The gas phase oxidation of HCOOH by Cl and NH₂ radicals. Proton coupled electron transfer versus hydrogen atom transfer. ‡

Josep M. Anglada,^a * Ramon Crehuet^a and Albert Solé^b

a) Departament de Química Biològica, (IQAC – CSIC), Jordi Girona, 18-26, E-08034 Barcelona. E-mail: anglada@iqac.csic.es and ramon.crehuet@iqac.csic.es

b) Departament de Ciència de Materials i Química Física, i Institut de Química Teòrica i Computacional (IQTCUB). Universitat de Barcelona, Martí i Franqués, 1, E-08028 Barcelona. E-mail: a.sole@ub.edu

‡ This paper is dedicated to the memory of Prof. Dieter Cremer

Keywords: Atmospheric chemistry, ab-initio calculations, proton coupled electron transfer, hydrogen atom transfer, reaction kinetics,

Abstract

The reaction of formic acid (HCOOH) with chlorine atom and amidogen radical (NH₂) have been investigated using high level theoretical methods such BH&HLYP, MP2, QCISD, and CCSD(T) with the 6-311+G(2df,2p), aug-cc-pVTZ, aug-cc-pVQZ and extrapolation to CBS basis sets. The abstraction of the acidic and formyl hydrogen atoms of the acid by the two radicals has been considered, and the different reactions proceed either by a proton coupled electron transfer (*pcet*) and hydrogen atom transfer (*hat*) mechanisms. Our calculated rate constant at 298 K for the reaction with Cl is $1.14 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ in good agreement with the experimental value $1.8 \pm 0.12 / 2.0 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ and the reaction proceeds exclusively by abstraction of the formyl hydrogen atom, via *hat* mechanism, producing HOCO + ClH. The calculated rate constant, at 298 K, for the reaction with NH₂ is $1.71 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, and the reaction goes through the abstraction of the acidic hydrogen atom, via a *pcet* mechanism, leading to the formation of HCOO + NH₃.

Introduction

Formic acid (HCOOH) is the most abundant carboxylic acid in the troposphere.[1] It is emitted to the atmosphere in great amounts from biogenic sources, as a results of photooxidation of volatile organic compounds, from biomass burning, as one of the products of ozonolysis of alkenes and from automobile exhaust. [2] The best known gas phase atmospheric oxidation process of formic acid is the reaction with hydroxyl radical, which can result in the abstraction of the acidic hydrogen (reaction 1), or the abstraction of the formyl hydrogen (reaction 2).

These reaction have been investigated experimentally [3] and theoretically,[4-6] and results indicate that the main reaction process corresponds to the abstraction of the acidic hydrogen, with estimated values of 93%, while the abstraction of the formyl hydrogen accounts for about 7%.[6]

As far as we know, the studies of the gas phase reaction of formic acid by other atmospheric radicals are very scarce, and few works have been devoted to the study of the oxidation of HCOOH by Cl radical. The experimental rate constant was determined to be $1.8 \pm 0.12 / 2.0 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, [7] and there is experimental evidence that the dominant mechanism involve the abstraction of the formyl hydrogen.[8] This reaction has been also investigated theoretically[9,10] reporting valuable information regarding the reaction mechanism and the kinetics. In this work we have carried out an extensive theoretical investigation of the reaction of HCOOH with Cl and NH₂ radicals, according to reactions 3-6, with the aim of achieving a deep knowledge of the main features of the reaction mechanisms and also of reporting high level theoretical values on the kinetics of these reactions.

The interest of the reactions investigated in this work lie in the importance of these species in the Earth's atmosphere and in combustion processes.

Chlorine atom is an important oxidant in the Earth's troposphere, as it is shown comparing the oxidation of alkanes by Cl and OH radicals. [11,12,13] The rate constant of the reaction with chlorine is about two orders of magnitude greater than the rate constant of the reactions with hydroxyl radical, which makes necessary to know the reactivity of this radical with atmospheric species. Its main tropospheric precursor is sea salt aerosol,[13,14] and recently, there has been measured chlorine concentrations of $3 \times 10^5 \text{ atoms} \cdot \text{cm}^{-3}$ in the marine boundary layer, along with the $6 \times 10^5 \text{ molecules} \cdot \text{cm}^{-3}$ measured for hydroxyl radical.[12]

Both, HCOOH and NH₃ have been detected in biomass burning plumes,[15] and ammonia is also emitted to the atmosphere from biogenic and anthropogenic sources and constitutes the third most abundant gaseous nitrogen compound in the troposphere.[16] Amidogen radical (NH₂) is formed in the gas phase oxidation of ammonia (NH₃) by hydroxyl radical, and is of interest in the combustion of fossil fuels. It is considered to play an important role in the atmospheric formation and elimination of NO_x [17] and in the oxygen isotopic exchange of N₂O. [18] Very recently, it has also been proposed that amidogen radical can also react with gas phase nitric acid. [19]

Technical details

We have considered different theoretical approaches in this study. In a first step, we have optimized and characterized all stationary points employing the BH&HLYP[20] density functional with the aug-cc- pVTZ basis set. At this level of theory we have also performed harmonic vibrational frequency calculations in order to confirm the nature of the stationary points (minima or saddle point) and to calculate the corresponding zero point energy and the enthalpic and the free energy contributions to the energy. We have performed intrinsic reaction coordinate (IRC) calculations[21] for all transition states to verify that they connect with the corresponding reactants and products.

In a second step, we have also reoptimized and characterized the most important stationary points using the QCISD level of theory[22] along with the 6 -311+G(2df,2p) basis set. [23] Finally, we have also optimized some relevant stationary points at MP2 and CCSD(T) level of theory[22] employing the 6-311+G(2df,2p) basis set.

In all cases, the final energies have been obtained by carrying out single point energy calculation at CCSD(T) level of theory employing the aug-cc-pVTZ and aug-cc-pVQZ basis sets, extrapolating to the complete basis set (CBS) limit, according to the scheme by Helgaker et al. [24]. The reliability of these results, with respect to the possible multi-reference character of the corresponding wave function, have been assessed by looking at the T1 diagnostic value of the CCSD wave function.[25]

The kinetic study has been carried out using the variational (VTST) and conventional (CTST) transition state theories, considering energies obtained at the CCSD(T)/CBS and partition functions computed at BH&HLYP/aug-cc-pVTZ level of theory. The tunneling effects have been obtained with the small curvature approach for the VTST calculations and the zero curvature approach for the CTST calculations.

The quantum chemical calculations carried out in this work were performed by using Gaussian[26] and ORCA program packages. [27] The Molden[28] and VMD[29] programs were employed to visualize and plot the geometric and electronic features. The kinetic study was done by using the Polyrate program.[30]

Reaction mechanisms and potential energy surfaces

There are two conformers (*syn*- and *anti*-) of formic acid and our results, displayed in Table S1, predict the *syn*-HCOOH to be 4.05 kcal·mol⁻¹ more stable than the *anti*-HCOOH conformer, and the energy barrier for their interconversion is computed to be 11.39 kcal·mol⁻¹ relative to the most stable conformer, in very good agreement with previous results from the literature.[10,31,32] According to our results, the corresponding equilibrium constant for the *syn*- *anti*- conformers is 1.05 x 10⁻³ at 298 K, implying that the population of the *syn*- conformer is 99.89%. Table S1 of the supplementary material contains the corresponding relative energies, and Table S2 the equilibrium constants in a wide range of temperatures.

Figure 1: Schematic potential energy surface for the reaction of *syn*-HCOOH with Cl and NH₂. The relative energy values are taken from Tables 1 and 2. Values in plain text, parenthesis, braces, and brackets correspond to optimized geometries computed at BY&HLYP, at QCISD, at MP2, and at CCSD(T) levels of theory respectively.

In this study we have considered the reaction of both conformers of formic acid with Cl and NH₂ radicals according reactions 3 to 6. The relative energies of the different

stationary points computed for these reactions are contained in Tables 1 and 2, and Figures 1 and 3 show a schematic picture of the potential energy surfaces of these reactions. Figure 2 contains the most relevant electronic features describing the processes investigated in this work. In all elementary reactions, the transition states are mediated by the formation of a pre-reactive complex in the entry channel, which is formed by interaction of the two reactants, and by a post-reactive complex in the exit channel before the release of the corresponding products. Along the text, we have named the pre-reactive complexes by the letters CR, the transition states by TS and the post-reactive complexes by CP, followed by a number to distinguish the different reaction paths. In order to differentiate the reaction of formic acid with the two radicals investigated, the acronym of each stationary point is preceded by the letter A for the reactions involving Cl radical and by the letter B for the reactions with NH₂ radical.

Table 1: Relative energies, energies plus ZPE, enthalpies and free energies at 298 K calculated for the reaction between HCOOH and Cl. All values are in kcal·mol⁻¹.

	Method ^{a, b}	ΔE	$\Delta (E+ZPE)$	ΔH	ΔG
<i>syn</i> -HCOOH + Cl					
<i>syn</i> -HCOOH + Cl	A/B/C/D	0.00	0.00	0.00	0.00
ACR1	A	-6.15	-5.47	-5.81	1.00
	B	-5.83	-5.23	-5.47	0.99
ATS1	A	12.39	8.60	7.78	15.80
	B	12.28	8.53	7.72	15.76
ACP1	A	11.45	7.77	8.17	12.33
	B	11.87	8.15	8.64	12.23
ATS2	A	22.35	15.77	15.51	22.21
ACP2	A	14.76	10.42	11.32	13.96
ACR2	A	-2.01	-1.89	-1.75	2.10
	B	-2.02	-1.85	-1.74	2.66
	C	-2.05	-1.89	-1.79	2.58
	D	-2.05	-1.89	-1.78	2.58
ATS3	A	4.43	-0.05	-0.49	6.47
	B	4.53	0.23	-0.20	6.77
	C	4.44	0.60	0.11	7.16

	D	4.55	0.71	0.22	7.27
ACP3	A	-1.78	-5.19	-4.41	-1.60
	B	-1.82	-5.10	-4.37	-1.44
	C	-1.79	-4.77	-4.20	-0.61
HCO₂ + HCl	A	15.01	6.88	7.41	5.77
cis-HOCO + Cl	A	-0.33	-4.50	-3.89	-6.09
anti-HCOOH + Cl					
anti-HCOOH + Cl	A/B/C/D	0.00	0.00	0.00	0.00
ACR3	A	-2.14	-1.87	-1.82	2.88
	B	-2.16	-1.83	-1.80	2.95
	C	-2.16	-1.83	-1.81	3.09
	D	-2.16	-1.83	-1.82	3.09
ATS4	A	-3.22	-6.90	-7.46	-0.27
	B	-3.08	-6.66	-7.19	-0.08
	C	-1.75	-3.44	-4.09	3.08
	D	-1.36	-3.05	-3.70	3.47
ACP4	A	-9.76	-12.72	-11.97	-8.84
	B	-9.86	-12.66	-11.99	-8.25
	C	-9.90	-12.49	-11.91	-7.74
ATS5	A	15.00	10.81	10.12	17.73
ACP5	A	6.53	3.21	3.46	8.24
HCO₂ + HCl	A	10.75	2.83	3.31	1.72
trans-HOCO + Cl	A	-6.35	-10.13	-9.55	-11.69

- a) A stands for CCSD(T)/CBS//BH&HLYP/aug-cc-pVTZ; B stands for CCSD(T)/CBS//QCISD/6-311+G(2df,2p); C stands for CCSD(T)/CBS//MP2/6-311+G(2df,2p) with enthalpic and entropic corrections at MP2/6-311+G(2df,2p); D stands for CCSD(T)/CBS//CCSD(T)/ 6-311+G(2df,2p) with enthalpic and entropic corrections at MP2/6-311+G(2df,2p)
- b) The T1 diagnostic values of the CCSD wave functions are 0.020, 0.036, 0.017, 0.035, 0.017, 0.014, 0.019, 0.018, 0.014, 0.019, 0.017, 0.044, and 0.018 for **ACR1**, **ATS1**, **ACP1**, **ATS2**, **ACP2**, **ACR2**, **ATS3**, **ACP3**, **ACR3**, **ATS4**, **ACP4**, **ATS5**, and **ACP5**, respectively.

As pointed out in the technical details section, we have employed different theoretical approaches in this work, namely geometry optimizations at BH&HLYP/aug-cc-pVTZ,

QCISD/6-311+G(2df,2p) theoretical approaches, and in some particular cases employing the MP2/-311+G(2df,2p) and CCSD(T)/6-311+G(2df,2p) levels of theory. Moreover for each stationary point we have performed single point energy calculations at CCSD(T)/CBS level of theory in order to obtain more accurate results. The computed relative energy values are collected in Tables 1 and 2, and, the relative energies obtained with different theoretical schemes differ utmost in $0.8 \text{ kcal}\cdot\text{mol}^{-1}$. Figures 1 and 3, and Figures S1-S4 show that BH&HLYP, QCISD and CCSD(T) approaches predict geometrical parameters differing up to $0.03 \text{ \AA}$, whereas the MP2 approach does not perform as well, predicting geometrical parameters which differ up to $0.09 - 0.10 \text{ \AA}$ with respect the most robust CCSD(T) method (see, for instance **ATS3** and **BTS1** in Figure 1). The exception is **ATS4** which will be analyzed in more detail. Along the text we will only discuss the results obtained with the most accurate theoretical approach in each case. For the *syn*-HCOOH + X (X = Cl and NH₂) reaction, the abstraction of the acidic hydrogen by the X radical produces HCOO + XH, and it is computed to be endothermic (by $6.88 \text{ kcal}\cdot\text{mol}^{-1}$ for HCOO + ClH, reaction 3 and by $4.34 \text{ kcal}\cdot\text{mol}^{-1}$ for HCOO + NH₃, reaction 5). Moreover, the HCOO radical decomposes into H and CO₂ in a process that has been already described in the literature, and we refer the reader to these works for a more detailed description of this process.[10,31,33]

Figure 2: Electronic features of the HOMO and SOMO natural orbitals describing the proton coupled electron transfer (*pcet*) reaction mechanism for **ATS1** and **BTS1**

transition states, and the hydrogen atom transfer (*hat*) reaction mechanism for **ATS2**, **ATS3**, **BTS2** and **BTS3** transition states.

Figure 1 and Tables 1 and 2 show that there are two elementary reactions for each of the reactions 3 and 5. The one having the lowest energy barrier occurs via **ATS1** (for X = Cl) and via **BTS1** (for X = NH₂), and the one having higher energy barrier takes place through **ATS2** and **BTS2** (for X = Cl and NH₂, respectively). These two elementary reactions have very different electronic features. Thus, reactions through **ATS1** and **BTS1** involve a proton coupled electron transfer mechanism whereas reactions via **ATS2** and **BTS2** follow a conventional hydrogen atom transfer process, in a similar way as described previously in the reactivity of other systems with radicals.

In the *pcet* mechanisms (via **ATS1** and **BTS1**), the radical approaches the *syn*-HCOOH acid in such a manner that unpaired electron interacts with a lone pair of the oxygen atom of the carbonyl group whereas the lone pair over the radical faces the hydrogen atom of the OH group in the acid. In such a situation, an electron jumps from the oxygen atom of the carbonyl group to the radical moiety and, at the same time, a proton moves from the acid moiety to the radical moiety. Figure 1 shows the most relevant geometrical parameters of these transition states. The most relevant parameter here is the distance between the oxygen atom of the carbonyl group and the chlorine or nitrogen atom of the radical, between which the electron is being transferred, computed to be 2.46 and 2.32 Å, respectively, which is in agreement with similar processes reported in the literature. In Figures 2 we have depicted the HOMO and SOMO natural orbitals which clearly show that this process is described by a two center three electron structure. The electronic density and spin densities lie between the oxygen atom of the carbonyl group and chlorine or nitrogen atoms of the radical, namely the atoms between which the electron transfer occurs, whereas no electronic density exist in the region where the proton is transferred. This is the common distance range where the electron transfer takes place in this kind of *pcet* processes, as it has been observed in similar reactions occurring in different systems. [5,6,19,34,35] We address the reader to these works for a more detailed discussion of these processes.

The conventional *hat* mechanism (taking place through **ATS2** and **BTS2**) is well known and involves the simultaneous breaking and making of two covalent bonds, as is shown in Figure 1. The radical approaches formic acid with the unpaired electron of the X radical

(X= Cl or NH₂) facing the -O-H bond. Along this process, the X-H bond is formed whereas the O-H or C-H bond breaks homolitically. The HOMO and SOMO natural orbitals depicted in Figure 2 show that this process is characterized by a three center three electron structure, and consequently, the spin density is shared between the acidic oxygen atom of the HCOOH moiety and the X atom (Cl or N) of the radical moiety, both being involved in the transfer of the hydrogen atom.

The abstraction of the formyl hydrogen is computed to be exothermic (by -4.50 kcal·mol⁻¹ for the production of *cis*-HOCO + ClH, reaction 4, and by -7.05 kcal·mol⁻¹ for the formation of *cis*-HOCO + NH₃, reaction 6). For this process, the transition states (**ATS3** for X = Cl and **BTS3** for X = NH₂) involve a conventional hydrogen atom mechanism, with electronic features similar to those described for **ATS2** and **BTS2**. Thus, the HOMO and SOMO natural orbitals of the transition states, displayed in Figure 2, show that the electronic and spin densities are shared between the carbon atom of the HCOOH moiety and the radical (Cl or N atoms, respectively), so that the **ATS3** and **BTS3** transition states are characterized by a three center three electron structure.

Table 1 and Figures 1 and 3 show that for the *syn*-HCOOH + Cl, reaction 3 begins with the pre-reactive complex **ACR1** having a binding energy of 5.23 kcal·mol⁻¹. After **ACR1** the reaction can proceed via **ATS1** (involving a *pcet* mechanism) or via **ATS2** (that corresponds to an *hat* mechanism). Our results predict **ATS1** and **ATS2** to lie 8.53 and 15.77 kcal·mol⁻¹, respectively. For the *anti*-HCOOH + Cl, reaction 3 starts with the formation of the pre-reactive complex **ACR3**, with binding energy of 1.83 kcal·mol⁻¹, and continues via **ATS5** lying 10.81 kcal·mol⁻¹ above the separate reactants to the post reactive complex **ACP5** and the HCO₂ + ClH products. Thus, the elementary reaction path going through the *pcet* mechanism requires to surmount a smaller energy barrier than the elementary reaction taking place through the *hat* mechanism. It is well known that the energy barrier associated to *hat* reaction mechanism depends on the strength of the Y-H bond of the hydrogen to be abstracted (Y-H stand for O-H or C-H in this case). Moreover, Zavitsas and co-workers [36] pointed out that the value of this energy barrier is related to the triplet repulsion energy of the Y•/•Cl pair at the transition structure. This triplet repulsion energy term does not occur in the *pcet* mechanism having thus a smaller energy barrier.

Regarding reaction 4, the *syn*-HCOOH + Cl, starts with the **ACR2** pre-reactive complex, with a computed binding energy of 1.89 kcal·mol⁻¹ and proceeds through **ATS3**, which lies just 0.71 kcal·mol⁻¹ above the energy of the separate reactants. Its fate is the post reactive complex **ACP3** occurring before the release of the *cis*-HOCO + ClH products. The *anti*-HCOOH + Cl is much more complex since different theoretical approaches predict very different structures for the **ATS4** transition state. Figure 3 shows that for the BH&HLYP and QCISD theoretical approaches, the Cl-H and H-C distances of the hydrogen being transferred are close to 1.5 and 1.3 Å, respectively. The MP2 approach predicts 1.853 and 1.156 Å, respectively, whereas the most accurate CCSD(T) method predicts distances of 1.979 and 1.135 Å, respectively, indicating an early transition state. These results reveal the important effect of allowing for higher excitations in the wavefunction, while the better results of the MP2 method compared, for instance with QCISD, suggests the existence of error compensation. These large differences in the predicted geometrical parameters of the stationary points also result in large differences in the CCSD(T)/CBS predicted relative energy. Thus, Table 1 shows that at BH&HLYP and QCISD optimized geometries, the calculations predict **ATS4** to lie below the reactants and the **ACR3** pre-reactive complex, even in terms of the free energy at 298 K whereas for the MP2 and CCSD(T) optimized structures the calculations predict **ATS4** to lie above the **ACR3** in terms of energy and above the **ACR3** and the separate reactants in terms of free energy at 298 K. The differences in the relative CCSD(T)/CBS energies at the geometries optimized with the distinct approaches rise up to 3.74 kcal·mol⁻¹

In summary, our calculations show that the abstraction of the formyl hydrogen by chlorine atom is much more favorable than the abstraction of the acidic hydrogen, which is in agreement with the fact that the bond dissociation energy of the C-H (96.2 ± 0.7 kcal·mol⁻¹) is much smaller than the bond dissociation energy of the O-H bond in formic acid (112.2 ± 3.1 kcal·mol⁻¹).^[37] Finally, it is worth noting at this point that, our results compare quite well with those reported by Ng and co-workers,^[10] who devoted great effort to the study of the processes involving the abstraction of the formyl hydrogen by chlorine atom (reaction 4).

	Method ^{a, b}	ΔE	$\Delta (E+ZPE)$	$\Delta H(298K)$	$\Delta G(298K)$
<i>syn</i>-HCOOH + NH₂					
<i>syn</i>-HCOOH + NH₂	A/B/C/D	0.00	0.00	0.00	0.00
BCR1	A	-9.18	-7.08	-7.48	0.73
	B	-9.14	-7.00	-7.35	0.74
	C	-9.17	-7.05	-7.46	0.83
	D	-9.16	-7.04	-7.45	0.84
BTS1	A	1.20	1.94	0.54	11.23
	B	1.24	1.95	0.60	11.19
	C	1.04	2.44	0.93	11.86
	D	1.16	2.56	1.05	11.98
BTS2	A	4.77	5.05	3.98	13.82
	C	5.86	6.36	5.13	15.33
BCP1	A	-1.12	1.82	1.18	10.29
	B	-1.15	1.58	0.92	10.13
BCR2	A	-3.98	-2.55	-2.51	4.26
	B	-3.98	-2.57	-2.50	4.21
	C	-3.99	-2.56	-2.53	4.37
	D	-3.98	-2.55	-2.53	4.38
BTS3	A	9.87	9.18	8.32	17.32
	B	9.92	9.22	8.38	17.36
	C	10.01	9.39	8.51	17.57
	D	9.98	9.36	8.48	17.55
BCP2	A	-21.66	-18.18	-18.66	-10.45
	B	-21.67	-18.08	-18.52	-10.44
	C	-21.74	-18.33	-18.83	-10.57
HCOO + NH₃	A	7.01	4.34	4.29	4.12
<i>cis</i>-HOCO + NH₃	A	-8.32	-7.05	-7.01	-7.74
<i>anti</i>-HCOOH + NH₂					
<i>anti</i>-HCOOH + NH₂	A/B/C/D	0.00	0.00	0.00	0.00
BCR3	A	-8.81	-6.88	-7.02	0.09
	B	-8.80	-6.64	-6.94	0.90

	C	-8.80	-6.81	-6.97	0.14
	D	-8.80	-6.81	-6.97	0.14
BTS4	A	5.54	5.39	4.43	13.64
	B	5.54	5.45	4.47	13.81
	C	5.61	5.63	4.61	14.03
	D	5.60	5.62	4.60	14.02
BCP3	A	-26.93	-23.21	-23.55	-16.08
	B	-26.95	-23.12	-23.42	-16.13
	C	-26.98	-23.29	-23.64	-16.15
BTS5	A	9.26	8.73	7.87	17.00
BCP4	A	-1.71	0.29	0.30	7.07
HCOO + NH₃	A	2.76	0.28	0.19	0.07
<i>trans</i>-HOCO + NH₃	A	-14.35	-12.68	-12.67	-13.33

- a) A stands for CCSD(T)/CBS//BH&HLYP/aug-cc-pVTZ; B stands for CCSD(T)/CBS//QCISD/6-311+G(2df,2p); C stands for CCSD(T)/CBS//MP2/6-311+G(2df,2p); D stands for CCSD(T)/CBS//CCSD(T)/6-311+G(2df,2p) with ZPE and enthalpy and free energy corrections at MP2 level of theory.
- b) The T1 diagnostic values of the CCSD wave functions are: 0.015, 0.032, 0.043, 0.033, 0.014, 0.022, 0.018, 0.015, 0.033, 0.018, 0.040, and 0.019 for **BCR1**, **BTS1**, **BTS2**, **BCP1**, **BCR2**, **BTS3**, **BCP2**, **BCR3**, **BTS4**, **BCP3**, **BTS5**, and **BCP4**, respectively.

These results show that the oxidation of formic acid by amidogen radical is quite different to the oxidation by chlorine atom. First, because the abstraction of the acidic hydrogen via *pcet* mechanism requires a much smaller energy barrier in the reaction of NH₂ (**BTS1**, 2.56 kcal·mol⁻¹) than in the reaction with Cl (**ATS1**, 8.53 kcal·mol⁻¹), which is due to the fact that chlorine atom is much more electronegative than nitrogen atom so that Cl hampers the transfer of the electron from the oxygen atom of the carbonyl group and second, because the abstraction of the formyl hydrogen is less favorable in the reaction with amidogen radical, even in the process through **BTS2** via *hat* mechanism. In **BTS2** there is an additional stabilizing effect due to the existence of a hydrogen bond between the oxygen atom of the carbonyl group of the acid moiety and one hydrogen atom of the amidogen moiety (see Figure 1) and consequently, the energy barrier of this process is smaller than the energy barrier of the abstraction of formyl hydrogen via **BTS3**, despite one would expect the opposite situation if one would take into account the bond

dissociation energy (BDE) of the C-H and O-H of formic acid only (see above). Again, the reaction through the *pcet* mechanism (via **BTS1**) requires to surmount a smaller energy barrier than the reaction through the *hat* mechanism (via **BTS2**). At this point it is also worth to compare the results of this investigation with the gas phase oxidation of formic acid by hydroxyl radical.[6] For the reaction with OH, calculations predict that the abstraction of the acidic hydrogen through a *pcet* mechanism, with the transition state lying just 0.51 kcal·mol⁻¹ above the energy of the separate reactants, whereas the transition states occurring via *hat* mechanism lie 3.40 and 1.17 kcal·mol⁻¹, above the energy of the reactants for the abstraction of the acidic and formyl hydrogen atoms respectively. Thus, it appears that the electronegativity of the radical involved in the *pcet* mechanism plays an important role in the energy barrier involved in this process.

Reaction kinetics

In the previous section we have shown that in all elementary reactions considered in this work except for **ATS4**, the interaction of the radical with formic acid proceeds via the formation of a pre-reactive complex (CR) followed by a transition state (TS) and a post-reactive complex (CP) before the release of the products (Reaction 7).

Moreover, all transition states lie higher in terms of free energy than the reactants and the pre-reactive complexes, so that we can consider that the pre-reactive complex (CR) are in equilibrium with the reactants, and consequently, the rate constants can be calculated according equation 1.

$$k_I = \frac{k_1}{k_{-1}} k_2 = K_{eq} k_2 \quad [1]$$

where K_{eq} is the equilibrium constant of the pre-reactive complex and k_2 is the rate constant of the unimolecular reaction between the pre-reactive complex to the reaction product. The K_{eq} values have been calculated according to equation 2.

$$K_{eq} = \frac{Q_{CR}}{Q_{syn-(anti)-HCOOH}Q_X} e^{\frac{-(E_C-E_R)}{RT}} \quad [2]$$

where the Q values correspond to the partition functions and E_C and E_R are the energies of the complex and reactants. For k_2 , we have used the conventional transition state theory (CTST) and the canonical variational transition state theory (CVTST),[39] following equation 3.

$$k_2 = \kappa \frac{k_B T}{h} \frac{Q_{GT}(S^*)}{Q_{CR}} e^{\frac{-V(S^*)}{k_B T}} \quad [3]$$

where s^* is the free energy maximum along the reaction path at temperature T , $Q_{Complex}$ is the partition function of the pre-reactive complex, $Q_{GT}(s^*)$ is the generalized transition state partition function and $V(s^*)$ is the potential energy and κ is the tunneling parameter, that has been computed with the small curvature approach (SCT) in the case of the CVTST calculations and with the zero curvature approach (ZCT) with the CST calculations. In all cases but for **ATS4**, these calculations have been done employing the Hessian matrices computed at the BH&HLYP/aug-cc-pVTZ level of theory and energies calculated at the best level of theoretical treatment CCSD(T)/CBS). In all cases, the partition functions have been calculated from a rigid rotor harmonic oscillator approximation. For the reaction via **ATS4** we calculated the rate constant according to conventional transition state theory with equation 4 where ΔG corresponds to the free energy of the transition state minus the free energy of the separated products, and we have considered the free energy computed with CCSD(T)/CBS energies and free energy corrections obtained at MP2 level of theory (see below).

$$k_{ATS4} = \frac{k_B T}{h} e^{\frac{-\Delta G}{RT}} \quad [4]$$

The two reactions for the removal of formic acid by Cl or NH_2 radicals, namely abstraction of the acidic hydrogen (reactions 3 and 5) and abstraction of the formyl hydrogen (reactions 4 and 6) can be written as:

(X = Cl or NH_2)

Where the whole reaction rates are given by

$$v = -\frac{d[HCOOH]}{dt} = k_a[HCOOH][X] + k_b[HCOOH][X] = (k_a + k_b) [HCOOH][X] \quad [5]$$

$$k_{\text{tot}} = k_a + k_b$$

The reaction rate for the abstraction of the acidic hydrogen can be written as

$$v_a = -\frac{d[\text{HCOOH}]}{dt} = (k_{\text{XTS1}} + k_{\text{XTS2}})[\text{syn-HCOOH}][\text{X}] + k_{\text{XTS5}}[\text{anti-HCOOH}][\text{X}]. \quad [6]$$

$$v_b = -\frac{d[\text{HCOOH}]}{dt} = k_{\text{XTS3}}[\text{syn-HCOOH}][\text{X}] + k_{\text{XTS4}}[\text{anti-HCOOH}][\text{X}]. \quad [7]$$

taking into account that

$$[\text{HCOOH}] = [\text{syn-HCOOH}] + [\text{anti-HCOOH}] \quad (10)$$

$$K_{eq-\text{HCOOH}} = \frac{[\text{anti-HCOOH}]}{[\text{syn-HCOOH}]} \quad [8]$$

$$\begin{aligned} v_a &= \frac{(k_{\text{XTS1}} + k_{\text{XTS2}})}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] + \frac{k_{\text{XTS5}} K_{eq-\text{HCOOH}}}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] \\ &= \frac{(k_{\text{XTS1}} + k_{\text{XTS2}}) + k_{\text{XTS5}} K_{eq-\text{HCOOH}}}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] = k_a [\text{HCOOH}][\text{X}] \end{aligned} \quad [9]$$

and

$$\begin{aligned} v_b &= \frac{k_{\text{XTS3}}}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] + \frac{k_{\text{XTS4}} K_{eq-\text{HCOOH}}}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] \\ &= \frac{k_{\text{XTS3}} + k_{\text{XTS4}} K_{eq-\text{HCOOH}}}{(1 + K_{eq-\text{HCOOH}})} [\text{HCOOH}][\text{X}] = k_b [\text{HCOOH}][\text{X}] \end{aligned} \quad [10]$$

where **XTS1**, **XTS2**, **XTS3**, **XTS4**, and **XTS5** stand for **ATS1**, **ATS2**, **BTS3**, **ATS4**, and **ATS5** for X = Cl, and stand for **BTS1**, **BTS2**, **BTS3**, **BTS4**, and **BTS5** for X = NH₂. Please note that k_a = k_{R3} for X = Cl and k_{R5} for X = NH₂ and k_b = k_{R4} for R = Cl and k_{R6} for X = NH₂

Table 3: Rate constants (in $\text{cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) calculated at 298 K with VTST and CTST levels of theory for the whole elementary reactions investigated in this work

	VTST	CTST		VTST	CTST
	(R3) $\text{HCOOH} + \text{Cl} \rightarrow \text{HCOO} + \text{ClH}$			(R5) $\text{HCOOH} + \text{NH}_2 \rightarrow \text{HCOO} + \text{NH}_3$	
k_{ATS1}	2.46×10^{-19}	9.19×10^{-19}	k_{BTS1}	1.69×10^{-15}	3.28×10^{-15}
k_{ATS2}	1.97×10^{-23}	1.31×10^{-22}	k_{BTS2}	1.77×10^{-17}	6.64×10^{-17}
k_{ATS5}	5.05×10^{-19}	5.40×10^{-19}	k_{BTS5}	5.73×10^{-20}	2.77×10^{-18}
k_{R3}^a	2.46×10^{-19}	9.18×10^{-19}	k_{R5}^a	1.71×10^{-15}	3.35×10^{-15}
	(R4) $\text{HCOOH} + \text{Cl} \rightarrow \text{HOCO} + \text{ClH}$			(R6) $\text{HCOOH} + \text{NH}_2 \rightarrow \text{HOCO} + \text{NH}_3$	
k_{ATS3}	1.13×10^{-13}	2.91×10^{-12}	k_{BTS3}	9.73×10^{-19}	1.61×10^{-17}
	$(2.00 \times 10^{-13})^b$				
k_{ATS4}	--	7.27×10^{-10}	k_{BTS4}	8.81×10^{-17}	8.65×10^{-15}
	$(1.48 \times 10^{-12})^b$				
k_{R4}^a	$1.14 \times 10^{-13}^d$	3.69×10^{-12}	k_{R6}^a	1.07×10^{-18}	2.53×10^{-17}
k_(R3+R4)	$1.14 \times 10^{-13}^d$	3.69×10^{-12}	k_(R5+R6)	1.71×10^{-15}	3.37×10^{-15}
Exp^c	$1.8 \pm 0.12 / 2.0 \times 10^{-13}$				

a) k_{R3} and k_{R5} are calculated according equation 9; k_{R4} and k_{R6} are calculated according equation 10.

b) Computed by Ng and co-workers at 300K.[10]

c) Experimental values. [7]

d) Computed according equation 10 with k_{ATS3} of our work and k_{ATS4} from Ng and co-workers.[10]

In Table 3 we have collected the rate constants of all elementary reactions investigated in this work along with the whole rate constants of reactions 3 to 6, computed at variational and conventional transition state theory at 298 K. Our results show that conventional transition state theory predicts rate constants between two times and two orders of magnitude greater than those predicted with variational transition state theory, which is mainly due to different tunneling corrections obtained with the ZCT approach (see supplementary information).

For reaction 3 (abstraction of the acidic hydrogen by Cl), our calculations predict a rate constant of $2.46 \times 10^{-19} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which correspond exclusively to the process taking place through the *pcet* mechanism (via **ATS1**). Our computed rate constant for the abstraction of the acidic hydrogen atom of the *anti*-HCOOH conformer is even greater, ($5.05 \times 10^{-19} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ via **ATS5**), but its contribution to the total rate constant is negligible because the rate constant is multiplied by the equilibrium constant of the *syn-anti*-HCOOH according 9. Reaction 4 (abstraction of formyl hydrogen atom by Cl) is much faster and our computed rate constant is about six orders of magnitude greater than reaction 3. Our computed rate constant for the process through **ATS3** is $1.13 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which compares well with the $2.00 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, reported by Ng and co-workers.[10] In that work, the authors report an extensive discussion on the different effects contributing to the rate constant and we refer the reader to this work for a more detailed discussion. For the reaction path through **ATS4**, all of our calculations employing different theoretical approaches predict the transition state to lie below the energies of the reactants and pre-reactive complex (see Table 1), except the relative free energies with the corrections computed at MP2 level of theory (see discussion in the previous section) and therefore we were not able to compute VTST rate constants for this process. Instead, we have performed CTST rate constants and the corresponding value at 298 K is $7.27 \times 10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. For this process, Ng and co-workers report a ICVT rate constant of $1.48 \times 10^{-12} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ at 300 K,[10] which is consistent with the differences between conventional and variational rate constants discussed above. With these values, Ng and co-workers[10] also conclude that the reaction via **ATS4** has a negligible effect of the whole rate constant, and if we take in equation 10 the rate constant of our CVT value for the process via **ATS3** and the Ng and co-workers value for the reaction through **ATS4**, we predict a whole rate constant of 1.14

$\times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, in very good agreement with the experimental measured values of $1.8 \pm 0.12 / 2.0 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. [7] All these results also confirm that chlorine atom exclusively abstracts the formyl hydrogen atom of formic acid.

For reaction 5, abstraction of the acidic hydrogen by NH_2 radical, we have computed a rate constants of the process through the *pcet* mechanism (via **BTS1** at 298 K) of $1.69 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which is two and five orders of magnitude greater than the reactions involving an *hat* mechanism (via **BTS2** and **BTS5**, see Table 3. The whole rate constant for reaction 5 is computed to be $1.71 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ at 298 K according equation 9. The abstraction of the formyl hydrogen atom by amidogen radical (via **BTS3** and **BTS4**, reaction 6) is slower and we have computed a rate constant of $1.07 \times 10^{-18} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ at 298 K, which is three orders of magnitude smaller than reaction 5 (see Table 3). Consequently, amidogen radical exclusively abstracts the acidic hydrogen atom of formic acid. This contrast with the results of the reaction with chlorine discussed previously, but are in concordance with the gas phase reaction of formic acid with hydroxyl radical, where the abstraction of the acidic hydrogen takes place predominantly, and occurs through a *pcet* mechanism. [6]

The atmospheric impact of the reactions investigated in this work depend on their rate constants but also on the concentration of these species in the troposphere and also on the competition of the reaction of these species with other atmospheric trace gasses. It is well known that one of the main sinks of gas phase formic acid in the atmosphere is the reaction with hydroxyl radical, whose rate constant at 298 K is $3.2 \pm 1 / 4.9 \pm 1.2 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. [3] The rate constant for the reaction of formic acid with chlorine atom is slightly smaller, of $1.8 \pm 0.12 / 2.0 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ [7] and, for a typical tropospheric concentration of $[\text{OH}]$ of $4.5 \cdot 10^6 \text{ molecules} \cdot \text{cm}^{-3}$, [40] the removal of formic acid by hydroxyl radical is dominant. However, Ng and co- workers, [10] have pointed out that, at low temperatures and in areas with large concentration of chlorine atoms, like in marine boundary layers, the role of chlorine atom cannot be ignored. In these regions, chlorine atom concentrations are of $3 \times 10^5 \text{ atom} \cdot \text{cm}^{-3}$ [12] with estimated upper limits of $[\text{Cl}]$ of $10^6 \text{ atmos} \cdot \text{cm}^{-3}$. [41] At the same time, hydroxyl radical concentration is measured to be $6 \times 10^5 \text{ molecules} \cdot \text{cm}^{-3}$ [12], thus increasing the potential role of chlorine atoms.

Our computed rate constants for the reaction of HCOOH with NH₂ is about two orders of magnitude smaller ($1.71 \times 10^{-15} \text{ cm}^3 \cdot \text{at 298 K}$) that the rate constants for the reaction with OH and Cl and therefore it would be expected that much higher concentrations of amidogen radical are needed for this reaction to play a role. However, it is known that amidogen radical can react with molecular oxygen and nitrogen dioxide, with rate constants of 6×10^{-21} and $2 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, respectively at 298 K, [42] and taking into account that the atmospheric concentration of these species are 5.15×10^{18} and up to $1.34 \times 10^{11} \text{ molecules} \cdot \text{cm}^{-3}$, [43] compared with the atmospheric concentration of formic acid, which can rise up to $1.96 \times 10^{11} \text{ molecules} \cdot \text{cm}^{-3}$. [44] According to these values, the oxidation of formic acid by amidogen radical is predicted to be about two orders of magnitude smaller that the reaction rate of the reaction of amidogen radical with molecular oxygen and about four orders of magnitude smaller than the reaction of NH₂ with NO₂, and therefore we conclude that that atmospheric relevance of the oxidation of formic acid by amidogen radical is very small.

Conclusions

In this work, the reaction mechanisms and kinetics for the gas phase oxidation of formic acid by chlorine atom and amidogen radical have been investigated employing high level theoretical methods. There are two possible processes for these reactions, namely the abstraction of the acidic hydrogen and the abstraction of the formyl hydrogen by the radicals. We have studied these processes for the *syn*- and *anti*- conformers of formic acid.

The energy barrier for the abstraction of the acidic hydrogen lies $8.53 \text{ kcal} \cdot \text{mol}^{-1}$ above the energy of the reactants for the reaction with Cl, but $2.56 \text{ kcal} \cdot \text{mol}^{-1}$ for the reaction with NH₂. In both cases the reaction proceeds through a *pcet* mechanism and the differences in the high of the energy barrier can be attributed to the difference on the electronegativity of the attacking radical.

The energy barrier for the abstraction of the formyl hydrogen lies 0.73 and $-3.05 \text{ kcal} \cdot \text{mol}^{-1}$ for the reaction of chlorine atom with *syn*- and *anti*-HCOOH, respectively, and 9.39 and $5.62 \text{ kcal} \cdot \text{mol}^{-1}$ for the equivalent processes of the reaction with NH₂.

The reaction of HCOOH with Cl produces exclusively HOCO and ClH, and our calculated rate constant at 298 K is $1.14 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ in good agreement

with the experimental value $1.8 \pm 0.12 / 2.0 \times 10^{-13} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. The reaction proceeds exclusively by abstraction of the formyl hydrogen atom, via *hat* mechanism.

The calculated rate constant, at 298 K, for the reaction of HCOOH with NH₂ is $1.71 \times 10^{-15} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. The reaction goes through the abstraction of the acidic hydrogen atom, via a *pcet* mechanism, and leads to the formation of HCOO + NH₃.

Acknowledgements

We thank the Generalitat de Catalunya (Grant 2017SGR348) for financial support. We also acknowledge the Consorci de Serveis Universitaris de Catalunya (CSUC) for providing computational resources.

Supplementary information:

Contains equilibrium and rate constants for all elementary processes investigated, Figures with the most relevant optimized geometrical parameters, absolute energies and geometries of all stationary points.

Disclosure statement

No conflict of interest was reported by the authors.

Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

References.

- [1] M. Legrand and M. de Angelis, *J. Geophys. Res.* **100**, 1445 (1995); Daniel Grosjean, *Environ. Sci. Technol.* **23**, 1506 (1989); H. Puxbaum, C. Rosenberg, M. Gregori, C. Lanzerstorfer, E. Ober, and W. Winiwarter, *Atmos. Environ.* **22** (12), 1841 (1988); Eugenio Sanhueza, Magaly Santana, and Mariela Hermoso, *Atmos. Environ.* **26A** (8), 1421 (1992); Kit Granby, Carsten S. Christensen, and Christian Lohse, *Atmos. environ.* **31** (10), 1403 (1997); J. Kesselmeier, *J. Atmos. Chem.* **39**, 219 (2001).
- [2] R. W. Talbot, K. M. Beecher, R. C. Harriss, and W. Cofer III, *J. Geophys. Res.* **93**, 1638 (1988); R. W. Talbot, M. O. Andreae, H. Berresheim, D. Jacob, and H. M. Beecher,

- J. Geophys. Res.* **95**, 16799 (1990); K. Kawamura, L. Ling, and I. R. Kaplan, *Environ. Sci. Technol.* **19**, 1082 (1985); F. Su, G. Calvert, and HJ. H. Shaw, *J. Phys. Chem.* **84**, 239 (1980); D. J. Jacob and S. C. Wofsy, *J. Geophys. Res.* **93**, 1477 (1988); Peter Neeb, Osamu Horie, and Geert K. Moortgat, *J. Phys. Chem. A* **102**, 6778 (1998); Eric Grosjean, Jailson Bittercourt de Andrade, and Danial Grosjean, *Environ. Sci. Technol.* **30**, 975 (1996); R. Atkinson, B. J. Finlayson, and J. N. Pitts Jr., *J. Am. Chem. Soc.* **95**, 7592 (1973); Roger Atkinson, *Atmospheric Environment* **24A**, 1 (1990); K. Granby, A. H. Egelov, T. Nielsen, and C. Lohse, *J. Atmos. Chem.* **28**, 195 (1997).
- [3]C. Zetzsch and F. Stuhl, in *Proceeding of the Second European Symposium*, edited by B. Versino and H. Ott (Reidel, Dordrecht, 1982) pp. 129; P. H. Wine, R. J. Astalos, and R. L. Mauldin III, *J. Phys. Chem.* **89**, 2620 (1985); Gurvinder S. Jolly, Donald J. McKenney, Donald L. Singleton, George Paraskevopoulos, and Alain R. Bossard, *J. Phys. Chem.* **90**, 6557 (1986); Philippe Dagaut, Tomothy J. Wallington, Renzhang Liu, and Michal J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988); Donald L. Singleton, George Paraskevopoulos, Robert S. Irwin, Gurvinder S. Jolly, and Donald J. Mckenney, *J. Am. Chm. Soc.* **110**, 7786 (1988).
- [4]Annia Galano, J. Raúl Alvarez-Idaboy, Ma. Esther Ruiz-Santoyo, and Annik Vivier-Bunge, *J. Phys. Chem. A* **106**, 9520 (2002).
- [5]S. Olivella, J. M. Anglada, A. Sole, and J. M. Bofill, *Chem. Eur. J.* **10**, 3404 (2004).
- [6]J. M. Anglada, *J. Am. Chem.Soc.* **126** (31), 9809 (2004).
- [7]Timothy J. Wallington, Jean M. Andino, James C. Ball, and Steven M. Japar, *J. Atmos. Chem.* **10** (3), 301 (1990); Qiang Li, Michael C. Osborne, and Ian W. M. Smith, *Int J Chem Kinet* **32**, 85 (2000).
- [8]B. Ruscic, M. Schwarz, and J. Berkowitz, *J. Chem. Phys.* **91**, 6780 (1989); Geoffrey S. Tyndall, Timothy J. Wallington, and Alan R. Potts, *Chem. Phys. Lett.* **186** (2), 149 (1991).
- [9]Guang-Hui Yang , Xiang Zhang , Hong-Xing Zhang , Ke-Li Han , and Jia-Chong Sun *Acta Chim. Sin.* **61**, 499 (2013).
- [10]M. Ng, D. K. W. Mok, E. P. F. Lee, and J. M. Dyke, *Mol. Phys.* **113** (13-14), 1511 (2015).
- [11]R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr, M. J. Rossi, and J. Troe, *J. Phys. Chem. Ref. Data* **26** (3), 521 (1997); B.J. Finlayson-Pitts, *Res. Chem. Intermed.* **19**, 235 (1993); H. B. Singh and J. F. Kasting, *J. Atmos. Chem.* **7** (3), 261 (1988).
- [12]Chang-Tang Chang, Tsun-Hsien Liu, and Fu-Tien Jeng, *Environ. Res.* **94** (1), 67 (2004).
- [13]William R. Simpson, Steven S. Brown, Alfonso Saiz-Lopez, Joel A. Thornton, and Roland von Glasow, *Chem. Rev.* **115** (10), 4035 (2015).
- [14]B. J. Finlayson-Pitts, *Chem. Rev.* **103** (12), 4801 (2003).
- [15]Matthew J. Alvarado, Karen E. Cady-Pereira, Yaping Xiao, Dylan B. Millet, and Vivienne H. Payne, *Atmosphere* **2** (4), 633 (2011).
- [16]W. H. Schlesinger and A. E. Hartley, *Biogeochemistry* **15** (3), 191 (1992); S. C. Wofsy and M. B. McElroy, *Can. J. Chem.* **52** (8), 1582 (1974); R. J. Cicerone, *Rev. Geophys.* **13** (3), 900 (1975); P. S. Monks, C. Granier, S. Fuzzi, A. Stohl, M. L. Williams, H. Akimoto, M. Amann, A. Baklanov, U. Baltensperger, I. Bey, N. Blake, R. S. Blake, K. Carslaw, O. R. Cooper, F. Dentener, D. Fowler, E. Fragkou, G. J. Frost, S. Generoso, P. Ginoux, V. Grewe, A. Guenther, H. C. Hansson, S. Henne, J. Hjorth, A. Hofzumahaus, H. Huntrieser, I. S. A. Isaksen, M. E. Jenkin, J. Kaiser, M.

- Kanakidou, Z. Klimont, M. Kulmala, P. Laj, M. G. Lawrence, J. D. Lee, C. Liousse, M. Maione, G. McFiggans, A. Metzger, A. Mieville, N. Moussiopoulos, J. J. Orlando, C. D. O'Dowd, P. I. Palmer, D. D. Parrish, A. Petzold, U. Platt, U. Poeschl, A. S. H. Prevot, C. E. Reeves, S. Reimann, Y. Rudich, K. Sellegri, R. Steinbrecher, D. Simpson, H. ten Brink, J. Theloke, G. R. van der Werf, R. Vautard, V. Vestreng, Ch Vlachokostas, and R. von Glasow, *Atmos. Environ.* **43** (33), 5268 (2009).
- [17] B. Finlayson-Pitts. and Jr J. Pitts, *Chemistry of the Upper and Lower Atmosphere. Theory, Experiments, and Applications* (Academic Press, San Diego, 2000).
- [18] Thomas Röckmann, Jan Kaiser, John N. Crowley, Carl A. M. Brenninkmeijer, and Paul J. Crutzen, *Geophys. Res. Lett.* **28** (3), 503 (2001); J. Kaiser and T. Rockmann, *Geophys. Res. Lett.* **32** (15) (2005).
- [19] Josep M. Anglada, Santiago Olivella, and Albert Solé, *J. Am. Chem. Soc.* **136** (19), 6834 (2014); Josep M. Anglada, Santiago Olivella, and Albert Sole, *Phys. Chem. Chem. Phys.* **16** (36), 19437 (2014).
- [20] Axel D. Becke, *J. Chem. Phys.* **98**, 1372 (1993).
- [21] K. Ishida, K. Morokuma, and A. Kormornicki, *J. Chem. Phys.* **66**, 2153 (1977); C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.* **90**, 2154 (1989); C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.* **94**, 5523 (1990).
- [22] John A. Pople, Martin Head-Gordon, and Krishnan Raghavachari, *J. Chem. Phys.* **87** (10), 5968 (1987).
- [23] M. J. Frisch, J. A. Pople, and J. S. Binkley, *J. Chem. Phys.* **80**, 3265 (1984); W. J. Hehre, L. Radom, P.v.R. Schleyer, and J. A. Pople, in *Ab Initio Molecular Orbital Theory* (John Wiley, New York, 1986) pp. 86-87.
- [24] K. L. Bak, J. Gauss, P. Jorgensen, J. Olsen, T. Helgaker, and J. F. Stanton, *J. Chem. Phys.* **114** (15), 6548 (2001).
- [25] D. Jayatilaka and T. J. Lee, *J. Chem. Phys.* **98** (12), 9734 (1993).
- [26] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, Jr. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian 03, Revision C.01 (Gaussian, Inc., Wallingford CT, 2004).
- [27] F. Neese, *Wires Comput. Mol. Sci.* **2** (1), 73 (2012).
- [28] G. Shafteenaar and J. H. Noordik, *J. Comput.-Aided Mol. Design* **14**, 123 (2000).
- [29] W. Humphrey, A. Dalke, and K. Schulten, *J. Molec. Graphics.* **14**, 33 (1996).
- [30] D. H. Lu, T. N. Truong, V. S. Melissas, G. C. Lynch, Y.-P. Liu, B. C. Garrett, R. Steckler, A. D. Isaacson, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, and D. G. Truhlar, *Comput. Phys. Commun.* **71**, 235 (1992).
- [31] J. M. Anglada, R. Crehuet, and J. M. Bofill, *Chem. Eur. J.* **5** (6), 1809 (1999).

- [32] John D. Goddard, Yukio Yamaguchi, and Henry F. Schaefer III, *J. Chem. Phys.* **96** (2), 1158 (1992); Mika Pettersson, Ermelinda M. S. Maçôas, Leonid Khriachtchev, Rui Fausto, and Markku Räsänen, *J. Am. Chem. Soc.* **125** (14), 4058 (2003).
- [33] D. Feller, E. S. Huyser, W. T. Borden, and E. R. Davidson, *J. Am. Chem. Soc.*, **105**, 1459 (1983).
- [34] J. M. Anglada, S. Olivella, and A. Sole, *J. Phys. Chem. A* **110** (5), 1982 (2006); J. Gonzalez and J. M. Anglada, *J. Phys. Chem. A* **114** (34), 9151 (2010); J. M. Anglada and J. Gonzalez, *ChemPhysChem* **10** (17), 3034 (2009).
- [35] Solvejg Jorgensen, Camilla Jensen, Henrik G. Kjaergaard, and Josep M. Anglada, *Phys. Chem. Chem. Phys.* **15** (14), 5140 (2013).
- [36] A. A. Zavitsas and C. Chatgililoglu, *J. Am. Chem. Soc.* **117** (43), 10645 (1995); Brian P. Roberts, *J. Chem. Soc., Perkin Trans. 2* (12), 2719 (1996); Andreas A. Zavitsas, *J. Chem. Soc., Perkin Trans. 2* (3), 391 (1996); Andereas A. Zavitsas, *J. Am. Chem. Soc.* **120**, 6578 (1998).
- [37] S. W. Benson, *Thermochemical Kinetics* 2nd ed. ed. (Wiley-Interscience, New York, 1976).
- [38] Josep M. Anglada and Albert Solé, *J. Phys. Chem. A* **121** (51), 9698 (2017).
- [39] Bruce C. Garrett and Donald G. Truhlar, *J. Phys. Chem.* **83** (8), 1052 (1979); Donald G. Truhlar and Bruce C. Garrett, *Acc. Chem. Res.* **13**, 440 (1980); Yi Ping Liu, Gillian C. Lynch, Thanh N. Truong, Da Hong Lu, Donald G. Truhlar, and Bruce C. Garrett, *J. Am. Chem. Soc.* **115** (6), 2408 (1993).
- [40] Paul S. Monks, *Chem. Soc. Rev.* **34**, 376 (2005).
- [41] C. J. Young, R. A. Washenfelder, P. M. Edwards, D. D. Parrish, J. B. Gilman, W. C. Kuster, L. H. Mielke, H. D. Osthoff, C. Tsai, O. Pikelnaya, J. Stutz, P. R. Veres, J. M. Roberts, S. Griffith, S. Dusanter, P. S. Stevens, J. Flynn, N. Grossberg, B. Lefer, J. S. Holloway, J. Peischl, T. B. Ryerson, E. L. Atlas, D. R. Blake, and S. S. Brown, *Atmos. Chem. Phys.* **14** (7), 3427 (2014).
- [42] R. Atkinson, D. L. Baulch, R. A. Cox, J. N. Crowley, R. F. Hampson, R. G. Hynes, M. E. Jenkin, M. J. Rossi, and J. Troe, *Atmos. Chem. Phys.* **4**, 1461 (2004).
- [43] Peter Warneck and Jonathan Williams, *The atmospheric Chemist's Companion* (Springer Netherlands, 2012).
- [44] J. J. Schultz Tokos, S. Tanaka, T. Morikami, H. Shigetani, and Y. Hashimoto, *J. Atmos. Chem.* **14** (1), 85 (1992).

Graphical Abstract