the 400 ppm mark, and continue to rise relentlessly. Because of its involvement in global warming, there is an immediate need to better understand the chemistry of CO₂ and identify sequestration or other processes for its removal. Utilizing CO₂ as a renewable source of carbon is an attractive strategy for a sustainable, low-carbon society. This has led to significant interest in developing CO₂ as a C₁ feedstock for carbon–carbon bond formation and carbon–heteroatom functionalization reactions in chemical synthesis.^[3] However, the considerable thermodynamic stability of CO₂ renders it relatively inert as a chemical reactant.^[4] Therefore, low-energy catalytic activation of CO₂ is highly desirable.

Several transition-metal catalysts have been employed to transform CO₂ into valuable commodity chemicals.^[5] Metal-free catalysis presents an alternative approach for CO₂ capture under ambient reaction conditions.^[6] The potential of N-heterocyclic carbenes,^[7,8] frustrated Lewis pairs (FLPs),^[9–13] and various other main-group catalysts^[14] for CO₂ activation has been recently established. FLPs contain sterically hindered Lewis acid and Lewis base that makes them catalytically interesting.^[15] For example, Grimme, Stephan, and Erker et al. have re-

ported the usefulness of phosphine–borane FLPs in CO₂ activation.^[9a] Piers and co-workers have used B(C₆H₅)₃ and amines to convert CO₂ into methane with silanes.^[10] Fontaine and co-workers have established the catalytic effect of R₂PC₆H₄B(O₂C₆H₄) in the hydroboration of CO₂ en route to methanol formation.^[11] Zhu and An have recently examined the CO₂ sequestration with a series of amidophosphoranes at the DFT level and suggested the role of the interplay of the ring strain and the *trans* influence in determining the reactivity, which provides a new platform for the design of FLPs for the CO₂ capture.^[12] In a subsequent study, An and Zhu performed a comparative analysis of the sequestration of CO₂ and CS₂ using the P/N-based FLPs and provided useful mechanistic insights into the factors controlling the sequestration.^[13]

Herein we report the role of metal-free dual organocatalysis in the CO₂ insertion into the S–H bond of hydrogen sulfide (H₂S) in the gas phase that leads to the unprecedented C–S bond formation. The mechanistic beauty of dual organocatalysis lies in the fact that the coexistence of acidic and basic sites in a catalyst (an organic or inorganic acid) causes the concerted activation of the electrophile CO₂ and nucleophile H₂S, and results in the low-energy reaction (Scheme 1). To the best of our knowledge, C–S bond formation in the presence of a metal-free dual catalyst has yet to be achieved.



Scheme 1. Proposed mechanism for the gas-phase formation of carbonyl sulfide by carbon dioxide insertion into the H–S bond of hydrogen sulfide under metal-free dual organocatalysis.

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The catalytic role of explicit water (H_2O) molecules in lowering the barrier of atmospherically important hydrogen atom transfer (HAT)-based reactions is well-documented.^[16] However, there are other species that can catalyze the HAT reactions in atmosphere. In fact, it is now increasingly becoming clear that organic acids, which are present in significant amounts in the Earth's atmosphere,^[17–19] can catalyze such reactions much more efficiently.^[20–25] For example, the role of acid catalysis in influencing the energetics of various atmospheric processes such as sulfuric acid (H_2SO_4) forming hydrolysis of SO_3 ,^[20,21] hydrolysis of ketene,^[23] and tautomerization of the Criegee intermediate^[24,25] has been recently reported. In the Venusian atmosphere, the inorganic acid, H_2SO_4 is expected to be present in appreciable amounts^[26] and may play a role in CO_2 activation.

H_2S is an important sulfur compound that is emitted into the atmosphere by natural and anthropogenic activities, with fossil fuel burning as its main source.^[27] The insertion of CO_2 into H_2S provides a new mechanism for the formation of carbonyl sulfide ($\text{O}=\text{C}=\text{S}$) in the troposphere (Scheme 1), where it is one of the most abundant sulfur compounds.^[27] This reaction also holds immense significance for the atmosphere of Venus, where CO_2 is the largest constituent (96.5%) and the formation mechanism of OCS continues to remain unclear.^[26]

Herein, we propose a new mechanism for the OCS formation that takes advantage of H_2S -induced CO_2 activation by metal-free dual catalysis (Scheme 1), and support its feasibility with gas-phase electronic structure calculations. All calculations were performed using the Gaussian 09^[28] software package. The reaction of H_2S with CO_2 leading to monothiolcarbonic acid (HCO_2SH), and subsequent decomposition of HCO_2SH resulting in OCS and H_2O in the gas phase, were extensively examined by means of first-principles quantum chemical calculations. Both reactions were calculated with and without catalysts. There are two possible decomposition pathways for HCO_2SH (Scheme 1). We have considered both in the present work. The catalysts studied in the present work were H_2S , H_2O , hydrogen fluoride (HF), hydrogen chloride (HCl), ammonia (NH_3), methylamine (CH_3NH_2), dimethylamine ($(\text{CH}_3)_2\text{NH}$), HCO_2SH , $\text{H}_2\text{CO}_2\text{S}$, HCOOH , and H_2SO_4 . For analyzing the HCO_2SH -induced catalysis, we have considered three possible modes of catalysis: $-\text{COOH}$, $-\text{COSH}$, and $-\text{CSOH}$. HCO_2SH is capable of undergoing intramolecular HAT, which results in the *cis,cis* conformer. We have used a different notation, $\text{H}_2\text{CO}_2\text{S}$, to represent that *cis,cis* conformer, which has no hydrogen atom directly bonded to sulfur atom. Considering that HCO_2SH and $\text{H}_2\text{CO}_2\text{S}$ can exist in multiple conformers depending upon the relative orientation of OH and/or SH moieties (Supporting Information, Schemes S1 and S2), we have only explored the catalysis that is due to their *cis,cis* and *cis,trans* conformations in our calculations because the *cis,cis* conformer is the most stable and the *cis,trans* form is involved in the sacrificial reactions. The equilibrium and transition-state structures were fully optimized using the M06-2X^[29] level of density functional theory and the augmented correlation-consistent triplet zeta basis set, aug-cc-pVTZ.^[30] The energetics of these reactions was

further refined using the coupled-cluster single and double substitution method with a perturbative treatment of triple excitations (CCSD(T))^[31] and the aug-cc-pVTZ basis set. Specifically, the zero-point-corrected CCSD(T)/aug-cc-pVTZ electronic energies at the M06-2X/aug-cc-pVTZ-optimized geometries have been used. For all of the reactions, the M06-2X/aug-cc-pVTZ calculated vibrational frequencies were used to estimate the zero-point correction for the reactants, products, transition states, and intermediates. The presence of zero or single imaginary frequency was used to identify all the stationary points as minima or transition states.

In the first step, the nucleophilic addition of H_2S across the $\text{C}=\text{O}$ bond in the CO_2 electrophile occurs. The reaction is initiated with the formation of a weak van der Waals association complex, Int_1 between H_2S and CO_2 , which has a nominal binding energy of $0.9 \text{ kcal mol}^{-1}$ (Figure 1). Int_1 then transforms into *trans,cis*-monothiolcarbonic acid (HCO_2SH) via 4-center transition state, $\text{TS}_{\text{H}_2\text{S}}$. The reaction has an effective barrier of $48.7 \text{ kcal mol}^{-1}$, measured relative to Int_1 , and is endothermic by $15.8 \text{ kcal mol}^{-1}$. Though the hydrolysis of CO_2 has been extensively explored,^[32–35] the reaction of CO_2 with H_2S has not received any attention until recently when Baltrusaitis et al. examined the gas-phase reaction between CO_2 and reduced sulfur compounds, H_2S and CH_3SH , using ground- and excited-state density functional theory and coupled-cluster methods.^[36] Our calculated barrier of $48.7 \text{ kcal mol}^{-1}$ and an endothermicity of $15.8 \text{ kcal mol}^{-1}$ are in reasonable agreement with their CR-CC(2,3)/6-311 + G(2df,2p)//CAM-B3LYP/6-311 + G(2df,2p) calculated values of 49.6 and $16.6 \text{ kcal mol}^{-1}$, respectively. Additional calculations suggest that the barrier to nucleophile addition across the $\text{C}=\text{O}$ bond of CO_2 is tunable depending upon the nature of a nucleophile, that is, the amine addition is more favorable than the H_2O or methanol addition, which, in turn, is preferred over the H_2S addition (Supporting Information, Figure S1). Significant barrier tuning for a nucleophilic addition reaction between XO_2 ($\text{X}=\text{C}, \text{N}, \text{or S}$) and H_2S is also achievable by judiciously changing the central atom in XO_2 ; sulfur dioxide, SO_2 , shows more reactivity than nitric oxide, NO_2 , which, in turn, does better than CO_2 (Supporting Information, Figure S2).

The gas-phase CO_2 activation in the presence of various catalysts with single activation site is also examined here. The effect of catalysis on the reaction is significant; for HF-, HCl-, and H_2O -catalyzed reactions, Int_1 has a binding energy of 3.7 – $4.5 \text{ kcal mol}^{-1}$, and the effective barrier is lowered to 34.0 – $35.4 \text{ kcal mol}^{-1}$. Int_2 is a postreaction complex in which *trans,cis*- HCO_2SH and the catalyst are H-bonded and now mediates the reaction. Int_2 is 2.6 – $6.9 \text{ kcal mol}^{-1}$ more stable than the separated products. The activation effect of N-based reagents, NH_3 , CH_3NH_2 , and $(\text{CH}_3)_2\text{NH}$ is even higher. The $\text{Int}_{1,\text{S}}$ and $\text{Int}_{2,\text{S}}$ are 4.3 – $6.3 \text{ kcal mol}^{-1}$ and 10.8 – $15.3 \text{ kcal mol}^{-1}$ more stable than separated reactants and products, respectively. The relatively larger stability of Int_2 implies that the endothermic formation of *trans,cis*- HCO_2SH can be achieved by judicious selection of catalysis. Interestingly, the calculated barrier for the CO_2 insertion correlates with the nature of amine; the barrier for the unsubstituted amine, NH_3 , is $25.2 \text{ kcal mol}^{-1}$, which is lowered to $19.8 \text{ kcal mol}^{-1}$ upon single methyl substitution

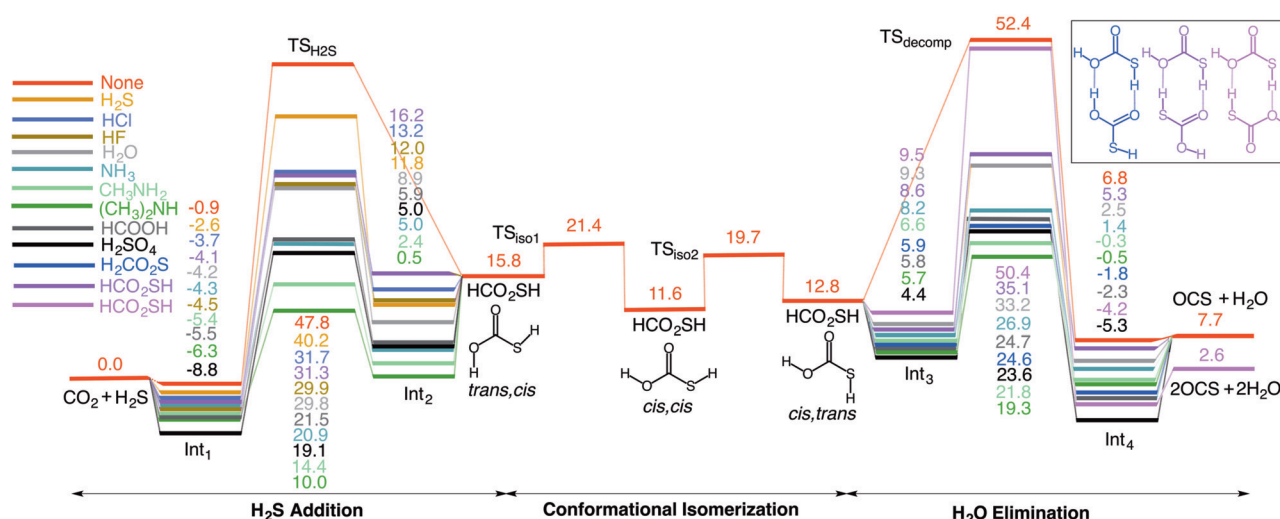


Figure 1. Calculated reaction profile for the formation of carbonyl sulfide via PATH-A, which involves insertion of carbon dioxide into the H–S bond of hydrogen sulfide, conformational isomerization in *trans,cis*-monothiolcarbonic acid (HCO_2SH), and decomposition of *cis,trans*- HCO_2SH . Inset: the dimer conformations of HCO_2SH that lead to the decomposition of *cis,trans*- HCO_2SH . The zero point-corrected electronic energies [kcal mol^{-1}] are calculated at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level.

(CH_3NH_2), and $16.3 \text{ kcal mol}^{-1}$ upon double methyl substitution ($(\text{CH}_3)_2\text{NH}$).

The effect of catalysts with dual activation site, HCOOH and H_2SO_4 on the gas-phase CO_2 insertion is investigated. The presence of carbonyl- and hydroxyl-type functionalities in these catalysts allows them to cause the concerted activation of CO_2 and H_2S by forming two point H-bonding interactions in a stereoeffective manner (Scheme 1). The effective barriers for the HCOOH and H_2SO_4 reactions are 27.0 and $27.9 \text{ kcal mol}^{-1}$, 21.7 and $20.8 \text{ kcal mol}^{-1}$ lower than that for the uncatalyzed reaction. These acid catalysts outperform HF , HCl , and H_2O , but turn out to be less effective than NH_3 , CH_3NH_2 , and $(\text{CH}_3)_2\text{NH}$.

The prospect of the CO_2 insertion being an autocatalytic process is explored by calculating the reaction profiles for the H_2S - and *cis,cis*- HCO_2SH -catalyzed gas-phase reactions. The H_2S reaction has an effective barrier of $42.8 \text{ kcal mol}^{-1}$, which is $5.9 \text{ kcal mol}^{-1}$ lower than that for the uncatalyzed reaction, but at least $7.4 \text{ kcal mol}^{-1}$ higher than that calculated with any monofunctional catalyst. On the other hand, the catalytic effect of *cis,cis*- HCO_2SH is appreciably higher; the effective barrier is $7.4 \text{ kcal mol}^{-1}$ lower than that for the H_2S reaction. It is interesting to note that though the catalysis mechanism of the *cis,cis*- HCO_2SH reaction is similar to that for the HCOOH and H_2SO_4 reactions, the effect of *cis,cis*- HCO_2SH on the reaction barrier is less pronounced. This is attributed to the lesser polarity of the S–H bond in *cis,cis*- HCO_2SH compared to the O–H bond in HCOOH and H_2SO_4 .

There are two mechanistic choices for converting *trans,cis*- HCO_2SH into OCS : 1) PATH-A, which involves direct decomposition, and 2) PATH-B, which involves intramolecular HAT followed by subsequent decomposition (Scheme 1). We calculated and compared both pathways to determine the most efficient route for the OCS formation. It is important to mention that HCO_2SH is produced in a *trans,cis* form, which is an inactive conformation for the direct decomposition (Figure 1). This

necessitates a double conformational change in the *trans,cis* form to produce the catalytically active *cis,trans* conformer. The calculations suggest that these conformational switches in the gas phase are moderately expensive, with barriers of 5.6 and $8.1 \text{ kcal mol}^{-1}$ (Figure 1). Moreover, *cis,trans*- HCO_2SH is $3.0 \text{ kcal mol}^{-1}$ more stable than the *trans,cis* analogue. From the *cis,trans* conformer, the OCS forming dehydration occurs, which involves the concerted cleavage of C–OH and S–H bonds. The uncatalyzed dehydration step is $5.1 \text{ kcal mol}^{-1}$ exothermic and has a barrier of $39.6 \text{ kcal mol}^{-1}$ (Figure 1). Overall, the gas-phase formation of OCS is $7.7 \text{ kcal mol}^{-1}$ endothermic, and the decomposition of *cis,trans*- HCO_2SH is the rate-limiting step of the reaction.

The barrier to dehydration is lowered to $23.9 \text{ kcal mol}^{-1}$ in the presence of a H_2O molecule (Figure 1). HCOOH and H_2SO_4 acids further lower the dehydration barrier by about $5.0 \text{ kcal mol}^{-1}$. Notably, Int_3 and Int_4 in the acid-catalyzed reactions are significantly more stable than those in the H_2O -catalyzed one, implying that acid catalysis is capable of tuning the energetics of the decomposition reaction. The effect of HCO_2SH on its own decomposition is also examined. The calculated barriers for the autocatalytic reactions are 18.7 and $26.5 \text{ kcal mol}^{-1}$ for the –COOH-based and –COSH-based catalysis, respectively. The larger barrier for the –COSH-based catalysis is due to lower polarity of S–H bond. The barrier of $40.9 \text{ kcal mol}^{-1}$ for the noncatalytic reaction is significantly higher than any of the catalytic reactions. The catalytic effect of substituted amines on the decomposition is larger than any of acid catalysts; the effective barrier of $13.6 \text{ kcal mol}^{-1}$ for the $(\text{CH}_3)_2\text{NH}$ -catalyzed reaction is $5.3 \text{ kcal mol}^{-1}$ lower than that calculated for the HCOOH -catalyzed reaction.

The PATH-B for the OCS formation from *trans,cis*- HCO_2SH initiates with the intramolecular HAT from thiol sulfur to carbonyl oxygen. This HAT reaction leads to the *cis,cis*- $\text{H}_2\text{CO}_2\text{S}$. The uncatalyzed HAT in the gas phase involves a significant barrier of

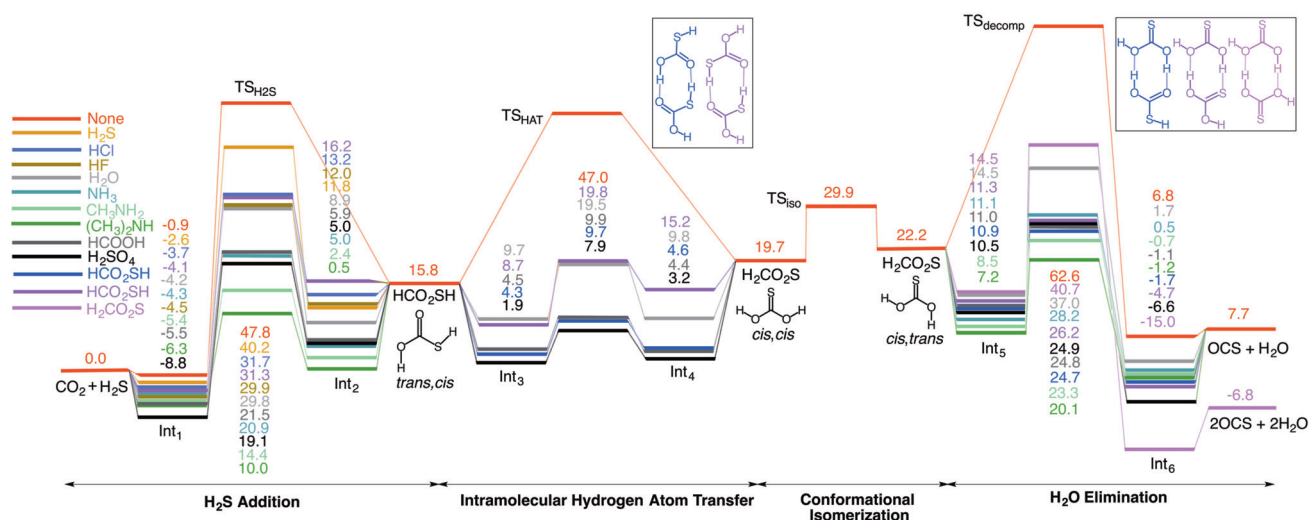


Figure 2. Calculated reaction profile for the formation of carbonyl sulfide via PATH-B, which involves insertion of carbon dioxide into the H–S bond of hydrogen sulfide, intramolecular hydrogen atom transfer (HAT) in *trans,cis*-HCO₂SH, conformational isomerization in *cis,cis*-monothiolcarbonic acid (H₂CO₂S) and decomposition of *cis,trans*-H₂CO₂S. Insets: the dimer conformations of HCO₂SH and H₂CO₂S that assist in the intramolecular HAT and the decomposition of *cis,trans*-H₂CO₂S. The zero point-corrected electronic energies [kcal mol⁻¹] are calculated at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level.

31.2 kcal mol⁻¹ and is 3.9 kcal mol⁻¹ endothermic. Baltrusaitis et al. have recently reported a similar barrier of 31.4 kcal mol⁻¹ and an endothermicity of 3.4 kcal mol⁻¹ for this intramolecular HAT reaction in the gas phase.^[36] Our calculations reveal that the reaction becomes appreciably favorable under H₂O or acid catalysis. Interestingly, the HAT barrier is tuned to the extent that the formation of *cis,cis*-H₂CO₂S from *trans,cis*-HCO₂SH is found to be barrierless under acid catalysis. Just like acids, *cis,cis*-HCO₂SH also makes its intramolecular HAT barrierless when the catalysis is –COOH-based (Figure 2). The –COSH-based autocatalytic HAT reaction is relatively less effective, as it involves a noticeable barrier of 11.1 kcal mol⁻¹.

The *cis,cis*-H₂CO₂S must be converted into the *cis,trans* form to allow the subsequent decomposition into OCS and H₂O (Figure 2). This conformational change in the gas phase involves a moderate barrier of 10.3 kcal mol⁻¹ and could be achieved under atmospheric conditions because the *cis,cis*-H₂CO₂S in the acid-catalyzed HAT reaction is produced as a H-bonded complex, Int₄, which has at least 14.0 kcal mol⁻¹ binding energy except in the –COSH-based autocatalytic reaction. This extra energy stored in Int₄ may drive the formation of *cis,trans*-H₂CO₂S.

The *cis,trans*-H₂CO₂S then dehydrates into OCS and H₂O. The gas-phase dehydration is 14.5 kcal mol⁻¹ exothermic and has a barrier of 40.4 kcal mol⁻¹. Though the barrier to the dehydration of the *cis,trans*-H₂CO₂S is 0.8 kcal mol⁻¹ higher than that for the *cis,trans*-HCO₂SH decomposition, the reaction is 9.4 kcal mol⁻¹ more exothermic, which should have a positive effect on the preceding conformational isomerization in the *cis,cis*-H₂CO₂S. The effect of H₂O or acid catalysis on the decomposition of *cis,trans*-H₂CO₂S is enormous. H₂O lowers the barrier for the H₂CO₂S dehydration by 22.5 kcal mol⁻¹. Acids HCOOH and H₂SO₄ produce greater catalysis, causing an additional barrier lowering of about 9.0 kcal mol⁻¹. Substituted amines produce optimum catalysis in the decomposition of *cis,trans*-H₂CO₂S;

the effective barrier for the (CH₃)₂NH-catalyzed reaction is 0.9 kcal mol⁻¹ lower than that calculated for the HCOOH-catalyzed reaction.

The scope for the self-assisted reaction is assessed by exploring the gas-phase decomposition from three dimer conformations. As far as autocatalysis is concerned, the HCO₂SH-mediated reaction has a 3.0 kcal mol⁻¹ lower barrier than that for the H₂CO₂S-mediated reaction and produces an acid-like catalytic effect on the reaction. The dehydration barrier for the noncatalytic reaction is larger than any of the autocatalytic reactions owing to the additional cleavage of a C–OH bond. Interestingly, the effect of catalysis on the decomposition of the *cis,trans*-H₂CO₂S is marginally greater than that on the *cis,trans*-HCO₂SH decomposition. This is due to the fact that *cis,trans*-H₂CO₂S has larger dipole moment ($\mu = 3.2$ D) than that of *cis,trans*-HCO₂SH ($\mu = 2.3$ D), which makes the catalytic cleavage of O–H bond in H₂CO₂S easier compared to that of S–H bond in HCO₂SH. The comparative analysis of PATH-A and PATH-B implies that the PATH-A would be favored in the absence of any catalysis due to relatively lower barrier for the rate-limiting decomposition of *cis,trans*-HCO₂SH. However, under acid or amine catalysis influence, both pathways might become equally likely because the intramolecular HAT in *trans,cis*-HCO₂SH becomes barrierless and the subsequent conformational isomerization of *cis,cis*-H₂CO₂S benefits from its coupling to the exothermic decomposition of the *cis,trans*-H₂CO₂S under catalysis.

The main conclusions are that substituted amines or organic and inorganic acids exert significant catalysis on both the gas-phase CO₂ activation step and the subsequent rate-limiting decomposition of *cis,trans*-HCO₂SH or *cis,trans*-H₂CO₂S. This implies that the insertion of H₂S into CO₂ can lead to OCS and H₂O for little energy cost within an effective dual organocatalysis scheme. The ability of these reagents to lower the energetics for the CO₂+H₂S reaction by inducing a stereoeffective proton wire makes them potentially interesting catalysts for

CO₂ activation. Such a mechanism may play a key role in improving our understanding regarding the coupled carbon and sulfur cycles in the atmospheres of Earth and even Venus.

Keywords: atmospheric chemistry · CCSD(T) theory · CO₂ activation · organocatalysis · potential energy profiles

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