



Highly toxic air
pollutants from
halogenated
formaldehydes

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A theoretical model on the formation mechanism and kinetics of highly toxic air pollutants from halogenated formaldehydes reacted with halogen atoms

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Abstract

The atmospheric reactions of halogenated formaldehydes with halogen atoms were investigated by high-accuracy molecular orbital calculation. Studies showed that halogen atoms could easily abstract hydrogen atom from halogenated formaldehydes to form halogenated formyl radical and hydrogen halide (HX). In specific areas with high concentration of halogen atoms, such as the marine boundary layer (MBL), halogenated formyl radical was easily to react with halogen atoms and finally transformed into HX and CO₂ in the presence of water; otherwise, this radical was degraded to CO₂, halogen gas, and halogenated oxide. By using the canonical variational transition state theory, the kinetics calculations were performed within a wide atmospheric temperature range of 200–368 K, and theoretical values agreed well with the available experimental data. Under atmospheric conditions, the rate constants decreased as altitude increased, and especially the rate constants of halogen atoms reaction with FCHO quickly reduced. Although the reactions of halogenated formaldehydes with F atoms were more easily occurred than did those with Cl and Br atoms, the two latter reactions were still important atmospheric degradation process, especially in the MBL. The modified Arrhenius formulas of rate constants within the atmospheric temperature range were fitted, which helped to understand the established atmospheric model and estimate the contribution of title reactions to atmospheric chemistry pollution.

1 Introduction

The Antarctic-like ozone hole was proposed in the Arctic in 2011 Nature paper (Manney et al., 2011). This proposal indicated that the implementation of the Montreal Protocol did not well restrain chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) to destroy the ozone and increase the stratospheric halogen loading (Manney et al., 2011; Newman et al., 2009) despite very low anthropogenic emission of CFCs, HCFCs and halogen (Manney et al., 1994; Newman et al., 2009). Halogenated

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tions of FCHO + F (Francisco et al., 1990; Wu et al., 2003) and FCHO + Cl (Wu et al., 2002). And these studies achieved different conclusions regarding the contribution of addition pathways. For instance, the result obtained by Francisco et al. (Francisco et al., 1990) concluded that addition of fluorine atom onto FCHO was competitive, which contradicted Wu et al.'s results (Wu et al., 2003). Furthermore, no studies on the kinetic data of the addition pathways have been conducted by these theoretical researchers. To our knowledge, no experimental or theoretical investigations have been reported on the title reactions, except the ClCHO + Cl and FCHO + F/Cl reactions. Thus, to gain insight into the environmental impact of halogenated formaldehydes, a systematic theoretical study is required to illustrate the detailed atmospheric reaction mechanisms and kinetics of the title reactions, and the potential importance of the title reactions as an atmospheric degradation pathway is also deserved to qualitatively investigate with theoretical calculation method.

In this study, the atmospheric reaction mechanisms and kinetics of halogenated formaldehydes reaction with halogen atoms were investigated using the dual-level direct dynamics (DLD) method. The temperature-dependent rate constants of the title reactions in atmospheric environment were deduced using canonical variational transition state theory (CVT) with small curvature tunneling (SCT) to simulate the troposphere temperature range within the atmospheric temperature range of 200–368 K. Furthermore, the calculated data were compared with the available experimental results to assess the reliability of the proposed model.

2 Methods

All quantum chemistry and computational kinetics were calculated with Gaussian 03 program (Frisch et al., 2003) and Polyrate 9.4.1 program (Corchado et al., 2002), respectively. Geometric parameters and frequency calculations were carried out at the second-order Møller–Plesset perturbation theory (MP2) with sets of polarization function, i.e., MP2/6-311G(d,p). The vibrational frequencies were performed to character-

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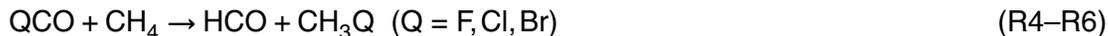
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indicated that the H atom of halogenated formaldehydes should be abstracted more easily from FCHO to ClCHO to BrCHO. To further investigate the reactivity of H atom, the C–H bond-dissociation energies ($D_{298}^0(\text{C–H})$) in carbonyl group were calculated, and the results were also listed in Table 1. For the three halogenated formaldehydes, the corresponding $D_{298}^0(\text{C–H})$ values were 96.42, 86.19, and 81.04 kcal mol⁻¹, respectively. This result was in line with the order of the ΔE , indicating that the halogen atom substitutions from F to Cl to Br atom can increase the reactivity of H atom. The reaction enthalpies obtained were -40.75 (F-R_{abs-F}), -50.89 (F-R_{abs-Cl}), and -56.04 (F-R_{abs-Br}) kcal mol⁻¹, exhibiting the same trend as that of potential barrier heights. Similar conclusions can be drawn regarding different halogenated formaldehydes reaction with Cl and Br atoms.

As for the attack of three halogen atoms to FCHO, the ΔE s and ΔH_{298}^0 s were increased when the halogen atoms changed from F to Cl to Br atoms. This finding suggested that halogenated formaldehydes could be more easily abstracted by F atoms than Cl or Br atoms. However, some differences were observed in the reactions of ClCHO and BrCHO with different halogen atoms. The lowest ΔE was obtained in Cl-R_{abs-Cl} (-1.25 kcal mol⁻¹) and Cl-R_{abs-Br} (-1.56 kcal mol⁻¹) pathways (Table 1). For F-R_{abs-Cl}, Cl-R_{abs-Cl}, F-R_{abs-Br}, Cl-R_{abs-Br}, and Br-R_{abs-Br} pathways, the energy barrier heights were positive without the ZPE corrections, while it became negative via the ZPE correction (Table 1). This result implied that all the aforementioned pathways can be nearly barrierless (see Supplement).

In addition, the standard formation enthalpy ($\Delta H_{f,298}^0$) of species is necessary to determine the kinetics of reaction process and the thermodynamic properties. Hence, the isodesmic reaction method (IUPAC) was performed to obtain the $\Delta H_{f,298}^0$ of main species without the experimental values, such as ClCHO, BrCHO, and the corresponding radicals, and are presented in Table S4. The method was used in this study as a hypothetical reaction, in which the chemical bond broken model in the reactants is the same as the formed model in the products. Therefore, the following isodesmic re-

actions were chosen due to the simple configuration of CH₄ (Ji et al., 2007):



5 The derivation procedure was as follows: (1) the SPE was calculated at the PMP2/6-311+G(3df,3pd) level using the geometries obtained by the MP2/6-311G(d,p) level for all products and reactants involved in Reactions (R1)–(R3) and Reactions (R4)–(R6). (2) The heat corrections were used to obtain the ΔH_{298}^0 of Reactions (R1)–(R3) and Reactions (R4)–(R6) at 298 K using standard statistical thermodynamic meth-
10 ods. (3) The aforementioned reaction enthalpies were combined with the known experimental data in Reactions (R1)–(R3) and (R4)–(R6) (HCHO $-27.69 \text{ kcal mol}^{-1}$; HCO $-10.39 \text{ kcal mol}^{-1}$; CH₃Cl, $-19.99 \text{ kcal mol}^{-1}$; CH₃F, $-55.97 \text{ kcal mol}^{-1}$; CH₃Br, $-9.08 \text{ kcal mol}^{-1}$; CH₄, $-17.89 \text{ kcal mol}^{-1}$) (NIST) to calculate the required $\Delta H_{f,298}^0$. As shown in Table S4, the calculated $\Delta H_{f,298}^0$ were -46.55 , -33.46 , -6.10 , and
15 $1.78 \text{ kcal mol}^{-1}$ for ClCHO, BrCHO, ClCO, and BrCO, respectively. Despite the lack of experimental data that prevents full comparison between the theoretical data and the experimental $\Delta H_{f,298}^0$, the calculated $\Delta H_{f,298}^0$ of FCHO ($-93.53 \text{ kcal mol}^{-1}$) and FCO ($-42.95 \text{ kcal mol}^{-1}$) were in line with the available experimental values ($-89.96 \text{ kcal mol}^{-1}$ and $-41.95 \text{ kcal mol}^{-1}$ for FCHO and FCO, respectively) in the refer-
20 ence (NIST). These results indicated that the PMP2//MP2 level can effectively model the $\Delta H_{f,298}^0$ of these species. Thus, it is expected that the calculated $\Delta H_{f,298}^0$ can provide reliable information for experimental investigations in the future.

3.1.2 X-addition pathways

For Cl or Br atoms addition to three halogenated formaldehydes, the ΔE s of these
25 addition pathways were too high to overcome (Table 1), and these addition pathways were endothermic at least with 10 kcal mol^{-1} (ΔH_{298}^0). Thus, as indicated by the ΔE

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and ΔH_{298}^0 , the addition pathways mentioned above were not likely to occur under the atmospheric conditions. Therefore, this section will mainly focus on the pathways of F atoms addition onto three halogenated formaldehydes (F-addition pathway).

For the F-addition pathways (Fig. S2), the formation of C–F bond was always the same. Thus, the earliness of the TSs can be directly inferred from the forming C ... F distance. That is, the longer the C ... F distance is, the earlier the TS is (Iuga et al., 2008). Fig. S2 showed that the F-TS_{add-Cl} pathway was the earliest among three addition TSs, suggesting that this pathway was more exothermic than the F-R_{add-F} and F-R_{add-Br} pathways according to the Hammond postulate (Hammond, 1955). From Table 1, the order of ΔH_{298}^0 s were in line with that of TSs' geometrical feature mentioned above, and the ΔH_{298}^0 s were -23.73 (F-R_{add-F}), -25.48 (F-R_{add-Cl}), and -23.02 (F-R_{add-Br}) kcalmol⁻¹, respectively. The ΔE s of F-R_{add-X} pathways were 6.20, 7.57, and 8.23 kcalmol⁻¹ (Table 1), respectively, with the increasing order of ΔE (F-R_{add-F}) < ΔE (F-R_{add-Cl}) < ΔE (F-R_{add-Br}). This result indicated that the addition pathways of F atom onto three halogenated formaldehydes would become increasingly more difficult as the molecular weight of halogen atom was increased in halogenated formaldehydes.

For the reaction of FCHO with F atoms, Francisco et al. asserted that the F-addition pathway should be competitive (Francisco et al., 1990); however, Wu et al. obtained a contrary conclusion (Wu et al., 2003). That is, this addition pathway can be completely disregarded. However, our calculation results mentioned above showed that the ΔE of F-addition pathway was higher than that of the corresponding H-abstraction pathway by only 4 kcalmol⁻¹, indicating a kinetic competition between the F-addition and H-abstraction pathways. On the other hand, the ΔH_{298}^0 of F-addition pathway was higher than that of the H-abstraction pathways at least 17 kcalmol⁻¹, suggesting that the F-addition pathway can be ignored thermodynamically. The similar trend was observed for other title atmospheric reactions (F + ClCHO and F + BrCHO reactions). Thus, the contribution of the addition pathway cannot only be determined from the mechanism aspect but also from the kinetic aspect.

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3.1.3 Natural bond orbital (NBO) calculation analysis

To further understand the nature of the title atmospheric reaction mechanisms, the distribution of molecular electrostatic potential as well as NBO charges were carried out at the MP2/6-311G(d,p) level. The results were illustrated in Fig. 1. The most positive and negative potential were assigned to be blue and red, respectively. The more positive potential bond (bluer) is preferred to the nucleophiles attack. Therefore, the blue color of H atoms was deeper than that of C atoms in three halogenated formaldehydes (Fig. 1). That is, the H atoms appeared to have stronger positive potential bond than the C atoms. This finding suggested that the H-abstraction pathways were expected to more likely occur than the corresponding X-addition pathways. The NBO charges estimated for H atoms were 0.105, 0.139, and 0.141 e, respectively, indicating an increased trend from FCHO to ClCHO to BrCHO. Therefore, the H atoms in three molecules were more and more easy to be abstracted by halogen atoms and could be explained in terms of the inductive effect of halogen substitution. For three halogenated formaldehydes, the inductive effect gradually weakens from the electron group -F to -Cl to -Br, and thus the lone pair of electrons on the C atom of carbonyl group were harder and harder to be attracted, thereby increasing the electron density of H atom. As expected, the reactivity of the H-abstraction pathway should be increased from FCHO to ClCHO and then to BrCHO.

3.2 Reaction kinetics

The theoretical predictions herein can help us to develop reliable models for the real atmospheric reactions occurring within the temperature range from the earth surface to tropopause (200–368 K). Therefore, in this section, the DLD calculations were performed with CVT plus interpolated single-point energies method (Chuang et al., 1999) using the PMP2//MP2 level to compute the rate constants at every 10 K as well as the temperature point with the experimental values. For the convenience of the following discussion, the calculated rate constants using CVT plus SCT were denoted as

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CVT/SCT rate constants. The obtained rate constants and the available experimental data were compared in Fig. S3. The temperature dependences of branching ratios between the H-abstraction and the X-addition pathways were also exhibited in Fig. S4. Tables S5 to S7 list the rate constants of each pathway and the total rate constants.

The CVT/SCT rate constants of the F-R_{abs-F} pathway (Fig. S3a) were in good agreement with most experimental data (Behr et al., 1993, 1998; Francisco et al., 1990; Hasson et al., 1998; Meagher et al., 1997). For example, the calculated rate constant of $9.26 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K perfectly matched with the experimental values of $(8.8 \pm 1.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Behr et al., 1993) and $(8.0 \pm 1.0) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Hasson et al., 1998), but was slightly lower than that of $2.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Francisco et al., 1990). With respect to Cl-R_{abs-F} pathway (Fig. S3b), the rate constants matched with the available experimental data (Bednarek et al., 1996; Edney et al., 1992; Meagher et al., 1997; Wallington et al., 1992) in the temperature range of 244–298 K due to the largest deviation within a factor of 1.6. For instance, the calculated rate constant of $1.99 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K agreed well with the experimental values of $(1.9 \pm 0.2) \times 10^{-15}$ (Meagher et al., 1997) and $(2.1 \pm 0.2) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Edney et al., 1992). For Cl-R_{abs-Cl} pathway (Fig. S3c), the calculated rate constant was slightly lower than the data achieved by Sanhueza et al. at 305 K (Sanhueza et al., 1975), but were well accord with other experimental data (Catoire et al., 1996; Libuda et al., 1990; Orlando, 1999; Wallington et al., 1996). Fitted by the CVT/SCT rate constants, the Arrhenius expression was obtained to be $0.99 \times 10^{-11} \exp(-813/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which was in agreement with the experimental expressions of $1.39 \times 10^{-11} \exp[(-866 \pm 168)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ within the temperature range 266–322 K (Libuda et al., 1990). On the basis of the previous discussion, the theoretical results matched well with the available experimental data owing to the largest deviation factor of 2.6. Thus, the rate constants obtained at the PMP2//MP2 levels were reliable within the atmospheric temperature range from 200 to 368 K, which is particularly important for the atmospheric reactions without experimental data.

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The total rate constants of same halogen atom reaction with different halogenated formaldehydes within the temperature range of 200–368 K were demonstrated in Fig. 2a–c. These rate constants at 298 K were also presented in Table 2. For the reactions of F atom with different halogenated formaldehydes (Table 2), the total rate constants obtained were 9.26×10^{-13} (F + FCHO), 1.40×10^{-12} (F + ClCHO), and 5.64×10^{-12} (F + BrCHO) $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ at 298 K. The rate constants increased in the order of $k(\text{F} + \text{FCHO}) < k(\text{F} + \text{ClCHO}) < k(\text{F} + \text{BrCHO})$, which was consistent with the analysis values of potential barrier and NBO calculation. The similar results can be drawn from the reactions of different halogenated formaldehydes with Cl or Br atoms. For the same halogenated formaldehyde reactions with different halogen atoms, the total CVT/SCT results were also summarized in Fig. 2d–f. For the reactions of ClCHO with different halogen atoms (Fig. 2d), the theoretical results decreased in the order of $k(\text{F} + \text{ClCHO}) > k(\text{Cl} + \text{ClCHO}) > k(\text{Br} + \text{ClCHO})$. The similar trend can also be observed for the reactions of FCHO and BrCHO with different halogen atoms. Although the results showed that the reactions of F atoms with halogenated formaldehydes were more important in the degradation processes than those with Cl and Br atoms, the halogenated formaldehydes reacted with Cl and Br atoms were still important under the atmospheric condition due to high concentration of Cl and Br atoms in the MBL. To confirm the contributions of halogen atoms in halogenated formaldehydes, the rate constants of parent formaldehyde reaction with halogen atoms reported by Beukes et al. (Beukes et al., 2000) were also presented in Table 2. The rate constants of formaldehydes with halogen atoms were larger than those of halogenated formaldehydes with the corresponding halogen atoms. This result indicated that the decrease in the atmospheric activities of three halogenated formaldehydes with halogen atom substitution compared with their parent formaldehydes.

Figure S4 showed that for all nine atmospheric reactions, the contribution of all X-addition pathways to the total rate constant was almost equal to zero. Such finding suggested that the addition–elimination pathways were negligible within the temperature range of 200–368 K. Therefore, the halogenated formyl radical (QCO, where Q = F,

Cl, Br) and hydrogen halide (HX, where $X = \text{F, Cl, Br}$) were the dominant products, and the addition intermediates (such as HC(O)F_2 , HC(O)ClF , etc.) were difficult to form at temperature range from 200 to 368 K.

To predict the rate constants of the title reactions in the temperatures without experimental data, the relationship was attempted between the temperature and the rate constants. Within the atmospheric temperature ranges of 200–368 K, the modified Arrhenius formulas were listed in Tables 3 and S8. The pre-exponential factor, the rate constants, and the activation energy can be drawn from these formulas.

3.2.1 The fate of main atmospheric intermediates

To better ascertain the environmental impact of the title atmospheric reactions, CICO and HC(O)ClF were used as examples of the reaction intermediates of the H-abstraction and X-addition channels, respectively. The four possible atmospheric degradation pathways of CICO radical were presented in Fig. 3, in which is corresponding to the elimination of Cl atom from CICO (pathways 1), the reactions of CICO with Cl atom (pathways 2 and 3) and oxygen atom (pathways 4). As shown in Fig. 3, the pathway 1 was difficult to occur because of higher potential barrier height than those of other pathways, whereas pathways 2–4 were all barrierless processes. To further confirm these barrierless processes, the point-wise potential curve was performed and the results were shown in Figs. S5–S7 (the detailed discussion is presented in Supplement). Pathways 2 and 3 were exothermic processes with the exothermic energies of -18.92 and $-19.54 \text{ kcal mol}^{-1}$ to form two isomers *cis*- ClCO_3 and *trans*- ClCO_3 with high activity, in which could be easily transformed to each other with a small internal rotation barrier ($6.43 \text{ kcal mol}^{-1}$). Furthermore, both species can be easily degraded. For *trans*- ClCO_3 , the most feasible pathway was to undergo a concerted O-shift and C–Cl bond cleavage, leading to the final products (CO_2 and ClO). Two *cis*- ClCO_3 could easily combine each other to produce CCl(O)OCCl(O) owing to the low potential barrier heights with $-19.91 \text{ kcal mol}^{-1}$ and strongly exothermic energy with $-35.37 \text{ kcal mol}^{-1}$. This intermediate CCl(O)OCCl(O) could be further decomposed to produce CO_2 and Cl_2 .

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displayed in Table S10 and Fig. S4, the QCO and HX were always found as dominated intermediates within the altitude between 0 and 12 km, but the products of addition pathways were difficult to produce. Particularly at sea level, the reaction intermediates of QCO and HX were obtained almost exclusively with the ratio of 100%. According to previously mentioned results, the intermediate, QCO, was willing to react with halogen atoms to form unstable compounds in specific areas with high concentrations of halogen atoms (for example, MBL). These compounds were slightly soluble and then yield CO₂ and HX as final gaseous products. Otherwise, the QCO were degraded to form CO₂, X₂, and XO. In particular, for the reaction of ClCHO with Cl atoms, the phosgene and ClO were found during the atmospheric degradation process. Phosgene is well known as a highly toxic colorless gas (Fu et al., 2007) that can endanger human health via inhalation and exposure (Stanek et al., 2011), and ClO is also a key ozone destruction catalyst (Solomon, 1999). Therefore, halogenated formaldehydes as intermediates of the atmospheric degradation of VOCs, need an ongoing comprehensive attention and further risk assessment in atmospheric environment.

Supplement

(1) Detailed descriptions of the computational methods and comparison of methods; (2) details on frequencies for species, parameters of energies, and ratios; (3) detailed comparison between the theoretical and the experimental values; and (4) CVT/SCT rate constants and Arrhenius formulas for each pathway within the temperature range of 200–368 K. These materials are available free of charge via the internet at <http://www.atmospheric-chemistry-and-physics.net/home.html>.

Supplementary material related to this article is available online at:
<http://www.atmos-chem-phys-discuss.net/13/18205/2013/acpd-13-18205-2013-supplement.pdf>.

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Table 1. Energy parameters, including the potential barrier heights (ΔE), reaction enthalpies (ΔH_{298}^0), and dissociation energies [$D_{298}^0(\text{C-H})$] for the title reactions $\text{QCHO} + X \rightarrow \text{products}$ (in kcal mol^{-1}).

QCHO \ X	F		Cl		Br		$D_{298}^0(\text{C-H})$
	ΔE	ΔH_{298}^0	ΔE	ΔH_{298}^0	ΔE	ΔH_{298}^0	
H-abstraction pathways							
FCHO	1.29	-40.75 ^a (-35.14)	2.64	-3.36 ^a (-2.15)	11.34	10.26 ^a (13.63)	96.42
ClCHO	-0.58	-50.89	-1.25	-14.13	5.69	0.07	86.19
BrCHO	-0.69	-56.04	-1.56	-18.63	-0.53	-5.07	81.04
OH-addition pathways							
FCHO	6.20	-23.73	16.14	15.17	23.12	25.88	
ClCHO	7.57	-25.48	15.24	20.49	20.54	23.93	
BrCHO	8.23	-23.02	15.14	10.05	20.12	56.68	

^a Experimental value (NIST).

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Table 2. Total rate constants of the $X + \text{QCHO}$ reactions at 298 K (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$).

QCHO \ X	F	Cl	Br
	$k_{\text{CVT/SCT}}$	$k_{\text{CVT/SCT}}$	$k_{\text{CVT/SCT}}$
FCHO	9.26×10^{-13}	2.11×10^{-15}	9.87×10^{-21}
ClCHO	1.40×10^{-12}	6.52×10^{-12}	1.53×10^{-15}
BrCHO	5.64×10^{-12}	1.71×10^{-12}	9.41×10^{-15}
HCHO ^a	4.5×10^{-11}	8.0×10^{-11}	1.8×10^{-12}

^a From the experimental data (Beukes et al., 2000).

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Table 3. The modified Arrhenius formulas for $k = AT^B \exp(-C/T)$ within the temperature range of 200–368 K.

Reaction	A^a	B	C^b
FCHO + F → products	4.39×10^{-16}	1.99	1102
ClCHO + F → products	4.48×10^{-17}	2.22	694
BrCHO + F → products	3.71×10^{-16}	1.91	374
FCHO + Cl → products	1.80×10^{-41}	9.78	-1275
ClCHO + Cl → products	5.39×10^{-18}	2.20	243
BrCHO + Cl → products	3.50×10^{-17}	1.91	31
FCHO + Br → products	4.21×10^{-21}	3.02	4866
ClCHO + Br → products	1.53×10^{-23}	3.96	1228
BrCHO + Br → products	5.41×10^{-24}	4.03	501

^aUnits in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b $B = \frac{E}{R}$, $E = E_a - nRT$, R is the gas constant (Zheng et al., 2010).

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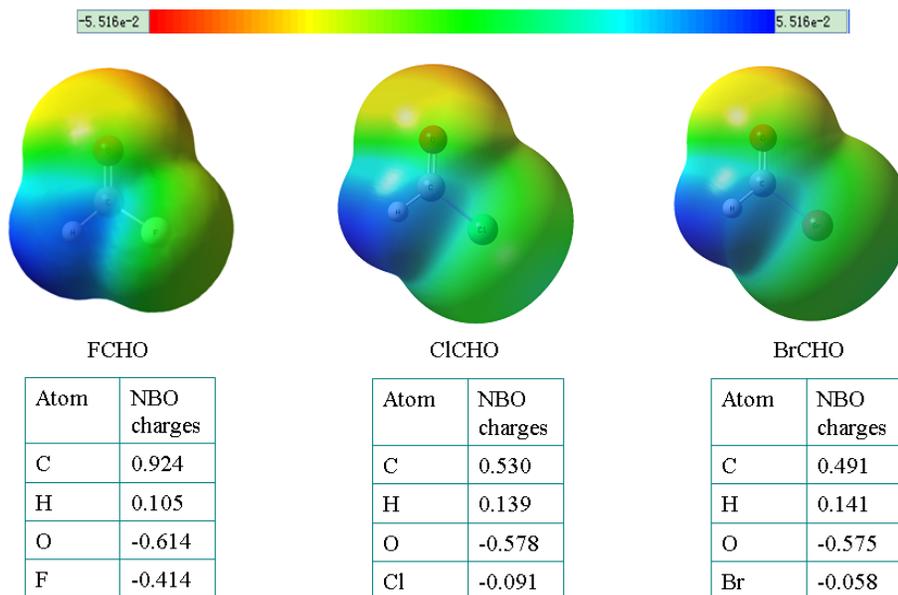


Fig. 1. Calculated molecular electrostatic potential and NBO charges (in e) for the reactants at the MP2/6-311G(d,p) level.

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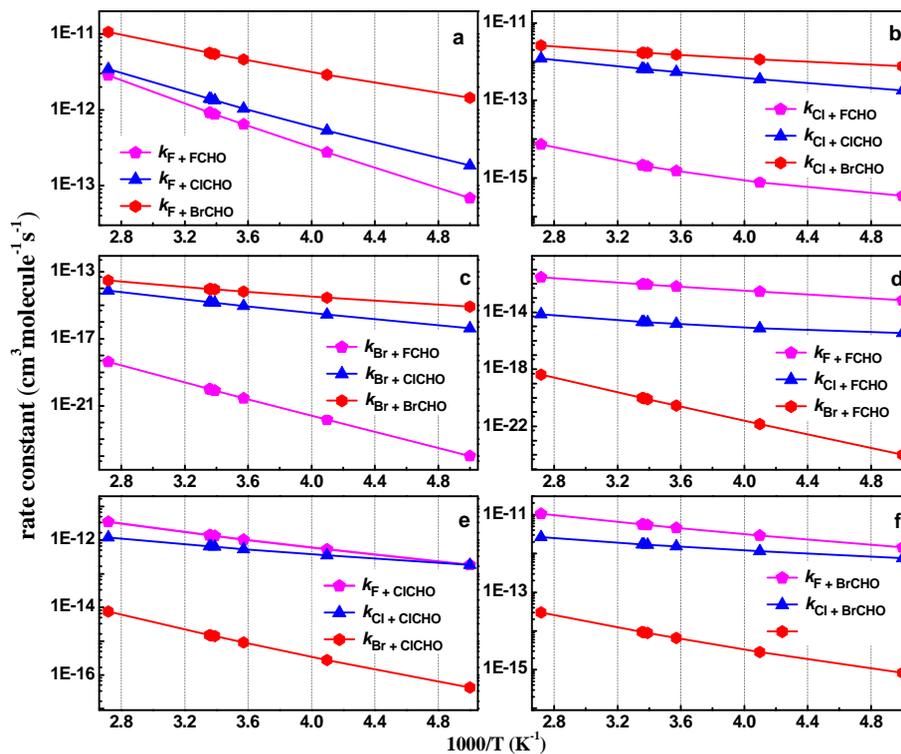


Fig. 2. Plot of the CVT/SCT rate constants for the different reaction systems within the temperature range of 200–368 K.

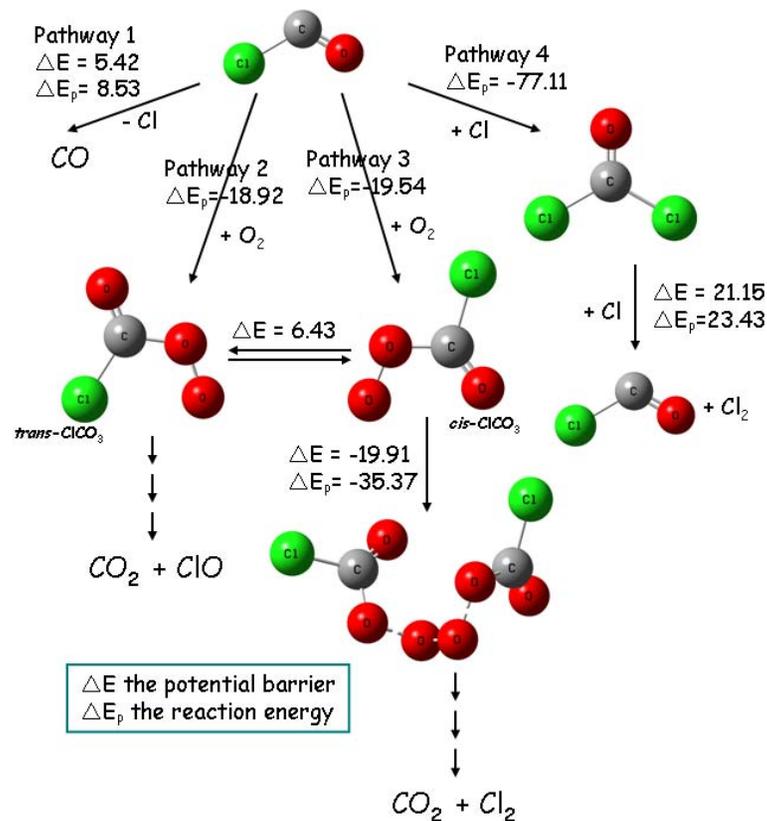


Fig. 3. Possible atmospheric degradation pathways of CICO radical at the PMP2/6-311+G(3df,3pd)//MP2/6-311G(d,p) level (in kcal mol⁻¹).

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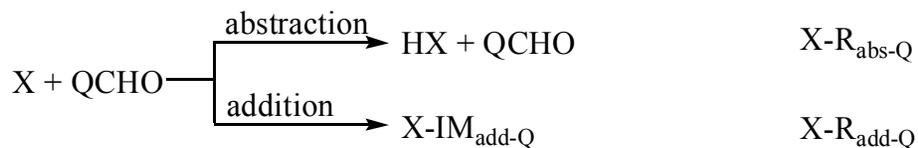


Fig. 4. Possible pathways for the title atmospheric reactions, where QCHO represents the halogenated formaldehydes as well as $Q = \text{F}, \text{Cl}, \text{and Br}$. X represents the halogen atoms as well as $X = \text{F}, \text{Cl}, \text{and Br}$, respectively.

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