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Catalytic effect of water and formic acid on the reaction of carbonyl sulfide with dimethyl amine under tropospheric conditions†

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CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculations were performed on the addition of amines [i.e. ammonia (NH₃), methyl amine (MA), and dimethyl amine (DMA)] to carbonyl sulfide (OCS), followed by transfer of the amine H-atom to either the S-atom or O-atom of OCS, assisted by a single water (H₂O) or a formic acid (FA) molecule, leading to the formation of the corresponding carbamothioic S- or O acids. For the OCS + NH₃ and OCS + MA reactions with or without the H₂O or FA, very high barriers were observed, making these reactions unfeasible. Interestingly, the barrier heights for the OCS + DMA reaction, involving H-atom transfer to either the S-atom or O-atom of OCS and assisted by a FA, were found to be $-4.2 \text{ kcal mol}^{-1}$ and $-3.9 \text{ kcal mol}^{-1}$, respectively, relative to those of the separated reactants. The barrier height values suggest that FA lowers the reaction barriers by $\sim 28.4 \text{ kcal mol}^{-1}$ and $\sim 35.9 \text{ kcal mol}^{-1}$ compared to the OCS + DMA reaction without the catalyst. Rate coefficient calculations were performed on the OCS + DMA reaction both without a catalyst, and assisted by a H₂O and a FA molecule using canonical variational transition state theory and small curvature tunneling at the temperatures between 200 and 300 K. The rate data show that the OCS + DMA + FA reaction proceeds through H-atom transfer to the S-atom of OCS, which was found to be $\sim 10^3$ – 10^{11} and 10^3 – 10^{10} times faster than the OCS + DMA and OCS + DMA + H₂O reactions, respectively, in the studied temperature range. For the same temperature range, the rate of the OCS + DMA + FA reaction was found to be $\sim 10^8$ – 10^{16} and 10^3 – 10^{12} times faster than the OCS + DMA and OCS + DMA + H₂O reactions in which H-atom transfer to the O-atom of OCS occurred. This suggests that the OCS + DMA reaction that is assisted by FA is more efficient than the H₂O assisted reaction. In addition, the rate of the OCS + DMA + FA reaction was found to be $\sim 10^{10}$ times slower than the OCS + •OH reaction at 298 K. This clarifies that the OCS + DMA + FA reaction may be feasible for the atmospheric removal of OCS under night-time forest fire conditions when the OCS and DMA concentrations are high and the •OH concentration is low.

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1. Introduction

Carbonyl sulfide (OCS) is well-known as a long-lived sulfur-containing atmospheric gas. It is considered to be a major S-carrier with an average mixing ratio of ~ 0.4 – 0.5 parts per billion (ppb) in the earth's troposphere,^{1–6} and is believed to contribute

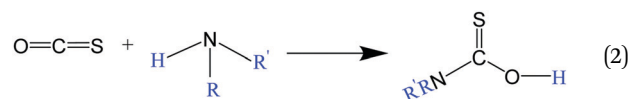
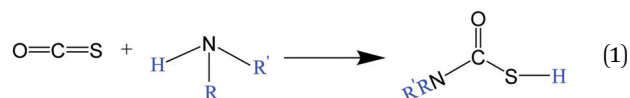
sulfur mainly to the stratospheric aerosol layer.^{7,8} This has an adverse effect on stratospheric ozone and significantly impacts radiative balance of the atmosphere.⁹ Various natural and anthropogenic sources are responsible for the OCS presence in the atmosphere.^{10,11} Primary emitters of OCS include soils, trees, marshes, plant roots, manure, microorganisms, biomass burning, volcanos, hot springs, and oceans.^{12,13} Importantly, oxidation of atmospheric dimethyl sulfide (Me₂S) and carbon disulfide (CS₂) generate up to one half of the terrestrial OCS as a secondary product in the global sulfur cycle.¹³ Anthropogenic emissions which occur as a consequence of aluminum production, coal and automobile fuel burning, and industrial desulfurization, also contribute to global OCS production, albeit to a much lower extent.¹⁴ Measurement of the OCS concentration in Antarctic ice cores suggests that its levels have risen over the past 350 years as a consequence of industrialization.⁶

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† Electronic supplementary information (ESI) available: Tables S1–S11 present the optimized geometries of all the stationary points, calculated total electronic energies including zero-point energy corrections, vibrational frequencies and rotational constants, and imaginary frequencies of various TSs as discussed in the text at the M06-2X level, relative energies of complexes at various levels, temperature dependent unimolecular and effective rate coefficients using the CVT/SCT method, equilibrium constants. Fig. S1 and S2 present the optimized geometries for the reaction of OCS + NH₃ and OCS + MA, Fig. S3–S8 present the IRC plots for the OCS + DMA, OCS + DMA + H₂O, and OCS + DMA + FA reactions. See DOI: 10.1039/d1cp00180a

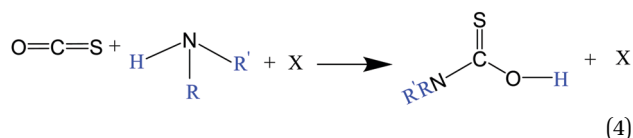
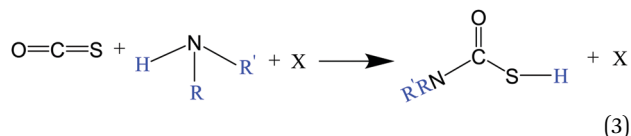
The number of studies on removal processes of OCS from the atmosphere are limited. The major sink for this molecule is reported to be loss to vegetation through hydrolysis by the enzymes primarily involved in photosynthesis.^{15–17} Another atmospheric loss process is its reaction with OH radicals. Various studies of the $\text{OCS} + \bullet\text{OH}$ reaction using experimental^{18–21} and *ab initio* quantum chemistry methods^{22–26} have been reported. Atkinson *et al.*¹⁸ determined the rate coefficient for the $\text{OCS} + \bullet\text{OH}$ reaction using a flash photolysis resonance fluorescence technique and found an upper limit rate coefficient of $7.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K. Using the same experimental technique, Kurylo determined the rate coefficient for the $\text{OCS} + \bullet\text{OH}$ reaction to be $(5.66 \pm 1.21) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K.¹⁹ The study of this reaction by Cox and Sheppard²⁰ using relative rate experiments furnished an upper limit rate coefficient of $4.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Ravishankara *et al.*²¹ determined an upper limit rate coefficient at 298 K of $8.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using a laser/flash photolysis resonance fluorescence technique. Using a similar experimental technique, Leu and Smith,²⁷ Wahner and Ravishankara,²⁸ and Cheng and Lee²⁹ determined room temperature rate coefficient values for the $\text{OCS} + \bullet\text{OH}$ reaction to be $(0.6 \pm 0.4) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $(1.92 \pm 0.25) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; and $(2.0 \pm 0.8) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. Subsequently, using the relative rate technique combined with computational calculations, Schmidt *et al.*³⁰ reported the rate coefficient to be $(5.3 \pm 3.6) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and 700 Torr.³⁰ The aforementioned rate coefficient results indicate that the $\text{OCS} + \bullet\text{OH}$ reaction is slow, and that its atmospheric lifetime with respect to $\bullet\text{OH}$ is from 2–4 years. Studies of additional atmospheric gas phase removal processes for OCS are required in order to learn more about the fate of this molecule in the atmosphere, since studies of alternative sinks for this molecule are very limited.

Amines are important atmospheric compounds due to their involvement in the formation of secondary organic aerosols (SOA) in the troposphere^{31–34} and formation of amino acids in interstellar space.^{35–37} The major sources of amines in the earth's atmosphere occur from both biogenic and anthropogenic emissions. These include motor vehicle exhaust, biomass burning, animal husbandry, industrial processes, and marine organisms.^{31,32} Atmospheric concentrations of amines such as methyl amine (CH_3NH_2 , MA), and dimethyl amine ($(\text{CH}_3)_2\text{NH}$, DMA) are typically found in the range of parts per trillion by volume (pptv), to tens of pptv,^{38–40} while ammonia (NH_3) is typically at the tens of parts per billion by volume (ppbv) level.^{41,42} Several recent studies have shown that addition of amines to certain atmospherically important species results in formation of a new C–N bond, followed by H-atom transfer to yield various products, and this has been shown to be an important removal pathway.^{43–48} In this work, we investigated the possible atmospheric removal of OCS through its gas phase reaction with the three amines NH_3 , MA, and DMA. In principle, these reactions can proceed by one of two possible pathways, given in eqn (1) and (2).



In eqn (1) and (2), R and R' can be either –H or –CH₃, and both reactions proceed through nucleophilic addition of the N-atom to the C-atom of OCS. The subsequent step involves transfer of the amine H-atom to either the S-atom (eqn (1)) or the O-atom (eqn (2)) of OCS, leading to formation of the corresponding carbamothioic S- and O- acids respectively as final products.

It is well-known that water is the third most abundant species present in the atmosphere with a concentration of $\sim 4.0 \times 10^{17} \text{ molecules cm}^{-3}$ at 298 K under 100% RH conditions. Yet another compound that has been found to be present in significant amounts is formic acid, which has been observed at the ~ 500 ppt level. Several studies have reported that water and formic acid form complexes with various atmospherically relevant volatile organic compounds (VOCs), volatile organo-sulfur compounds (VOSCs), and free radicals.^{49–56} In addition, a number of studies have shown that single water and FA molecules successfully act as catalysts in reducing the energy barriers for several reactions, which in turn significantly influences reaction rates at atmospherically relevant temperatures and pressures.^{55–57} Therefore, we also investigated the single water (H_2O) and single formic acid (HC(O)OH , FA) molecule assisted catalysis of the reactions presented in eqn (1) and (2) (*i.e.* eqn (3) and (4)), where X represents a catalyst ($\text{X} = \text{H}_2\text{O}$ or FA).



The energetics of the reactions presented in eqn (1)–(4) were computed by quantum chemistry calculations. The results were then used to determine the rate coefficients with canonical variational transition state theory^{58,59} combined with small curvature tunneling.⁶⁰ This study also explored the effect of single water and single FA molecules on the reaction barrier heights, when compared to the reactions in the absence of a catalyst. The results from these investigations can provide insight into the reaction mechanism, energies, and reaction rates for amine addition reactions with OCS to form the corresponding carbamothioic acids in the troposphere.

2. Computational methods

High level *ab initio* quantum chemistry calculations were performed for the reaction of OCS with three amines in the absence and presence of a water and a FA as catalysts using the

Gaussian-16 program suite.⁶¹ Molecular geometry optimization of isolated reactants, pre-reactant complexes (PRCs), two body complexes (RCs), transition states (TSs), post-reactive complexes (PCs) and individual products involved in the present work was performed using the M06-2X functional⁶² in conjunction with the augmented correlation consistent polarized valence-triple-zeta basis set (aug-cc-pVTZ).^{63,64} The M06-2X method is a global hybrid meta generalized gradient approximation with 54% HF exchange, and it provides good results in calculations of thermochemistry and rate coefficients.^{55,65–68} Normal mode frequency calculations were performed at the same level of theory. All TSs were located using the OPT = TS routine of the Gaussian-16 program. The reactants, products, PRCs, RCs, and PCs all involved positive normal mode frequencies, and the TSs involved single imaginary frequencies. The optimized molecular geometries represent the minima on the respective potential energy surfaces (PESs). Intrinsic reaction coordinate (IRC) calculations⁶⁹ were performed at the M06-2X/aug-cc-pVTZ level for the TSs optimized at the same level of theory to confirm that the predicted TSs were connected with the corresponding PRCs and PCs. To improve the calculated energies for all the geometries optimized at the M06-2X/aug-cc-pVTZ level, we performed single point energy calculations at the CCSD(T) level with the same aug-cc-pVTZ basis set. Various studies have tested the combination of CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ (designated as CCSD(T)//M06-2X) level calculations for determining the energetics and rate coefficients for various atmospherically important reactions and it has been shown to be a reasonably accurate method.^{70–72} The results obtained from T1 diagnostic calculations at the CCSD(T)/aug-cc-pVTZ level suggest that multi-reference character is not significant in the studied reactions.

The basis set superposition error (BSSE) might lead to increased stability of the pre-reactant complexes compared to the separated adducts. In this work, no BSSE corrections were performed because BSSE is difficult to treat in a uniform manner for all the complexes representing all the possible reaction paths. In addition, barrier heights for all the reaction paths were found to be ~ 5 –45 kcal mol^{−1} above that of the pre-reactive complexes. This indicates that the reaction barriers are large and hence the BSSE should be relatively small for the pre-reactive complexes studied here.

3. Results and discussion

3.1. Stationary points on the PESs and energetics

3.1.1. The reaction of OCS with amines in the absence of a catalyst. The present calculations were performed to determine the energies of OCS with three different amine addition reactions. The PES diagrams for the three selected amines, (NHRR', where R and R' refer to either -H or -CH₃), namely NH₃, MA, and DMA involved in each addition pathway with OCS leading to the formation of the corresponding carbamothioic acid (see eqn (1) and (2)) are shown in Fig. 1a and b. All the stationary point energies on the PESs were calculated at the CCSD(T)//M06-2X level. In Fig. 1a, the symbols RC1, TS1, and P₁ correspond

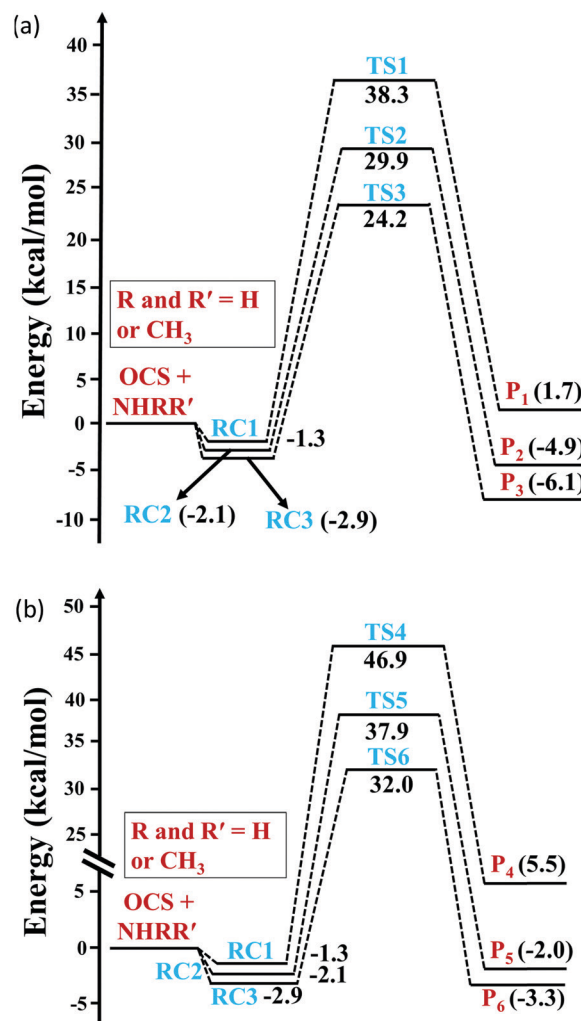


Fig. 1 Potential energy surface diagrams for: (a) addition of three different amines to OCS followed by transfer of the amine hydrogen atom to the S-atom of OCS; and (b) addition of three different amines to OCS followed by transfer of the amine hydrogen atom to the O-atom of OCS. The energies of all minima on the PESs were obtained at the CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ level. The symbols RC_n (*n* = 1–3), TS_n (*n* = 1–6), and P_n (*n* = 1–6) refer to dimer complexes, transition states, and carbamothioic acid products, respectively.

to the OCS + NH₃ reaction; RC2, TS2, and P₂ correspond to the OCS + MA reaction; and RC3, TS3, and P₃ correspond to the OCS + DMA reaction, respectively.

The computed total electronic energies (E_{total}) and zero-point energy (ZPE) corrected electronic energies [$E_{\text{total}}(\text{ZPE})$] for all the minima obtained at the M06-2X and CCSD(T) levels are given in Table S1 (ESI†). The geometries, imaginary frequencies of the various TSs, vibrational frequencies and rotational constants obtained in this work are provided in Tables S2–S5 (ESI†). The optimized geometries of the reactants, RCs, PRCs, TSs, PCs, and products involved in the OCS + NH₃ and OCS + MA reactions both without a catalyst and assisted by H₂O and FA single molecules are shown in Fig. S1 and S2 of the ESI†. The PES profile shown in Fig. 1a suggests that each amine addition with OCS proceeds *via* the formation of a two-body

complex (RC1, RC2, and RC3) that is below the separated reactants. The formed RCs proceed to the corresponding three transition states (TS1, TS2, and TS3) *via* addition of the amine N-atom to the C-atom of OCS, forming a new C–N bond, followed by simultaneous transfer of the amine's hydrogen to the S-atom of OCS (see Fig. S1, ESI†). The barrier heights for the formation of TS1, TS2, and TS3 were computed to be 38.3, 29.9, and 24.2 kcal mol^{−1}, respectively, above that of the starting reactants. The formed TSs proceed further to form carbamothioic acid (P₁), *N*-methyl carbamothioic acid (P₂), and *N,N*-dimethyl carbamothioic acid (P₃), as products from the reaction of ammonia, MA and DMA respectively. The barrier heights presented in Fig. 1a indicate that the reaction of OCS with DMA to form P₃ is the most energetically feasible, as it was found to differ from those of the OCS + NH₃ and OCS + MA reactions by ~14.1 and ~5.7 kcal mol^{−1} respectively.

Next, calculations were performed for the reaction of each of the three amines with OCS, in which nucleophilic addition of nitrogen to carbon is followed by H-atom transfer to the O-atom of OCS to form the corresponding products. The PES diagram obtained at the CCSD(T)//M06-2X level is shown in Fig. 1b. The symbols RC1, TS4, and P₄ correspond to the OCS + NH₃ reaction; RC2, TS5, and P₅ correspond to the OCS + MA reaction; and RC3, TS6, and P₆ correspond to the OCS + DMA reaction. From this figure, each addition reaction pathway proceeds *via* formation of RC1, RC2, and RC3, which then form the corresponding transition states (TS4, TS5, and TS6) with barrier heights of 46.9, 37.9, and 32.0 kcal mol^{−1}, respectively. The TSs lead to the formation of the corresponding products (P₄, P₅, and P₆), respectively. The barrier heights shown in Fig. 1b indicate that the DMA + OCS reaction *via* TS6 is lower than those of the OCS + NH₃ (TS4) and OCS + MA (TS5) reactions by ~15.0 and ~6.0 kcal mol^{−1} respectively. Overall, the calculated barrier heights for the OCS + amine addition reactions were found to be very high (see Fig. 1a and b) and require high energies. While the reaction that proceeds by eq. 1 is more energetically favorable, neither of the reactions in eqn (1) or (2) is feasible under normal tropospheric temperatures and pressures.

3.1.2. The reaction of OCS with NH₃ assisted by a single H₂O molecule. Water (H₂O) and formic acid (FA) are two important and ubiquitous molecules that are present in significant amounts in the troposphere.^{43,55,56} Both have been previously shown to catalyze various atmospherically important reactions.^{43,44,48,55,56} Therefore, we investigated the energetics of the three amine addition reactions at the CCSD(T)//M06-2X level to determine the potential impact of single H₂O and FA molecules on the atmospheric removal of OCS. First, the OCS + NH₃ reaction assisted by a single H₂O molecule and leading to the formation of the corresponding carbamothioic acid was investigated. The obtained PES profiles involving all the minima for the two possible reaction channels (*i.e.* eqn (3) and (4)) are shown in Fig. 2, which illustrates the addition of ammonia to the C-atom of OCS, followed by H-atom transfer to the S- or O-atom of OCS, assisted by a single H₂O molecule. The energies indicated on the PES profiles were calculated at the CCSD(T)//M06-2X level.

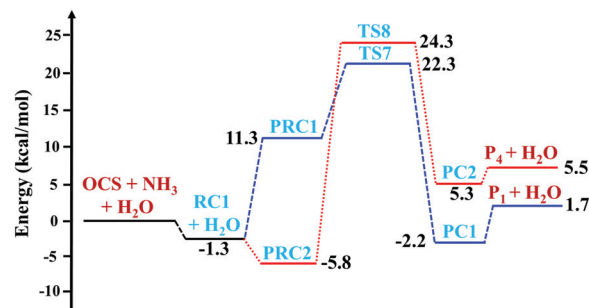


Fig. 2 The CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of ammonia to OCS followed by migration of the H-atom to either the S-atom (indicated using blue lines) or O-atom (indicated using red lines) of the OCS catalyzed by a single H₂O molecule to form carbamothioic acid. The symbols RC1; PRC1 and PRC2; TS7 and TS8; PC1 and PC2; and P₁ and P₄ refer to the OCS·NH₃ dimer complex, the pre-reactant complexes, the transition states, the post-reactive complexes, and the carbamothioic acid products, respectively.

Fig. 2 shows that the OCS + NH₃ reaction catalyzed by a H₂O molecule initially leads to the formation of a OCS·NH₃ complex (RC1) with a binding energy of ~1.3 kcal mol^{−1} below that of the starting reactants. The complex then reacts with a H₂O molecule leading to the formation of a pre-reactant complex (PRC1) at 11.3 kcal mol^{−1} above the starting reactants. The reaction further proceeds from PRC1 to the formation of a transition state (TS7) with a barrier height of 22.3 kcal mol^{−1} relative to that of the starting reagents. The structure of TS7 shows addition of the N-atom of ammonia to the C-atom of OCS, followed by transfer of the ammonia H-atom to the O-atom of H₂O and then to the S-atom of OCS (see Fig. S1, ESI†). TS7 continues through formation of the post reactive complex (PC1) and then to the formation of carbamothioic acid (P₁) + H₂O as final products. The barrier height for this reaction reveals that in comparison to the reaction in the absence of water, the presence of a single H₂O molecule reduces the transition state energy by ~16.0 kcal mol^{−1}.

The reaction of ammonia addition to the C-atom of OCS followed by H-atom migration to the O-atom of OCS, assisted by a single H₂O molecule is also shown in Fig. 2. This pathway also occurs *via* OCS·NH₃ (RC1) + H₂O leading to the formation of a pre-reactant complex (PRC2) with an energy of ~5.8 kcal mol^{−1} below that of the starting reactants. The formed PRC2 proceeds to a transition state (TS8) with a barrier height of 24.3 kcal mol^{−1} with respect to the starting OCS + NH₃ + H₂O reactants. The formation of TS leads to the corresponding post-reactive complex (PC2) and then on to form carbamothioic acid (P₄) + H₂O as final products (see Fig. 2). Therefore, the presence of a H₂O molecule lowers the barrier height for the OCS + NH₃ reaction by ~22.6 kcal mol^{−1} when compared to the value of the same reaction in the absence of the catalyst.

3.1.3. The reaction of OCS with NH₃ assisted by a single HC(O)OH molecule. We next examined the impact on the barrier height of the OCS + NH₃ reaction of a single FA molecule in place of a H₂O molecule. The obtained PES profiles involving all the minima are shown in Fig. 3. Like the OCS + NH₃ + H₂O

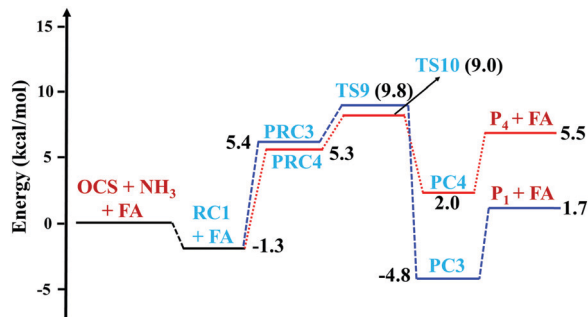


Fig. 3 The CCSD(T)/aug-cc-pVTZ//M0-62X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of ammonia to OCS followed by migration of the H-atom to either the S-atom (indicated with blue lines) or O-atom (indicated with red lines) of OCS catalyzed by a formic acid to form carbamothioic acid. The symbols RC1; PRC3 and PRC4; TS9 and TS10; PC3 and PC4; and P₁ and P₄ refer to the OCS·NH₃ dimer complex, the pre-reactant complexes, the transition states, the post-reactive complexes, and the carbamothioic acid products, respectively.

reaction, OCS + NH₃ + FA also progresses through the OCS·NH₃ + FA reaction, leading to formation of a pre-reactant complex (PRC3). The reaction then proceeds further to form a transition state (TS9) with a barrier height of ~9.8 kcal mol⁻¹ above that of the starting reactants. The TS structure for this reaction suggests that it proceeds *via* addition of the ammonia N-atom to the C-atom of OCS, followed by transfer of the ammonia H-atom to the O-atom of FA and then to the S-atom of OCS. The reaction continues by forming a post reactive complex (PC3), which then undergoes unimolecular decomposition to form final products (P₁ + FA). Similarly, the addition of ammonia to OCS followed by H-atom shift towards the O-atom of OCS assisted by a FA molecule, also proceeds from the OCS·NH₃ + FA reaction to form the corresponding pre-reactant complex (PRC4), and then to transition state (TS10) with a corresponding barrier height of ~9.0 kcal mol⁻¹. The reaction then proceeds further *via* PC4 and then to final products (P₄ + FA). The results for the reaction of OCS + NH₃ assisted by FA suggest that a FA molecule reduces the barrier height for the H-atom transfer to the S-atom of OCS by ~28.5 kcal mol⁻¹ and ~12.5 kcal mol⁻¹ compared to the uncatalyzed and single H₂O catalyzed reactions. For the alternative reaction path (H-atom transfer to the O-atom of OCS), a single FA molecule reduces the barriers by ~37.9 kcal mol⁻¹ and ~15.3 kcal mol⁻¹ compared to the uncatalyzed and water catalyzed reactions.

3.1.4. The reaction of OCS with CH₃NH₂ assisted by a single H₂O molecule. We also performed calculations on the addition of MA to OCS that is followed by H-atom transfer from the -NH₂ moiety to either the S- or O-atoms of OCS, assisted by a single H₂O molecule. The PESs involving all the minima for the two possible reaction paths obtained at the CCSD(T)//M06-2X level are shown in Fig. 4, which illustrates the energies of the minima on the PESs that were estimated relative to the OCS + MA + H₂O starting reagents.

The OCS + MA + H₂O reaction initially proceeds through the bimolecular interaction of OCS·MA (RC2) with a H₂O molecule,

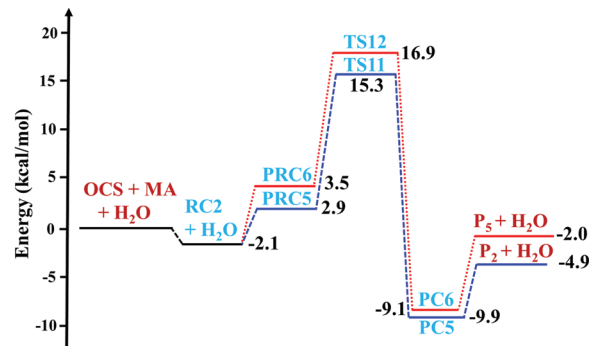


Fig. 4 The CCSD(T)/aug-cc-pVTZ//M0-62X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of methyl amine to OCS followed by migration of the H-atom to either the S-atom (indicating using blue lines) or O-atom (indicating using red lines) of OCS catalyzed by a single H₂O molecule to form *N*-methyl carbamothioic acid. The symbols RC2; PRC5 and PRC6; TS11 and TS12; PC5 and PC6; and P₂ and P₅ refer to the OCS·MA complex, the pre-reactant complexes, the transition states, the post reactive complexes, and the *N*-methyl carbamothioic acid products, respectively.

leading to the formation of a pre-reactant complex (PRC5). The reaction then progresses to the formation of a transition state (TS11) from PRC5 with a barrier height of ~15.3 kcal mol⁻¹ relative to that of the starting reactants. TS11 advances to formation of PC5 and then on to form *N*-methyl carbamothioic acid (P₂) + H₂O as products. Similarly, the alternative pathway proceeds from OCS·MA (RC2) + H₂O to form PRC6, which then proceeds to form TS12 with a barrier height of ~16.9 kcal mol⁻¹ above that of the starting reactants. A post reactive complex (PC6) forms from TS12 which then leads to the formation of P₅ + H₂O as products. Therefore, for the MA + OCS reaction that proceeds *via* addition of the amine N-atom followed by H-atom transfer from nitrogen to either the S- or O-atom of OCS, a single H₂O molecule reduces the barrier heights by ~14.6 kcal mol⁻¹ and ~21 kcal mol⁻¹ respectively when compared to the same reaction in the absence of water.

3.1.5. The reaction of OCS with CH₃NH₂ assisted by a single HC(O)OH molecule. Similarly, calculations on the OCS + MA reaction assisted by a single FA molecule were performed at the CCSD(T)//M06-2X level, and the observed PES is shown in Fig. 5. The reaction begins with the OCS + MA + FA reactants by forming a OCS·MA (RC2) dimer, which then reacts with FA, leading to the formation of two different pre-reactant complexes (PRC7 and PRC8) with binding energies of ~3.3 and ~4.1 kcal mol⁻¹ below that of the starting reactants. PRC7 and PRC8 further proceed to form the corresponding transition states (TS13 and TS14) with barrier heights of 1.0 kcal mol⁻¹ and -0.2 kcal mol⁻¹ respectively when compared to that of the starting reactants. These two pathways further proceed to form the corresponding post-reactive complexes (PC7 and PC8) and then on to form the corresponding bimolecular products P₂ + FA and P₅ + FA respectively. Therefore, the present calculations suggest that a single FA reduces the TS barrier heights for the H-atom transfer to the S-atom of OCS by ~29 kcal mol⁻¹ and ~14.3 kcal mol⁻¹, whereas for H-atom transfer to the O-atom of

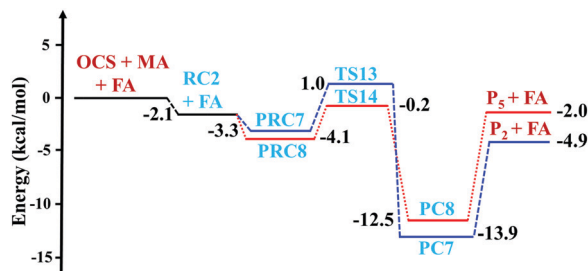
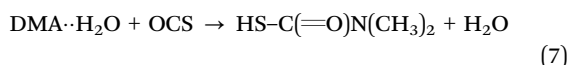
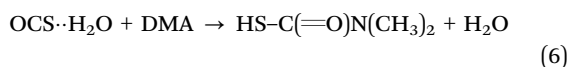
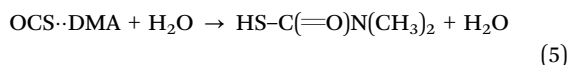


Fig. 5 The CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of methyl amine to OCS followed by migration of the H-atom to either the S-atom (indicated with blue lines) or O-atom (indicated with red lines) of OCS catalyzed by a formic acid to form *N*-methyl carbamothioic acid. The symbols RC2; PRC7 and PRC8; TS13 and TS14; PC7 and PC8; and P₂ and P₅ refer to the OCS·MA dimer complex, the pre-reactant complexes, the transition states, the post reactive complexes, and the *N*-methyl carbamothioic acid products, respectively.

OCS, the barrier heights are reduced by ~ 38.1 kcal mol⁻¹ and 17.1 kcal mol⁻¹ compared to the values for OCS + MA in the absence and presence of a single water molecule respectively.

3.1.6. The reaction of OCS with CH₃NH assisted by a single H₂O molecule. We next examined the OCS + DMA reaction catalyzed by a single water molecule. The simultaneous collision of three reactant species (OCS, DMA, and H₂O) in the atmosphere is not feasible. Therefore, the OCS + DMA + H₂O reaction was considered as taking place through the collision of a dimer complex with another reactant species. Accordingly, the OCS + DMA + H₂O reaction was modelled to occur *via* the three bimolecular reaction paths given in eqn (5)–(7).



The CCSD(T)//M06-2X calculated PES profiles for the OCS + DMA + H₂O reaction are shown in Fig. 6 and the optimized geometries of all the stationary points at the M06-2X/aug-cc-pVTZ level are shown in Fig. 7. The DMA·H₂O + OCS reaction (eqn (7)) was not considered further because the structure of the DMA·H₂O complex (RC6) (see Fig. 7) clearly shows the existence of a hydrogen bond between the N-atom of DMA and the H-atom of H₂O, which blocks the N-atom from attacking the C-atom of OCS. Therefore the OCS + DMA + H₂O reaction could in principle proceed *via* eqn (5) and (6). The PES for the OCS + DMA + H₂O reaction shows that the reaction initially forms three different dimer complexes: OCS·DMA (RC3); OCS·H₂O (RC4); and OCS·H₂O (RC5) with binding energies below that of the starting reactants of ~ 2.9 , ~ 1.0 , and ~ 1.2 kcal mol⁻¹ respectively. The formed OCS·DMA (RC3) and OCS·H₂O (RC4) dimer complexes further react with H₂O and DMA reactants. The reaction then leads to formation of a pre-reactant complex (PRC9)

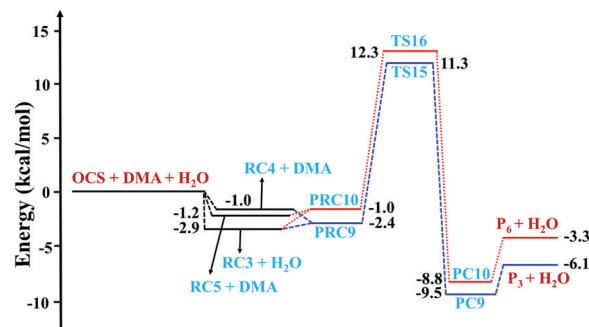
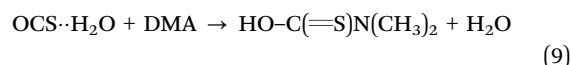
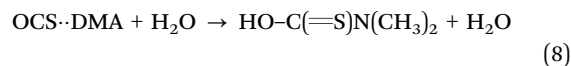


Fig. 6 The CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of dimethyl amine to OCS followed by migration of the H-atom to either the S-atom (indicated using blue lines) or O-atom (indicated using red lines) of OCS catalyzed by a single water molecule to form *N,N*-dimethyl carbamothioic acid. The symbols RC3, RC4 and RC5; PRC9 and PRC10; TS15 and TS16; PC9 and PC10; and P₃ and P₆ refer to the dimer complexes, the pre-reactant complexes, the transition states, the post reactive complexes, and the *N,N*-dimethyl carbamothioic acid products, respectively.

with an energy of ~ 2.4 kcal mol⁻¹ below that of the initial starting reactants. PRC9 proceeds through the addition of DMA to OCS followed by transfer of the H-atom of the -NH moiety to the S-atom of OCS with help of a H₂O molecule to form a transition state (TS15) with a barrier height of ~ 11.3 kcal mol⁻¹. The reaction further advances through the formation of a post-reactive complex (PC9) and then on to the formation of *N,N*-dimethyl carbamothioic acid (P₃) + H₂O products.

Similarly, the OCS·DMA (RC3) + H₂O and the OCS·H₂O (RC5) + DMA reaction channels lead to the formation of alternative reaction paths (eqn (8) and (9)).



The PES profiles and the corresponding energies of all the minima on the PES are presented in Fig. 6. The OCS·DMA (RC3) + H₂O and OCS·H₂O (RC5) + DMA reaction channels proceed to form an alternative pre-reactant complex (PRC10), which then leads to a transition state (TS16) with a barrier height of ~ 12.3 kcal mol⁻¹ above that of the starting reactants. The structure of TS16 suggests that the DMA addition to OCS is followed by transfer of the H-atom to the O-atom of OCS with the assistance of a water molecule. The reaction continues to form PC10, which then undergoes decomposition to form P₆ + H₂O as products. Therefore, when a single water molecule is involved in the OCS + DMA reaction, which proceeds through an H-atom shift to the S-atom of OCS, the barrier height is reduced by ~ 12.9 kcal mol⁻¹, whereas in the case of H-atom transfer to the O-atom of OCS, it is reduced by ~ 20 kcal mol⁻¹ compared to the value for the uncatalyzed OCS + DMA reaction.

3.1.7. The reaction of OCS with (CH₃)₂NH assisted by a single HC(O)OH molecule. Calculations were also performed on DMA + OCS assisted by a FA, and leading to the formation of

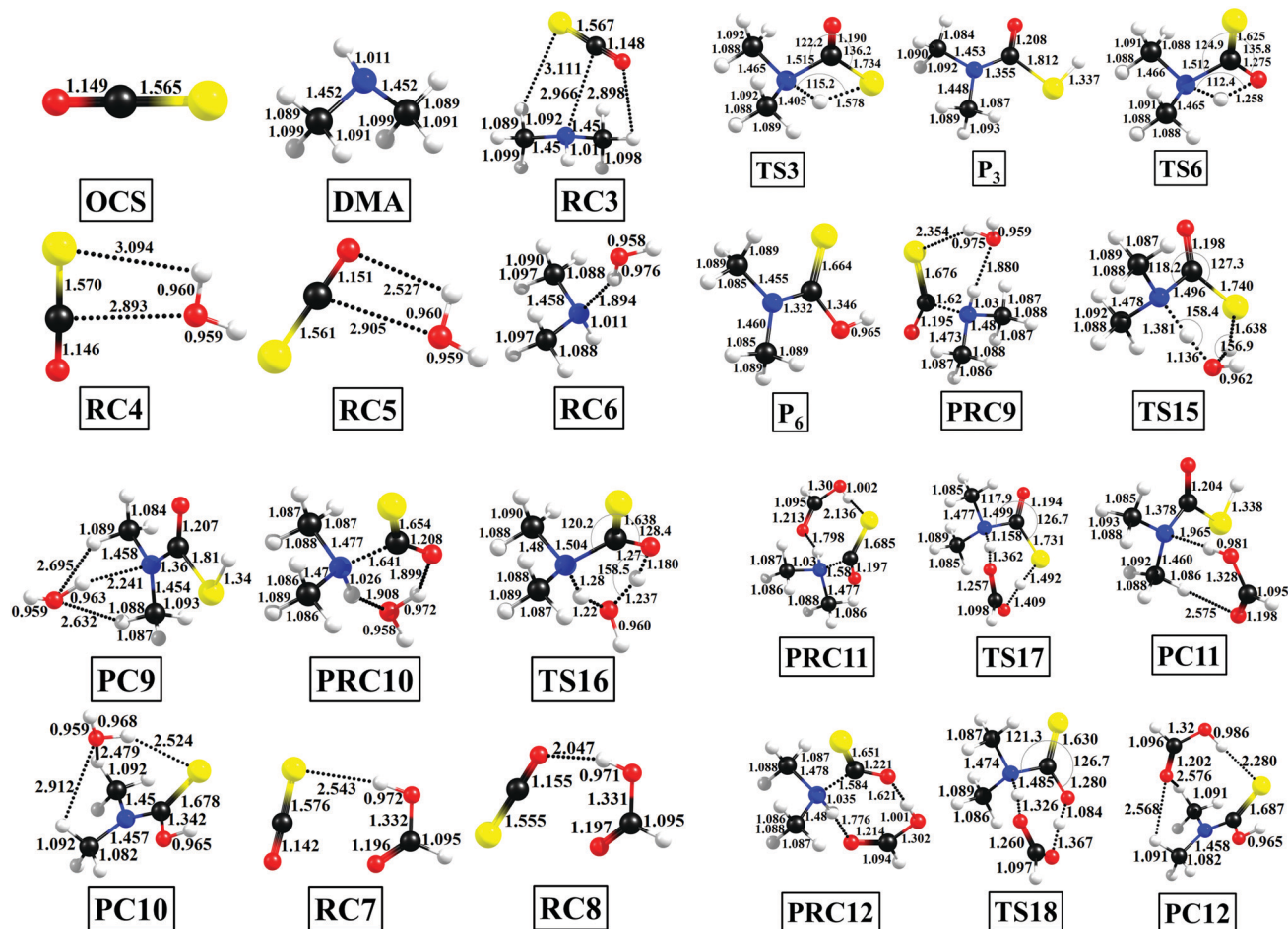
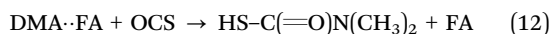
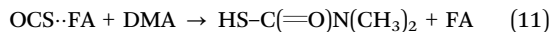
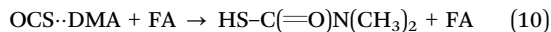


Fig. 7 The M06-2X/aug-cc-pVTZ optimized geometries for the addition of dimethyl amine to OCS without a catalyst and assisted by a water and a formic acid leading to the formation of *N,N*-dimethyl carbamothioic acid. The yellow, black, white, blue, and red colors represent sulfur, carbon, hydrogen, nitrogen, and oxygen atoms, respectively.

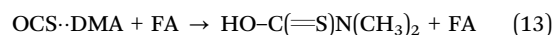
N,N-dimethyl carbamothioic acid. The PES profiles are shown in Fig. 8. The M06-2X/aug-cc-pVTZ optimized geometries for the OCS + DMA + FA reaction are shown in Fig. 7. Like the aforementioned OCS + DMA + H₂O reaction, the present OCS + DMA + FA reaction also proceeds *via* bimolecular collision pathways. Three possible elementary reactions defined by the three possible dimer complexes OCS·DMA, OCS·FA, and DMA·FA are presented in eqn (10)–(12)



The structures of OCS·DMA (RC3), OCS·FA (RC7), and OCS·FA (RC8) are shown in Fig. 7. We did not take into account the DMA·FA + OCS reaction channel (eqn (12)) because the structure of DMA·FA shows that the H-atom of FA blocks the DMA nitrogen site by forming a hydrogen bond, and it is therefore not available to attack the C-atom of OCS. The binding energies of RC3 and RC7 were both calculated to be ~ 2.9 kcal mol^{−1} at the CCSD(T)/M06-2X level of theory. The OCS·DMA (RC3) and

OCS·FA (RC7) dimer complexes further react with the other remaining reactant molecule through OCS·DMA + FA and OCS·FA + DMA (eqn (10) and (11)). This can be seen from the PES profile for the OCS + DMA + FA reaction entrance channels in Fig. 8. These OCS·DMA + FA and OCS·FA + DMA reaction paths proceed further to form a pre-reactant complex (PRC11) with a binding energy of ~ 9.4 kcal mol^{−1}. The formed PRC11 leads to the formation of TS17 with a barrier height that is -4.2 kcal mol^{−1} below that of the separated OCS + DMA + FA reactants (see Fig. 8). The structure of TS17 suggests that the addition of DMA to the C-atom of OCS followed by H-atom transfer from the -NH moiety of DMA to the S-atom of OCS is assisted by a FA molecule (see Fig. 7). The reaction further progresses *via* the formation of a post reactive complex (PC11) and then on to the formation of P₃ + FA as separated products.

We next performed calculations on the addition of DMA to OCS, followed by transfer of the H-atom from the -NH group to the O-atom of OCS, assisted by a FA. The possible bimolecular reaction channels are given in eqn (13) and (14).



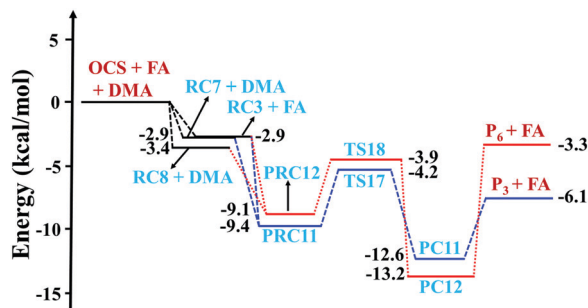
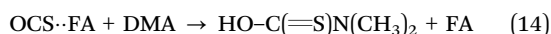


Fig. 8 The CCSD(T)/aug-cc-pVTZ//M0-62X/aug-cc-pVTZ calculated potential energy surface diagram for the addition of dimethyl amine to OCS followed by migration of the H-atom to either the S-atom (indicated using blue lines) or O-atom (indicated with red lines) of OCS catalyzed by a formic acid to form *N,N*-dimethyl carbamothioic acid. The symbols RC3, RC7 and RC8; PRC11 and PRC12; TS17 and TS18; PC11 and PC12; TS17 and TS18; and P₃ and P₆ refer to the dimer complexes, the pre-reactant complexes, the transition states, the post reactive complexes, and the *N,N*-dimethyl carbamothioic acid products, respectively.



The PES profile for these two reaction paths are also shown in Fig. 8. The OCS + DMA + FA reaction first forms OCS·DMA (RC3) and OCS·FA (RC8) dimer complexes. RC3 and RC8 further react with another species *via* OCS·DMA + FA and OCS·FA + DMA leading to the formation of TS18 with a barrier height of $\sim 3.9 \text{ kcal mol}^{-1}$ below that of the separated reactants. The formed TS18 is located between the corresponding pre-reactant complex (PRC12) and post-reactive complex (PC12), and finally leads to the formation of P₆ + FA as products. The barrier heights in Fig. 8 suggest that the OCS + DMA + FA reaction leading to the formation of TS17 and then to product (P₃) is energetically more favorable compared to the formation of the alternative TS18 to form product (P₆).

The CCSD(T)/M06-2X level calculated barrier heights for the addition of three different amine molecules with OCS without catalysis, and assisted by a H₂O or a FA molecule were shown in Fig. 1–6, and 8. We observed the trend that the barrier heights for the reactions in eqn (1)–(4) decrease along the series NH₃, MA, and DMA. It is also apparent from the figures that this trend aligns with the increase in the nucleophilic character of the reactants along the series for the reactions without catalysis and with catalysis by a H₂O and a FA molecule. In addition, the transition states for the unassisted reaction, and for the reactions assisted by a H₂O and a FA, involve four, six, and eight membered ring-like structures, respectively. Similar TS structures were reported for the reaction of isocyanic acid (HNCO) with DMA catalyzed by a single H₂O molecule.⁴³ The present work shows that in the case of FA as a catalyst, the reaction barrier associated with carbamothioic S- or O acid formation can be decreased by varying the R group on the amine nitrogen (see eqn (3) and (4)). In the case of NH₃, the barrier height was found to be 9.8 and 9.0 kcal mol^{−1}, respectively. For methylamine, the barrier energy reduces to 1.0 and −0.2 kcal mol^{−1}, and in the case of dimethylamine, the barrier energies drop to

−4.2 and −3.9 kcal mol^{−1} relative to those of the starting reactants, respectively. Therefore, by varying the R group on the nitrogen, the barrier height changes over a range of ~ 14 and $\sim 13 \text{ kcal mol}^{-1}$, respectively.

The transition states (TS1–TS18) in the present work clearly show that the C–N bond length ($\sim 1.50 \pm 0.01 \text{ \AA}$) is very close to the normal C–N bond length of $\sim 1.47 \text{ \AA}$. This suggests the possibility that the mechanism for the OCS + amine reaction may proceed in two steps (*i.e.* C–N bond formation followed by hydrogen transfer). Thus, we performed optimization of the transition states for the addition of the three different amines to OCS, proceeding to the formation of the C–N bond both without catalysis and in the presence of water and formic acid at the M06-2X/aug-cc-pVTZ level. Although we searched extensively, we did not find a transition state associated with the C–N bond formation step for any of the possible OCS + amine reactions at the present level of theory. Therefore, we conclude that the OCS + amine reaction mainly proceeds *via* a single step mechanism as suggested earlier. As an example, the IRC plots obtained at the M06-2X/aug-cc-pVTZ level for the addition of DMA to OCS followed by transfer of the H-atom to either the S-atom or O-atom of OCS without catalysis and in the presence of water and FA are shown in Fig. S3–S8 (ESI[†]), respectively. For the OCS + DMA reaction shown in Fig. S3 (ESI[†]), the structures presented from left to right in the IRC plot indicate that the reactant molecules OCS and DMA initially approach each other by forming the C–N bond, and then the H-atom of DMA starts to migrate to the S-atom of OCS before reaching the transition state. After passing the transition state, the H-atom of DMA finally forms a bond with the S-atom of OCS (see Fig. S3, ESI[†]). The structures in the IRC plot for the OCS + DMA + H₂O reaction (see Fig. S4, ESI[†]) suggest that OCS and DMA primarily approach each other by forming the C–N bond and then hydrogen atom transfer occurs at the DMA to the O-atom of H₂O before reaching the transition state. After passing the transition state, the H-atom of DMA forms a bond with the O-atom of H₂O and simultaneously, the H-atom of H₂O migrates to the S-atom of OCS (see Fig. S4, ESI[†]). Similarly, in the case of the OCS + DMA + FA reaction, the OCS and DMA approach one another before reaching the transition state. Then the reaction proceeds after passing the transition state through the H-atom of DMA, and forms a single bond with the O-atom of FA with simultaneous transfer of the H-atom of FA to the S-atom of OCS (see Fig. S5, ESI[†]). A similar mechanism was observed for the addition of DMA to OCS followed by transfer of the H-atom to the O-atom of OCS without catalysis and in the presence of water and FA (see Fig. S6–S8, ESI[†]). In addition, we have also found a similar mechanism for the OCS + NH₃, OCS + NH₃ + H₂O, OCS + NH₃ + FA, OCS + MA, and OCS + MA + FA reactions. The results for all these reaction mechanisms indicate that the displacements of heavy atoms and H-atom transfers occur concertedly throughout the reaction. Therefore, the present analysis suggests that the OCS + amine reaction proceeds *via* C–N bond formation followed by hydrogen transfer in a single step mechanism.

The complexes formed in the OCS + NH₃ reaction in the presence of water and formaldehyde were optimized at the M06-2X/aug-cc-pVTZ level with Grimme's third generation

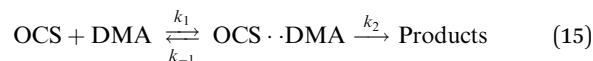
dispersion correction (M06-2X-D3).⁷³ The energies of the complexes were also refined by performing CCSD(T)/aug-cc-pVTZ on the M06-2X-D3 level optimized geometries. The comparison of energies for the various complexes involved in the OCS + NH₃ reaction assisted by a water and formic acid calculated at the M06-2X, M06-2X-D3 and their corresponding CCSD(T)/aug-cc-pVTZ levels are displayed in Table S6 (ESI†). All the energies of the stationary points displayed in Table S6 (ESI†) were calculated relative to the separated starting reactants. The data from the table clearly suggests that the M06-2X-D3 level energies of the complexes varied by ~0.1 kcal mol⁻¹ compared to the values at the M06-2X level. We also observed no change in the energies for the complexes at the CCSD(T)/M06-2X-D3 level compared to the values at the CCSD(T)/M06-2X level. Therefore, the empirical dispersion correction calculations were not performed for the OCS + MA + H₂O, OCS + MA + FA, OCS + DMA + H₂O, and OCS + DMA + FA reactions, respectively.

The energies of the pre-reactant complexes (PRC1 and PRC2) involved in the OCS + NH₃ + H₂O reaction at the CCSD(T)/M06-2X level were found to be 11.3 and -5.8 kcal mol⁻¹ respectively (see Table S6, ESI† and Fig. 2). In the case of the OCS + NH₃ + FA reaction, the energies of the pre-reactant complexes (PRC3 and PRC4) calculated at the CCSD(T)/M06-2X level were found to be 5.4 and 5.3 kcal mol⁻¹ above that of the starting reactants (see Table S6, ESI† and Fig. 3). We note that the calculated energies of PRC1, PRC3, and PRC4 that are associated with the OCS + NH₃ + H₂O and OCS + NH₃ + FA reactions indicate that they are located above the starting reactants (see Table S6, ESI† and Fig. 2, 3). We also observed a similar trend in the energies of the pre-reactant complexes, which are located above the separated reactants for the analogous reaction (HNCO + NH₃ + H₂O) reported in the literature.⁴³ The energies of the post-reactive complexes (PC1, PC2, PC3, and PC4) associated with the OCS + NH₃ + H₂O and OCS + NH₃ + FA reactions calculated at the CCSD(T)/M06-2X level were determined to be -2.2, 5.3, -4.8, and 2.0 kcal mol⁻¹, respectively. Similar trends in energies were observed for all the stationary points in Table S6 (ESI†) for the OCS + NH₃ + H₂O and OCS + NH₃ + FA reactions at various levels of theory, such as the M06-2X, M06-2X-D3, and CCSD(T)/M06-2X-D3 levels.

3.2. Theoretical kinetic analysis

The OCS + NH₃ and OCS + MA reactions in the absence of catalysts and presence of a single molecule of H₂O or FA exhibit very high barriers (see Fig. 1a/b through Fig. 5). Therefore, these reactions are energetically not feasible under normal atmospheric conditions. The OCS + DMA reaction catalyzed by a single FA molecule shows negative barrier heights for the formation of *N,N*-dimethyl carbamothioic acid (see Fig. 8). Therefore, rate coefficient calculations for the OCS + DMA reaction for both the absence of catalysis and the presence of single H₂O and FA molecules were calculated to determine the quantitative effect of these two catalysts, in comparison with the absence of catalysis in the atmospheric removal of OCS in the presence of DMA. In doing so, we followed previously published procedures for computing the reaction kinetics.^{43,55,56}

The reaction scheme for OCS + DMA in the absence of a catalyst can be represented by eqn (15):



The reaction between the two reactant species OCS and DMA primarily forms a two-body OCS⋅DMA complex (eqn (15)) which undergoes unimolecular isomerization through a TS leading to the formation of final products. The symbols k_1 and k_{-1} represent the forward and reverse rate coefficients for the OCS + DMA reactions to form a OCS⋅DMA complex. The symbol k_2 represents the unimolecular rate coefficient for product formation from the OCS⋅DMA complex *via* a well-defined TS. We assumed that the two-body complex is in equilibrium with the reactants, and that the rate of the uncatalyzed reaction under pre-equilibrium conditions can be approximated by:

$$\text{Rate} = k[\text{OCS}][\text{DMA}] \quad (16)$$

In eqn (16), k represents the rate coefficient (in cm³ molecule⁻¹ s⁻¹) for the uncatalyzed OCS + DMA reaction; $k = K_{\text{eq1}}k_2$; and the equilibrium constant K_{eq1} represents the formation of the OCS⋅DMA complex from the OCS and DMA reactants. Using eqn (15), K_{eq1} can be defined as $K_{\text{eq1}} = \frac{k_1}{k_{-1}}$.

As an example, the OCS⋅DMA complex primarily reacts with a catalyst X (X = H₂O or FA) to form a OCS⋅DMA⋅X pre-reactant complex, which then undergoes intramolecular isomerization to form a post-reactive complex (PC) *via* a TS. The reaction scheme for the OCS⋅DMA + X (X = H₂O or FA) can be represented by eqn (17)



Similar to the uncatalyzed OCS + DMA reaction mechanism given in eqn (15), the pre-reactant complex (OCS⋅DMA⋅X) is assumed to be in equilibrium with the OCS⋅DMA and X (X = H₂O or FA) reactants. The symbols k_3 and k_{-3} represent the forward and reverse rate coefficients for the OCS⋅DMA + X reaction to form the OCS⋅DMA⋅X complex. The symbol k_4 represents the unimolecular rate coefficient for the reaction step involving conversion of the OCS⋅DMA⋅X complex to the PC *via* a well-defined TS. The rate of the OCS⋅DMA + X reaction under pre-equilibrium conditions is given in eqn (18):

$$\text{Rate} = k_{\text{X}}[\text{OCS} \cdots \text{DMA}][\text{X}] \quad (18)$$

In eqn (18), k_{X} represents the rate coefficient for the reaction of OCS⋅DMA + X (X = H₂O or FA) $k_{\text{X}} = K_{\text{eqX}}k_4$; and the equilibrium constant K_{eqX} represents the formation of the OCS⋅DMA⋅X complex from the isolated reactants. Using eqn (17), K_{eqX} can be defined as: $K_{\text{eqX}} = \frac{k_3}{k_{-3}}$. The unimolecular rate coefficients (k_2 and k_4) were computed with Polyrate (2016) kinetic code⁷⁴ by employing canonical variational transition state theory,^{58,59} and tunneling contributions were calculated with the small curvature tunneling⁶⁰ method using eqn (19):

$$k_2, (k_4)(\text{CVT/SCT}) = \kappa^{\text{SCT}} \frac{k_{\text{B}} T Q_{\text{GT}}(s^*)}{h Q_{\text{RC}}} e^{-\frac{V(s^*)}{k_{\text{B}} T}} \quad (19)$$

In eqn (19), κ^{SCT} is the small curvature tunneling factor; s^* is the value of the reaction coordinate at the free energy maximum along the reaction path; $V(s^*)$ is the potential energy at the barrier maximum; k_B is Boltzmann's constant; h is Planck's constant; T is the temperature in Kelvin; and Q_{RC} and $Q_{\text{GT}}(s^*)$ are the partition functions of the pre-reactant complex and transition state, respectively.

The equilibrium constants (K_{eq1} and K_{eqX}) were calculated using eqn (20) and (21):

$$K_{\text{eq1}} = \frac{Q_{\text{OCS}\cdots\text{DMA}}}{Q_{\text{OCS}}Q_{\text{DMA}}} \exp\left(-\frac{E_{\text{OCS}\cdots\text{DMA}} - E_{\text{OCS}} - E_{\text{DMA}}}{k_B T}\right) \quad (20)$$

$$K_{\text{eqX}} = \frac{Q_{\text{RCX}}}{Q_{\text{OCS}\cdots\text{DMA}}Q_X} \exp\left(-\frac{E_{\text{RCX}} - E_{\text{OCS}\cdots\text{DMA}} - E_X}{k_B T}\right) \quad (21)$$

In eqn (20), the partition function of a OCS·DMA dimer complex formed from the OCS and DMA reactants are represented by the symbols $Q_{\text{OCS}\cdots\text{DMA}}$, Q_{OCS} , and Q_{DMA} , respectively. $E_{\text{OCS}\cdots\text{DMA}}$, E_{OCS} , and E_{DMA} are the zero-point corrected total energies of the OCS·DMA dimer complex, OCS, and DMA reactants respectively. Similarly, using eqn (21), the partition function of RC (RC_X) derived from the respective OCS·DMA dimer complex and the other reactant X ($X = \text{H}_2\text{O}$ or FA) are represented by the symbols Q_{RCX} , $Q_{\text{OCS}\cdots\text{DMA}}$, and Q_X , respectively. E_{RCX} , $E_{\text{OCS}\cdots\text{DMA}}$, and E_X represent the zero-point corrected total energies of the respective RC and reactant species.

The pre-reactant complexes such as OCS·DMA·H₂O and OCS·DMA·FA are formed from their corresponding reactants (OCS, DMA, H₂O, FA) as shown in the first step of eqn (17). Various studies have demonstrated that the presence of pre-reactive complexes has a significant effect on the progress of the reaction.^{75–77} This can occur because the formed complexes can spatially direct the site of the reaction by either steric hindrance or through provision of a pre-reactant potential energy well. Therefore, complex formation can have a major impact on the rate coefficients.

The bimolecular rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the OCS + DMA uncatalyzed reaction (eqn (1) and (2)) were calculated using the expressions: $k_{\text{TS3}} = K_{\text{eq1}}k_2$ and $k_{\text{TS6}} = K_{\text{eq1}}k_6$, respectively. In these expressions, the equilibrium constant K_{eq1} is associated with the formation of the OCS·DMA complex from the OCS and DMA reactants. The calculated temperature dependent unimolecular rate coefficients (k_2 and k_6), equilibrium constant (K_{eq1}), bimolecular rate coefficients (k_{TS3} and k_{TS6}), and tunneling contributions in the temperature range 200–300 K are provided in Tables S7 and S9 (ESI†) and Table 1. The bimolecular rate coefficient data in Table 1 suggest that in the studied temperature range, addition of DMA to OCS followed by H-atom transfer to the S-atom of OCS through TS3 is $\sim 10^5$ – 10^7 times faster than the addition of DMA to OCS that is followed by H-atom transfer to the O-atom of OCS through TS6. This difference is mainly because the barrier height for TS3 is $\sim 7.8 \text{ kcal mol}^{-1}$ lower than that for TS6. The calculated rate coefficients at 300 K for the OCS + DMA reaction *via* TS3 and TS6 were found to be $k_{\text{TS3}} = 5.28 \times 10^{-31}$ and $k_{\text{TS6}} = 4.20 \times 10^{-36} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The small curvature tunneling contributions ($\kappa_{\text{TS3}}^{\text{SCT}}$ and $\kappa_{\text{TS6}}^{\text{SCT}}$) given in

Table 1 The calculated rate coefficients (k_{TS3} and k_{TS6} in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and the corresponding tunneling factors (κ) for the OCS + DMA uncatalyzed reaction to form *N,N*-dimethyl carbamothioic acid in the temperatures between 200 and 300 K

T (K)	k_{TS3}	$\kappa_{\text{TS3}}^{\text{SCT}}$	k_{TS6}	$\kappa_{\text{TS6}}^{\text{SCT}}$
200	1.61×10^{-36}	9.39×10^4	5.62×10^{-43}	1.42×10^7
210	7.64×10^{-36}	2.41×10^4	3.32×10^{-42}	1.81×10^6
220	3.37×10^{-35}	7.50×10^3	2.22×10^{-41}	3.67×10^5
230	1.36×10^{-34}	2.70×10^3	1.35×10^{-40}	9.27×10^4
240	5.21×10^{-34}	1.11×10^3	7.50×10^{-40}	2.75×10^4
250	1.87×10^{-33}	5.15×10^2	3.79×10^{-39}	9.44×10^3
260	6.35×10^{-33}	2.63×10^2	1.77×10^{-38}	3.65×10^3
270	2.05×10^{-32}	1.47×10^2	7.66×10^{-38}	1.58×10^3
280	6.33×10^{-32}	8.83×10^1	3.09×10^{-37}	7.46×10^2
290	1.86×10^{-31}	5.67×10^1	1.17×10^{-36}	3.84×10^2
298	4.37×10^{-31}	4.12×10^1	3.33×10^{-36}	2.36×10^2
300	5.28×10^{-31}	3.86×10^1	4.20×10^{-36}	2.13×10^2

Table 1 show that the magnitude of the tunneling factor is significant, as it varies between ~ 1 –4 orders for TS3 and ~ 2 –7 orders for TS6 in the studied temperature range.

The rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the OCS·DMA + H₂O (k_5) and OCS·H₂O + DMA (k_6) reaction paths that proceed *via* H-atom transfer to the S-atom of OCS, and alternatively, *via* H-atom transfer to the O-atom of OCS for the OCS·DMA + H₂O (k_8), and OCS·H₂O + DMA (k_9) reactions, respectively were calculated using the expressions: $k_5 = K_{\text{eq2}}k_7$, $k_6 = K_{\text{eq3}}k_7$, $k_8 = K_{\text{eq4}}k_{15}$, and $k_9 = K_{\text{eq5}}k_{15}$, respectively. In these expressions, k_7 and k_{15} represent the unimolecular rate coefficients, and the equilibrium constants (K_{eq2} , K_{eq3} , K_{eq4} , and K_{eq5}) are associated with the PRC9 and PRC10 formation steps of the OCS·DMA + H₂O, and OCS·H₂O + DMA reactants. The calculated equilibrium constants, unimolecular and corresponding bimolecular rate coefficients for these dimer reactions were determined in the temperatures between 200 and 300 K and the values are displayed in Tables S8, S9 (ESI†) and Table 2. The data in Table 2 suggest that at 300 K, the rate coefficients for the OCS·DMA + H₂O (k_5) and OCS·H₂O + DMA (k_6) reactions for the addition of DMA followed by H-atom transfer to the S-atom of OCS (TS15) were found to be $5.16 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $2.02 \times 10^{-25} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. On the other hand, for the alternative pathways involving OCS·DMA + H₂O (k_8), and OCS·H₂O + DMA (k_9) with H-atom transfer to the O-atom of OCS (TS16), they were found to be $1.22 \times 10^{-26} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5.18 \times 10^{-27} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively at the same temperature. The data also show that at 300 K, the OCS·DMA + H₂O (k_5) and OCS·H₂O + DMA (k_6) rate coefficients that proceed *via* TS15 are ~ 1 order of magnitude higher than the values observed for the OCS·DMA + H₂O (k_8), and OCS·H₂O + DMA (k_9) reactions that occur *via* TS16.

Similarly, rate coefficients for the OCS·DMA + FA (k_{10}) and OCS·FA + DMA (k_{11}) reaction channels that proceed *via* H-atom transfer to the S-atom of OCS were calculated using the expressions: $k_{10} = K_{\text{eq6}}k_{16}$, and $k_{11} = K_{\text{eq7}}k_{16}$, respectively. The rate coefficients for the alternative pathways for the OCS·DMA + FA (k_{13}) and OCS·FA + DMA (k_{14}) reactions that proceed through H-atom transfer to the O-atom of OCS, were calculated using

Table 2 The calculated bimolecular rate coefficients (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the $\text{OCS} \cdot \text{DMA} + \text{H}_2\text{O}$ (k_5), $\text{OCS} \cdot \text{H}_2\text{O} + \text{DMA}$ (k_6), $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{10}), and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{11}) reaction paths that proceed via H-atom transfer to the S-atom of OCS, and the $\text{OCS} \cdot \text{DMA} + \text{H}_2\text{O}$ (k_8), $\text{OCS} \cdot \text{H}_2\text{O} + \text{DMA}$ (k_9), $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{13}), and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{14}) reaction paths that proceed via H-atom transfer to the O-atom of OCS, respectively to form *N,N*-dimethyl carbamothioic acid

<i>T</i> (K)	k_5	k_6	k_8	k_9	k_{10}	k_{11}	k_{13}	k_{14}
200	1.15×10^{-27}	1.83×10^{-27}	2.40×10^{-30}	3.58×10^{-30}	2.98×10^{-15}	6.50×10^{-16}	7.06×10^{-16}	1.35×10^{-16}
210	2.54×10^{-27}	3.29×10^{-27}	7.65×10^{-30}	9.53×10^{-30}	2.04×10^{-15}	4.39×10^{-16}	4.99×10^{-16}	9.97×10^{-17}
220	5.30×10^{-27}	5.75×10^{-27}	2.23×10^{-29}	2.37×10^{-29}	1.45×10^{-15}	3.11×10^{-16}	3.67×10^{-16}	7.64×10^{-17}
230	1.06×10^{-26}	9.67×10^{-26}	5.99×10^{-29}	5.46×10^{-29}	1.08×10^{-15}	2.26×10^{-16}	2.79×10^{-16}	5.99×10^{-17}
240	2.03×10^{-26}	1.59×10^{-26}	1.50×10^{-28}	1.19×10^{-28}	8.23×10^{-16}	1.71×10^{-16}	2.18×10^{-16}	4.84×10^{-17}
250	3.74×10^{-26}	2.56×10^{-26}	3.56×10^{-28}	2.49×10^{-28}	6.47×10^{-16}	1.33×10^{-16}	1.75×10^{-16}	4.01×10^{-17}
260	6.69×10^{-26}	4.02×10^{-26}	7.91×10^{-28}	4.93×10^{-28}	5.21×10^{-16}	1.06×10^{-16}	1.44×10^{-16}	3.39×10^{-17}
270	1.16×10^{-25}	6.19×10^{-26}	1.67×10^{-27}	9.37×10^{-28}	4.29×10^{-16}	8.67×10^{-17}	1.21×10^{-16}	2.92×10^{-17}
280	1.95×10^{-25}	9.32×10^{-26}	3.38×10^{-27}	1.72×10^{-27}	3.58×10^{-16}	7.19×10^{-17}	1.03×10^{-16}	2.54×10^{-17}
290	3.22×10^{-25}	1.38×10^{-25}	6.57×10^{-27}	3.04×10^{-27}	3.05×10^{-16}	6.08×10^{-17}	8.88×10^{-17}	2.25×10^{-17}
298	4.74×10^{-25}	1.89×10^{-25}	1.09×10^{-26}	4.71×10^{-27}	2.71×10^{-16}	5.36×10^{-17}	7.96×10^{-17}	2.06×10^{-17}
300	5.16×10^{-25}	2.02×10^{-25}	1.22×10^{-26}	5.18×10^{-27}	2.63×10^{-16}	5.20×10^{-17}	7.76×10^{-17}	2.01×10^{-17}

equations: $k_{13} = K_{\text{eq}8}k_{17}$ and $k_{14} = K_{\text{eq}9}k_{17}$. In these expressions, k_{16} and k_{17} refer to the unimolecular rate coefficients, and the equilibrium constants $K_{\text{eq}6}$, $K_{\text{eq}7}$, $K_{\text{eq}8}$, and $K_{\text{eq}9}$ are associated with PRC11 and PRC12 formation steps from the two possible $\text{OCS} \cdot \text{DMA} + \text{FA}$, and $\text{OCS} \cdot \text{FA} + \text{DMA}$ dimer reaction pathways. The estimated equilibrium constants, and unimolecular and bimolecular rate coefficients for these reactions are also provided in Tables S8, S9 (ESI†) and Table 2.

The data in Table 2 show that at 300 K, the rate coefficients for the $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{10}) and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{11}) reactions proceeding via TS17 were $2.63 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $5.20 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively. For the alternative pathways $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{13}), and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{14}) which proceed via TS18, the rate coefficients were $7.76 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $2.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively at the same temperature. The data also show that the rate coefficients for the $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{10}) and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{11}) reactions that proceed via TS17 are ~ 3 times larger than the values for the $\text{OCS} \cdot \text{DMA} + \text{FA}$ (k_{13}) and $\text{OCS} \cdot \text{FA} + \text{DMA}$ (k_{14}) reactions that occur via TS18 in the studied temperature range.

The effectiveness of a catalyst on a specific reaction in the atmosphere depends not only on the rate coefficient, but also on the rate of the reaction. Therefore, it is very important to compare the rates of reactions. Information such as the rate coefficient and the concentrations of the participating reactants allow comparisons to be made of the impacts of different catalysts on a specific reaction. For this reason, we compared the rates of the reactions involving $\text{OCS} + \text{DMA}$ both without catalysis and in the presence of single H_2O and FA molecules. The rates of the $\text{OCS} + \text{DMA}$ reaction, proceeding via TS3 and TS6 are given in eqn (22) and (23).

$$\text{rate} = k_{\text{TS}3}[\text{OCS}][\text{DMA}] = k_{\text{TS}3}^{\text{eff}}[\text{OCS}] \quad (22)$$

$$\text{rate} = k_{\text{TS}6}[\text{OCS}][\text{DMA}] = k_{\text{TS}6}^{\text{eff}}[\text{OCS}] \quad (23)$$

In eqn (22) and (23), $k_{\text{TS}3}^{\text{eff}}$ and $k_{\text{TS}6}^{\text{eff}}$ represent effective first order rate coefficients for the uncatalyzed reactions of $\text{OCS} + \text{DMA}$, and can be defined as $k_{\text{TS}3}^{\text{eff}} = k_{\text{TS}3}[\text{DMA}]$ and $k_{\text{TS}6}^{\text{eff}} = k_{\text{TS}6}[\text{DMA}]$. The rate for the $\text{OCS} \cdot \text{DMA} + \text{H}_2\text{O}$ and $\text{OCS} \cdot \text{H}_2\text{O} + \text{DMA}$ reactions via TS15 and TS16 can be written in terms of the

bimolecular rate coefficients and the corresponding reactant and dimer concentrations using eqn (24)–(27).

$$\text{rate} = k_5[\text{OCS} \cdot \text{DMA}][\text{H}_2\text{O}] = k_5 K_{\text{eq}1}[\text{OCS}][\text{DMA}][\text{H}_2\text{O}] = k_5^{\text{eff}}[\text{OCS}] \quad (24)$$

$$\text{rate} = k_6[\text{OCS} \cdot \text{H}_2\text{O}][\text{DMA}] = k_6 K_{\text{eq}10}[\text{OCS}][\text{DMA}][\text{H}_2\text{O}] = k_6^{\text{eff}}[\text{OCS}] \quad (25)$$

$$\text{rate} = k_8[\text{OCS} \cdot \text{DMA}][\text{H}_2\text{O}] = k_8 K_{\text{eq}1}[\text{OCS}][\text{DMA}][\text{H}_2\text{O}] = k_8^{\text{eff}}[\text{OCS}] \quad (26)$$

$$\text{rate} = k_9[\text{OCS} \cdot \text{H}_2\text{O}][\text{DMA}] = k_9 K_{\text{eq}11}[\text{OCS}][\text{DMA}][\text{H}_2\text{O}] = k_9^{\text{eff}}[\text{OCS}] \quad (27)$$

In eqn (24)–(27), k_5^{eff} , k_6^{eff} , k_8^{eff} , and k_9^{eff} represent the effective first order rate coefficients for the removal of OCS through these reactions. They were defined as: $k_5^{\text{eff}} = k_5 K_{\text{eq}1}[\text{DMA}][\text{H}_2\text{O}]$, $k_6^{\text{eff}} = k_6 K_{\text{eq}10}[\text{DMA}][\text{H}_2\text{O}]$, $k_8^{\text{eff}} = k_8 K_{\text{eq}1}[\text{DMA}][\text{H}_2\text{O}]$, and $k_9^{\text{eff}} = k_9 K_{\text{eq}11}[\text{DMA}][\text{H}_2\text{O}]$. The symbols $K_{\text{eq}1}$, $K_{\text{eq}10}$ and $K_{\text{eq}11}$ represent the equilibrium constants for the formation of the corresponding dimer complexes.

Similarly, the rate for the $\text{OCS} \cdot \text{DMA} + \text{FA}$ and $\text{OCS} \cdot \text{FA} + \text{DMA}$ reactions via TS17 and TS18 were calculated using the corresponding parameters k_{10}^{eff} , k_{11} , and $K_{\text{eq}1}$, with $k_{10}^{\text{eff}} = k_{10} K_{\text{eq}1}[\text{DMA}][\text{FA}]$; k_{11}^{eff} , k_{11} , and $K_{\text{eq}12}$ with $k_{11}^{\text{eff}} = k_{11} K_{\text{eq}12}[\text{DMA}][\text{FA}]$; k_{13}^{eff} , k_{13} , and $K_{\text{eq}1}$ with $k_{13}^{\text{eff}} = k_{13} K_{\text{eq}1}[\text{DMA}][\text{FA}]$; and k_{14}^{eff} , k_{14} , and $K_{\text{eq}13}$ with $k_{14}^{\text{eff}} = k_{14} K_{\text{eq}13}[\text{DMA}][\text{FA}]$. The k_{10}^{eff} , k_{11}^{eff} , k_{13}^{eff} , and k_{14}^{eff} refer to the effective first order rate coefficients for the reaction of $\text{OCS} + \text{DMA}$ assisted by a single FA molecule. The symbols $K_{\text{eq}1}$, $K_{\text{eq}12}$, and $K_{\text{eq}13}$ represent the equilibrium constants for the formation of dimer complexes. The equilibrium constants for the various dimer complexes are given in Table S7 of the ESI†. The temperature dependent concentrations of H_2O (assumed to be 10%–100% RH) are displayed in Table S10 (ESI†). The concentrations of other participating reactants used in this work were as follows: $[\text{DMA}] = 2.0 \times 10^8 \text{ molecules cm}^{-3}$; and $[\text{FA}] = 4.4 \times 10^{11} \text{ molecules cm}^{-3}$.^{43,56} In the cases of the $\text{OCS} + \text{DMA} + \text{H}_2\text{O}$ and $\text{OCS} + \text{DMA} + \text{FA}$ reactions involving multiple reaction pathways, the total effective rate coefficients (in s^{-1}) for the overall reaction were calculated by summing the individual effective rate coefficients for each branch using the

expressions: $k_{\text{TS15}}^{\text{eff}} = k_5^{\text{eff}} + k_6^{\text{eff}}$; $k_{\text{TS16}}^{\text{eff}} = k_8^{\text{eff}} + k_9^{\text{eff}}$; $k_{\text{TS17}}^{\text{eff}} = k_{10}^{\text{eff}} + k_{11}^{\text{eff}}$; and $k_{\text{TS18}}^{\text{eff}} = k_{13}^{\text{eff}} + k_{14}^{\text{eff}}$, where the symbols $k_{\text{TS15}}^{\text{eff}}$ and $k_{\text{TS16}}^{\text{eff}}$ represent the total rate coefficients for the OCS + DMA + H₂O reaction involving H-atom transfer to either the S-atom or O-atom of OCS, and $k_{\text{TS17}}^{\text{eff}}$ and $k_{\text{TS18}}^{\text{eff}}$ represent the total rate coefficient for the OCS + DMA + FA reaction involving H-atom transfer to either the S-atom or O-atom of OCS. The calculated effective first order rate coefficient values for the OCS + DMA, OCS + DMA + H₂O, and OCS + DMA + FA reactions involving two possible H-atom transfer reaction paths are given in Tables S10 and S11 (ESI[†]).

To better understand the impact of temperature, the effective first order rate coefficients were plotted against temperature, and the results for the two possible H-atom transfers involving OCS + DMA in the absence and presence of H₂O and FA single molecules are presented in Fig. 9. It is clear from the plot that the effective rate coefficients for the two possible H-atom transfers involving the OCS + DMA, and OCS + DMA + H₂O reaction pathways increase with temperature, whereas the effective rate coefficient values for the OCS + DMA + FA channels decrease with temperature. This difference in rate coefficient trends occurs because while the OCS + DMA reaction (*via* TS3 and TS6), and the OCS + DMA + H₂O reactions (*via* TS15 and TS16) show significant positive barrier heights, the OCS + DMA + FA reactions (*via* TS17 and TS18) have negative energy barriers. The effective first order rate coefficient data in Table S10 (ESI[†]) and Fig. 9 suggest that for the OCS + DMA + H₂O reaction, H-atom transfer to the S-atom of OCS is ~ 1 order of magnitude more dominant than the values for the OCS + DMA reaction in the temperatures between 200 and 300 K. For example, the effective rate coefficients for the OCS + DMA, and

OCS + DMA + H₂O reactions at 298 K were calculated to be $8.74 \times 10^{-23} \text{ s}^{-1}$, and $4.51 \times 10^{-22} \text{ s}^{-1}$ respectively. The OCS + DMA + FA reaction was $\sim 10^3$ – 10^{10} times more dominant compared to the values for the OCS + DMA + H₂O reaction in the studied temperature range.

At 298 K, the effective rate coefficient for the OCS + DMA + FA reaction was found to be $1.77 \times 10^{-19} \text{ s}^{-1}$, which is $\sim 10^3$ times larger than the value for the OCS + DMA + H₂O reaction, which had an effective rate coefficient of $4.51 \times 10^{-22} \text{ s}^{-1}$ at the same temperature. This shows that the rate of the FA catalyzed reaction of OCS + DMA is faster than that for the water catalyzed reaction, even though the concentration of FA is ~ 3 – 6 orders of magnitude smaller compared to the concentration of water in the atmosphere. This is mainly due to the fact that the OCS + DMA + FA reaction barrier is $\sim 15.5 \text{ kcal mol}^{-1}$ lower than that for the OCS + DMA + H₂O reaction. Similarly, Table S11 (ESI[†]) and Fig. 9 clearly show that the effective rate coefficients for the OCS + DMA + H₂O reaction involving the H-atom shift to the O-atom of OCS is larger by $\sim 10^4$ – 10^5 times the values for the uncatalyzed OCS + DMA reaction in the same temperature range. For example, at 298 K, the effective rate coefficient for the uncatalyzed and water catalyzed OCS + DMA reactions were found to be $6.66 \times 10^{-28} \text{ s}^{-1}$ and $1.04 \times 10^{-23} \text{ s}^{-1}$, respectively. For the OCS + DMA + FA reaction, the effective rate coefficient data suggest that this reaction rate is $\sim 10^3$ – 10^{12} times larger than the values for the OCS + DMA + H₂O reaction in the temperatures within 200–300 K. At 298 K, the effective rate coefficient for the OCS + DMA + FA was found to be $5.22 \times 10^{-20} \text{ s}^{-1}$, which is $\sim 10^3$ times larger than the value for the OCS + DMA + H₂O reaction. This suggests that a single molecule of FA is a more effective catalyst for the OCS + DMA reaction than a single water molecule. Overall, FA was found to be a more effective catalyst than water in catalyzing the OCS + DMA reaction. It was also observed that for the OCS + DMA + FA reaction, H-atom transfer to the S-atom of OCS is more favorable than H-atom transfer to the O-atom of OCS.

We also calculated the rate of atmospheric removal of OCS *via* the OCS + $\bullet\text{OH}$ reaction in order to compare it with the rate of the OCS + DMA + FA reaction. The rate coefficient for the OCS + $\bullet\text{OH}$ reaction reported by various groups at 298 K temperature has been reported to range between $5.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ – $6.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. To get the effective first order rate coefficient for the OCS + $\bullet\text{OH}$ reaction, the rate expression can be given by eqn (28).

$$\text{rate} = k_{\text{OH}}[\text{OCS}][\text{OH}] = k_{\text{OH}}^{\text{eff}}[\text{OCS}] \quad (28)$$

Using eqn (28), the effective rate coefficient can be defined as $k_{\text{OH}}^{\text{eff}} = k_{\text{OH}}[\text{OH}]$, where k_{OH} is the reported bimolecular rate coefficient for the OCS + $\bullet\text{OH}$ reaction. Using the average atmospheric concentration of $[\bullet\text{OH}] = 1.0 \times 10^6 \text{ molecules cm}^{-3}$ and the reported bimolecular rate coefficients, the effective rate coefficients for the OCS + $\bullet\text{OH}$ reactions at 298 K were calculated to be in the range of $5.70 \times 10^{-8} \text{ s}^{-1}$ – $6.0 \times 10^{-10} \text{ s}^{-1}$. This suggests that the effective rate coefficients for the OCS + $\bullet\text{OH}$ reaction are $\sim 10^{10}$ times higher than those for the OCS + DMA + FA reaction. Therefore, we concluded that atmospheric removal of

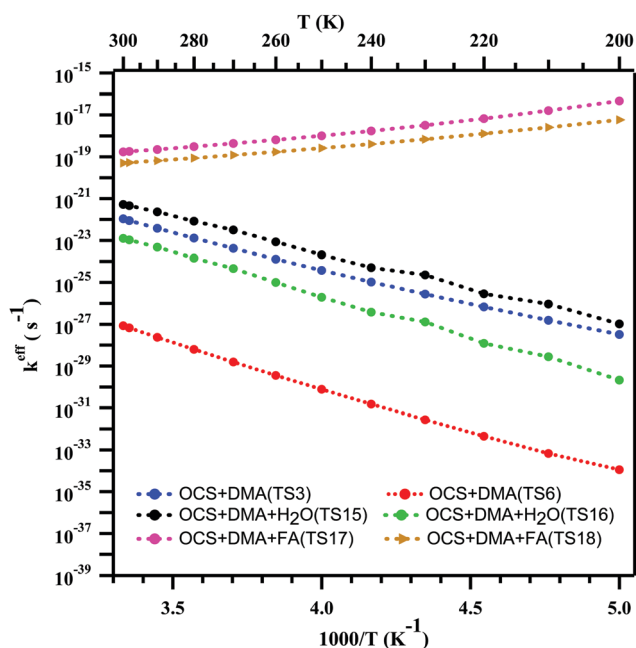


Fig. 9 Calculated effective rate coefficient (in s^{-1}) comparison for the reaction of OCS + DMA in the absence of a catalyst, versus assisted by a single water molecule and a formic acid molecule.

OCS through reaction with $\bullet\text{OH}$ is more favorable than *via* the OCS + DMA reaction assisted by either a single water or formic acid molecule. In summary, OCS + DMA + FA, OCS + DMA + H_2O , and OCS + $\bullet\text{OH}$ reactions are found to be slow under typical atmospheric conditions, and further studies are required to determine other possible catalysts that can facilitate removal of OCS from the atmosphere.

4. Conclusions

Atmospheric removal of OCS through reaction with three different amines both in the absence of, and assisted by a single H_2O or formic acid (FA) catalyst, were investigated at the CCSD(T)/M06-2X level of theory. The calculated barrier heights were observed to decrease with increasing methylation on the amine nitrogen atom. Addition of ammonia or methylamine (MA) to OCS assisted by a H_2O or FA and leading to the formation of the corresponding carbamothioic acids were deemed unfeasible under atmospheric conditions because of high energy barriers. On the other hand, dimethylamine (DMA) + OCS assisted by FA to form *N,N*-dimethyl carbamothioic acid, was found to be an energetically more favorable reaction compared to the uncatalyzed and single H_2O catalyzed reactions. The temperature dependent rate coefficients were computed for the OCS + DMA reactions both without catalysts and in the presence of a single H_2O and a single FA in the temperatures between 200 and 300 K. The results suggest that small curvature tunneling plays an important role in the OCS + DMA reaction when compared to the OCS + DMA reaction assisted by H_2O and FA. The effective rate coefficient results showed that a FA catalyst is more effective for the OCS + DMA reaction by larger than $\sim 10^3$ – 10^{10} times for the pathway involving H-atom shift to the S-atom of OCS, and $\sim 10^3$ – 10^{12} times for that involving the H-atom transfer to the O-atom of OCS when compared to the values for the OCS + DMA + H_2O reaction. Even though the OCS + DMA + FA reaction rate is lower compared to the OCS + $\bullet\text{OH}$ reaction, it could be a viable path for the atmospheric removal of OCS under night-time forest fire conditions when the OCS and DMA concentrations are high. Thus, although the OCS + DMA + FA reaction was shown to be less important in the gas phase based on its lower rate coefficient values, further extensive investigations are required to determine the impact of various other possible catalysts on the OCS + DMA reaction to determine the presence of alternative fates of OCS in the troposphere.

Conflicts of interest

There are no conflicts to declare.

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