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. Our studies showed that compared to X-addition pathway, the H-abstraction pathway was demonstrated to be more preferred to form halogenated formyl radicals and hydrogen halides (HX). In specific areas with abundant halogen atoms, such as the marine boundary layer (MBL), halogenated formyl radical was reacted easily 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 in the presence of O₂ and halogen atoms. 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, rate constants decreased as altitude increased, and especially the rate constants of halogen atoms reacted with FCHO quickly reduced. The kinetic results showed that although the reactions of halogenated formaldehydes with F atoms occurred more easily 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 equations of rate constants within the atmospheric temperature range were fitted, which helped to understand the established atmospheric model and estimated the contribution of title reactions to atmospheric chemistry pollution.

1 Introduction

The Antarctic-like ozone hole was proposed in the Arctic in the 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 formaldehydes are one of the halogenated molecules in the atmosphere, and are reactive molecules to form the atmospheric degradation intermediates of several halocarbons such as CFCs and HCFCs (Hasson et al., 1998; Sanhueza et al., 1975; Wallington et al., 1992) as well as from the tropospheric reactions of halogen atoms with volatile organic compounds (VOCs) such as isoprene (Fantechi et al., 1998). On the other hand, halogen species, such as chlorine and bromine, play an important role in the atmospheric chemical processes. Apart from anthropogenic organohalogen source, another important sources is from sea-salt aerosols (Finlayson-Pitts, 2003) and the heterogeneous reactions on these aerosol surfaces (Rossi, 2003). Thus, abundant halogen species could be frequently found in the marine boundary layers (MBL) (Sommariva et al., 2012; Wingenter et al., 2005). Moreover, these halogen species are reactive toward various VOCs as well as ozone (Foster et al., 2001; Ofner et al., 2012; Riedel et al., 2012). Especially in occurences of the depletion of surface ozone in the Atlantic and Arctic, the presence of abundant halogen atoms has been

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proven (Jobson et al., 1994; Read et al., 2008; Solberg et al., 1996). Thus, as a prelude to understand the role of VOCs in the atmospheric transformation, the atmospheric reactions of halogenated formaldehydes with halogen atoms are expected to be a significant process in some particular areas such as MBL.

So far, some of the atmospheric reactions of three halogenated formaldehydes (FCHO, CICHO and BrCHO) with three halogen atoms (F, Cl and Br), have been investigated experimentally: FCHO + F (Behr et al., 1993, 1998; Francisco et al., 1990; Hasson et al., 1998; Meagher et al., 1997), FCHO + Cl (Bednarek et al., 1996; Edney et al., 1992; Meagher et al., 1997; Wallington et al., 1992), and CICHO + Cl (Catoire et al., 1996; Libuda et al., 1990; Orlando, 1999; Sanhueza et al., 1975; Wallington et al., 1996). However, these experimental studies only focused on the kinetics data, and never involved in the reaction mechanisms. Nevertheless, to understand the transformation mechanisms and fate of atmospheric reaction intermediates (IM) is an indispensable component to assess the risk of various toxic VOCs (Blotevogel et al., 2010). As for the theoretical studies, only limited published data was reported on the reactions 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. (1990) concluded that addition of fluorine atom onto FCHO was competitive, which contradicted the results of 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 CICHO + 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 necessary to qualitatively investigate with a 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 PMP2/6–311 + G(d,p) level. The vibrational frequencies were performed to characterize the nature of each point on the potential energy surface (PES) and make zero-point-energy (ZPE) corrections. Using the intrinsic reaction coordinate (IRC) theory, the minimum-energy path (MEP) was constructed to verify that each transition state (TS) uniquely connected the designated reactants with the products. The DLD method (Hu et al., 1996; Truhlar et al., 1996) was employed to investigate the reaction mechanisms and kinetics. The energy profiles of the title atmospheric reactions were refined at the high-accuracy QCISD(T)/6–311 + G(2df,2p) level based on the geometries mentioned above. For simplicity, a double slash “//” was used to denote the dual-level dynamics approach such as QCISD(T)//PMP2. Based on the aforementioned results of quantum chemistry calculations, the products distributions and the rate constants of all the possible reaction pathways were computed using CVT (Truhlar et al., 1980) plus SCT (Liu et al., 1993).

### 3 Results and discussion

#### 3.1 Atmospheric reaction mechanism

Generally, two different attack sites were present on the halogenated formaldehydes (QCHO, Q = F, Cl, and Br) by halogen atoms (X = F, Cl, and Br): the H atom was abstracted from the carbonyl group position (X−Rabs-Q) and the halogen atom was added onto the carbon atom of carbonyl group (X−Radd-Q) (Scheme 1). Figures S1 and S2 illustrated the geometries of reactants, products, TSs, complexes, and IMs calculated at the MP2/6-311G(d,p) level. To confirm the calculated geometry corresponding to a saddle point with only one imaginary frequency or a local minimum without imaginary frequency; the harmonic vibrational frequencies of the main stationary points were also listed in Table S1. The energy parameters were also presented in Table 1, including the reaction enthalpies with heat corrections (ΔH°98) and potential barrier heights with ZPE correction (ΔE) obtained.
at the QCISD(T)/6–311 + G(2df,2p)//PMP2/6–311 + G(d,p) level. All geometries optimized at the PMP2/6–311 + G(d,p) level and all energies obtained at the QCISD(T)//PMP2 level agreed with the available experimental data (Groner et al., 2001; Huisman et al., 1979; Nagai et al., 1981; NIST). The maximum relative errors were less than 0.01 % and 1.7 kcal mol$^{-1}$ for the geometric parameters and energy parameters, respectively.

### 3.1.1 H-abstraction pathways

To compare the earliness of H-abstraction TS structures, a geometry parameter L was calculated using the variation in geometry parameter L was calculated using the variation in the breaking bond distance between TSs and reactants ($\delta$ (C–H)) as well as the forming bond distance between TSs and products ($\delta$ (H–X)): $L = \delta$ (C–H)/$\delta$ (H–X) (Table S2). This parameter L denoted not only a TS structure associated with a reactant-like or a product-like (L < 1 or L > 1) character, but also the quantification of the corresponding trend (Rayez et al., 1994). As shown in Table 1, except for Br-R$_{abs-F}$ and Br-R$_{abs-Cl}$ pathways (L > 1), all other pathways were exothermic reactions (L < 1). That is, the reaction pathways with TS having a reactant-like character (L < 1) were exothermic reactions. Otherwise, it was expected to be endothermic. This conclusion was in accordance with the Hammond postulate (Hammond, 1955); in addition, a positive correlation was observed between L and $\Delta H^0_{298}$; the lowest (highest) value of L corresponded to the lowest (highest) value of $\Delta H^0_{298}$. For instance, the minimum (0.07) and maximum (1.42) L values of F-R$_{abs-Br}$ and Br-R$_{abs-F}$ pathways (Table S2) corresponded to the lowest and the highest $\Delta H^0_{298}$ with −48.18 kcal mol$^{-1}$ and 12.05 kcal mol$^{-1}$, respectively (Table 1). For the attack of F atoms to three halogenated formaldehydes, the $\Delta E$s of H-abstraction pathways were −2.68 kcal mol$^{-1}$ for F-R$_{abs-F}$, −4.98 kcal mol$^{-1}$ for F-R$_{abs-Cl}$, and −5.75 kcal mol$^{-1}$ for F-R$_{abs-Br}$, decreasing with the order of $\Delta E$(F-R$_{abs-F}$) > $\Delta E$(F-R$_{abs-Cl}$) > $\Delta E$(F-R$_{abs-Br}$). This result indicated that the H atom of halogenated formaldehydes should be abstracted more easily from FCHO to CICOH to BrCHO. To further investigate the reactivity of H atom, the C–H bond-dissociation energies ($D^0_{298}$ (C–H)) in carbonyl group were calculated, and the results were also listed in Table 1. For the three halogenated formaldehydes, the corresponding $D^0_{298}$ (C–H) values were 97.71, 87.61, and 82.74 kcal mol$^{-1}$. This result was in line with the order of the $\Delta E$, 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 −33.94 (F-R$_{abs-F}$), −43.33 (F-R$_{abs-Cl}$), and −48.18 (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 $\Delta H^0_{298}$, the attack of three halogen atoms to FCHO, the $\Delta E$s and $\Delta H^0_{298}$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. Similar feature can be found from the reaction of three halogen atoms and CICOH and BrCHO. On the other hand, for F-R$_{abs-Cl}$ and Cl-R$_{abs-Cl}$ channels (Fig. S1), there is a complex on the reactants and products side, respectively, denoted as CR and CP, in which the relative energies were −0.47 (F-CR$_{abs-Br}$), −43.94 (F-CP$_{abs-Cl}$), −2.41 (Cl-CR$_{abs-Cl}$), and −11.05 (Cl-CP$_{abs-Cl}$) kcal mol$^{-1}$ below the corresponding reactants, respectively (Table S3). Also, there exist two Cl-CR$_{abs-Br}$ and Br-CR$_{abs-F}$ complexes located at the entrance of Cl-CR$_{abs-Br}$ and Br-CR$_{abs-F}$ channels, and the stabilization energies are all lower than the corresponding reactants by about 0.7 kcal mol$^{-1}$.

In addition, the standard formation enthalpy ($\Delta H^0_{f,298}$) 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 $\Delta H^0_{f,298}$ of main species without the experimental values, such as CICOH, BrCHO, and the corresponding radicals, and presented in Table S4. The method was used in

### Table 1. Energy parameters, including the potential barrier heights (ΔE), reaction enthalpies (ΔH$^0_{298}$), and dissociation energies [D$^0_{298}$ (C–H)] for the title reactions QCHO + X → products (in kcal mol$^{-1}$).

<table>
<thead>
<tr>
<th>X</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>$D^0_{298}$ (C–H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QCHO</td>
<td>ΔE</td>
<td>ΔH$^0_{298}$</td>
<td>ΔE</td>
<td>ΔH$^0_{298}$</td>
</tr>
<tr>
<td>FCHO</td>
<td>−2.68</td>
<td>−33.94*(−35.14)</td>
<td>5.79</td>
<td>−0.59*(−2.15)</td>
</tr>
<tr>
<td>CICOH</td>
<td>−4.98</td>
<td>−43.33</td>
<td>−0.58</td>
<td>−10.05</td>
</tr>
<tr>
<td>BrCHO</td>
<td>−5.75</td>
<td>−48.18</td>
<td>−1.81</td>
<td>−14.91</td>
</tr>
<tr>
<td>QCHO</td>
<td>5.70</td>
<td>−23.62</td>
<td>14.19</td>
<td>13.07</td>
</tr>
<tr>
<td>FCHO</td>
<td>7.38</td>
<td>−24.32</td>
<td>14.27</td>
<td>18.70</td>
</tr>
<tr>
<td>BrCHO</td>
<td>7.60</td>
<td>−21.74</td>
<td>14.02</td>
<td>8.08</td>
</tr>
</tbody>
</table>

* Experimental value (NIST).
this study as a hypothetical reaction, in which the chemical bond broken model in the reactants is the same as the former model in the products. Therefore, the following isodesmic reactions were chosen due to the simple configuration of CH₄ (Ji et al., 2007):

\[
\text{QCHO} + \text{CH}_4 \rightarrow \text{HCHO} + \text{CH}_3Q \quad (Q = \text{F, Cl, Br}) \quad (\text{R1–R3})
\]

\[
\text{QCO} + \text{CH}_4 \rightarrow \text{HCO} + \text{CH}_3Q \quad (Q = \text{F, Cl, Br}) \quad (\text{R4–R6})
\]

The derivation procedure was as follows: (1) the SPE was calculated at the QCISD(T)/6–311 + G(2df,2p) level using the geometries obtained by the PMP2/6–311 + G(d,p) level for all products and reactants involved in R1–3 and R4–6; (2) the heat corrections were used to obtain the \(\Delta H^0_{298} \) of Reaction (R1)–(R3) and Reaction (R4)–(R6) at 298 K using standard statistical thermodynamic methods; (3) the aforementioned reaction enthalpies were combined with the known experimental data in Reaction (R1)–(R3) and Reaction (R4)–(R6) (HCHO \(-27.69 \text{ kcal mol}^{-1}\), HCO \(-10.39 \text{ kcal mol}^{-1}\), CH₃F, \(-55.97 \text{ kcal mol}^{-1}\), CH₃Cl, \(-19.99 \text{ kcal mol}^{-1}\), CH₃Br, \(-9.08 \text{ kcal mol}^{-1}\), CH₄, \(-17.89 \text{ kcal mol}^{-1}\)) to calculate the required \(\Delta H^0_{298} \) for the reference (NIST). As shown in Table S4, the calculated \(\Delta H^0_{298} \) were \(-46.2, -32.8, -51.4, \) and 3.4 kcal mol\(^{-1}\) for FCHO, BrCHO, CICO, and BrCO, respectively. Despite the lack of experimental data, the values \(-98.96 \text{ kcal mol}^{-1}\) and \(-41.95 \text{ kcal mol}^{-1}\) for FCHO and FCHO, respectively) in the reference (NIST). In this study, the Hammond postulate (Hammond, 1955). From Table 1, the order of \(\Delta H^0_{298} \) was in line with that of the geometrical features of TS mentioned above, and the \(\Delta H^0_{298} \) were \(-23.62 \) (F-R\(_{\text{add-F}} \)), \(-24.32 \) (F-R\(_{\text{add-Cl}} \)), and \(-21.74 \) (F-R\(_{\text{add-Br}} \)) kcal mol\(^{-1}\), respectively. The \(\Delta E\) of F-R\(_{\text{add-X}} \) pathways were 5.70, 7.38, and 7.60 kcal mol\(^{-1}\) (Table 1), respectively, with the increasing order of \(\Delta \Delta E(F-R_{\text{add-F}}) < \Delta \Delta E(F-R_{\text{add-Cl}}) < \Delta \Delta E(F-R_{\text{add-Br}})\). This result indicated that the addition pathways of F atom onto three halogenated formaldehydes would become increasingly more difficult as the electronegativity of halogen atoms was decreased in halogenated formaldehydes.

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 QCISD(T)/6–311 + G(2df,2p) 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 occur more likely than the corresponding X-addition pathways. The NBO charges estimated for H atoms were 0.109, 0.104, and 0.144 e, respectively, indicating an increased trend from FCHO to CICO 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 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 CICHO 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 CVT calculations were performed with the CVT interpolated single-point energies method (Chuang et al., 1999) using the QCISD(T)//PMP2 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 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-Rabs-F pathway (Fig. S3a) were in good agreement with most experimental data (Behr et al., 1993, 1998; Francisco et al., 1990; Has-son et al., 1998; Meagher et al., 1997). For example, the calculated rate constant of $8.1 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K perfectly matched with the experimental values of $(8.8 \pm 1.4) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Behr et al., 1993) and $(8.0 \pm 1.0) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Has-son et al., 1998), but was slightly lower than that of $2.11 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Francisco et al., 1990). With respect to Cl-Rabs-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 1.5. For instance, the calculated rate constant of $1.7 \times 10^{-15}$ cm$^3$ molecule$^{-1}$ 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 $(2.1 \pm 0.2) \times 10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ (Edney et al., 1992). For Cl-Rabs-Cl pathway (Fig. S3c), the calculated rate constant was slightly lower than the data achieved by Sanhueza et al. (1975) at 305 K, but were well accorded 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 $1.70 \times 10^{-11} \exp(-940 K/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which was in agreement with the experimental expressions of $1.39 \times 10^{-11} \exp(-(866 \pm 168) K/T)$ cm$^3$ molecule$^{-1}$ 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 1.6. Thus, the rate constants obtained at the QCISD(T)//PMP2 levels were reliable within the atmospheric temperature range from 200 to 368 K, which is particularly important for the atmospheric reactions without experimental data.

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 $8.08 \times 10^{-13}$ (F + FCHO), $4.23 \times 10^{-12}$ (F + CICHO), and $8.28 \times 10^{-12}$ (F + BrCHO) cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. The rate constants increased in the order of $\kappa$(F + BrCHO) < $\kappa$(F + CICHO) < $\kappa$(F + FCHO), which was consistent with the analysis values of potential barrier and NBO calculation. In addition, from Fig. 2a, it can be found that as the temperature rises, the rate constants increase, implying that increasing temperature will be benefit from the reaction of F atom with different halogenated formalde-ynes. 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 CICHO with different halogen atoms (Fig. 2d), the theoretical results decreased in the order of $\kappa$(F + CICHO) > $\kappa$(Cl + CICHO) > $\kappa$(Br + CICHO). The similar trend can also be observed for the reactions of FCHO and BrCHO with different halogen atoms. The kinetics results showed that the reactions of F atoms with halogenated formaldehydes were faster than those with Cl and Br atoms, but due to abundant Cl and Br atoms in the MBL, the halogenated formaldehydes reacted with Cl and Br atoms were still important even more than those with F atoms under 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. (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

<table>
<thead>
<tr>
<th>Table 2. Total Rate Constants of the X + QCHO Reactions at 298 K (in cm$^3$ molecule$^{-1}$ s$^{-1}$).</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
</tr>
<tr>
<td>QCHO</td>
</tr>
<tr>
<td>FCHO</td>
</tr>
<tr>
<td>CICHO</td>
</tr>
<tr>
<td>BrCHO</td>
</tr>
<tr>
<td>HCHO*</td>
</tr>
</tbody>
</table>

* From the experimental data; Beukes et al. (2000).
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 = F, Cl, Br) were the dominant products, and the addition intermediates (such as HC(O)F₂, HC(O)ClF, etc.) were difficult to form at temperatures without experimental data, the relationship was attempted between the temperature and the rate constants. To predict the rate constants of the title reactions in the temperatures within the range from 200 to 368 K.

Table 3. The modified Arrhenius formulas for within the temperature range of 200–368 K.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FCHO + F → products</td>
<td>$1.74 \times 10^{-16}$</td>
<td>1.63</td>
<td>256</td>
</tr>
<tr>
<td>CICHO + F → products</td>
<td>$1.17 \times 10^{-15}$</td>
<td>1.41</td>
<td>-40</td>
</tr>
<tr>
<td>BrCHO + F → products</td>
<td>$4.60 \times 10^{-15}$</td>
<td>1.31</td>
<td>-6</td>
</tr>
<tr>
<td>FCHO + Cl → products</td>
<td>$1.55 \times 10^{-19}$</td>
<td>3.08</td>
<td>2415</td>
</tr>
<tr>
<td>CICHO + Cl → products</td>
<td>$1.97 \times 10^{-19}$</td>
<td>2.74</td>
<td>140</td>
</tr>
<tr>
<td>BrCHO + Cl → products</td>
<td>$3.70 \times 10^{-19}$</td>
<td>2.54</td>
<td>-182</td>
</tr>
<tr>
<td>FCHO + Br → products</td>
<td>$1.09 \times 10^{-19}$</td>
<td>3.44</td>
<td>7165</td>
</tr>
<tr>
<td>CICHO + Br → products</td>
<td>$7.94 \times 10^{-19}$</td>
<td>2.72</td>
<td>2309</td>
</tr>
<tr>
<td>BrCHO + Br → products</td>
<td>$8.33 \times 10^{-20}$</td>
<td>2.73</td>
<td>1113</td>
</tr>
</tbody>
</table>

a Units in cm³ molecule⁻¹ s⁻¹.

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, in the presence of O₂ and halogen atoms. The four possible atmospheric degradation pathways of CICO radical were presented in Fig. 3, in which the reactions of CICO with Cl atom (pathways 2 and 3) and oxygen atom (pathways 4) corresponds to the elimination of
Cl atom from CICO (pathways 1). As shown in Fig. 3, pathway 1 had difficulty occurring because of higher potential barrier height than those of other pathways, whereas pathways 2–4 were all barrier-free processes. To further confirm these barrier-free processes, the point-wise potential curve was performed and the results were shown in Figs. S5–S7 (the detailed discussion is presented in Supplementary Material). Pathways 2 and 3 were exothermic processes with the exothermic energies of −23.03 and −23.91 kcal mol$^{-1}$ to form two isomers cis-CICO and trans-CICO with high activity, in which could be easily transformed to each other with a small internal rotation barrier (5.10 kcal mol$^{-1}$). Furthermore, both species can be easily degraded. For trans-CICO, 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), in which the potential barrier height and reaction energy (Δ$E_p$) was 21.31 and −61.97 kcal mol$^{-1}$. In the absence of other radicals, two cis-CICO could easily combine each other to produce CCl(O)OCCl(O) owing to the low potential barrier heights with −2.03 kcal mol$^{-1}$ and strongly exothermic energy with −6.98 kcal mol$^{-1}$. This intermediate CCl(O)OCCl(O) could dissociated directly to give products ClCO$_2$ and Cl(O)CO$_3$ (Δ$E_p$ = −4.04 kcal mol$^{-1}$). The Cl(O)CO$_3$ could further dissociated to produce ClCO$_2$ and O$_2$ (Δ$E$ = −6.21 kcal mol$^{-1}$), and finally, due to high exothermic energy (−27.21 kcal mol$^{-1}$), the ClCO$_2$ could be decomposed to produce CO$_2$ and Cl$_2$. As for pathway 4, the CICO radical could be prefer to react with Cl atom to form phosgene by a strongly exothermic process with an energy decrease of −73.05 kcal mol$^{-1}$. Phosgene is well known to be slightly soluble in liquid water, in which it may yield CO$_2$ and HCl as final gaseous products (Hatakeyama et al., 1989). Based on the aforementioned results, the CICO radical could primarily react with Cl atoms to produce phosgene where there is abundant Cl atoms in the atmosphere. Otherwise, the CICO radical could be transformed into CO$_2$, Cl$_2$, and ClO in the presence of O$_2$.

For the addition intermediate HC(O)ClF, there may exist three degradation pathways: H-elimination, Cl-elimination, and HF-elimination pathways (Scheme S1, as denoted F-R$_{elm-Cl}$1, F-R$_{elm-Cl}$2, and F-R$_{elm-Cl}$3). Table S9 listed the energies at different pathways, in which the energy of the corresponding intermediate was set to zero as reference. As shown in table, the Δ$E$ of F−R$_{elm-Cl}$2 pathway was much lower at least 10 kcal mol$^{-1}$ than those of F−R$_{elm-Cl}$1 and F−R$_{elm-Cl}$3 pathways. This result suggested that F−R$_{elm-Cl}$2 pathway could easily occur from the viewpoint of kinetics to release Cl atoms. However, the exothermic energy of the F−R$_{elm-Cl}$3 pathway (−19.73 kcal mol$^{-1}$) was lower (6 kcal mol$^{-1}$) than that of the F−R$_{elm-Cl}$2 pathway. This indicated that the formation of HF and CICO was thermodynamically favorable. Anyway, the addition pathways were difficult to occur, thus these products were not obtained under the atmospheric conditions.

4 Environmental implications

To evaluate the specific atmospheric region where the reactions of the halogenated formaldehydes with halogen atoms occur, the rate constants at different altitudes were also calculated (Table 4). From table, the rate constants decreased with increasing the altitudes, and the decrease in the halogen atom reaction with FCHO was faster than those of halogen atoms with other halogenated formaldehydes. For example, the rate constants at sea level were 4.8 (F + FCHO), 2.2 (F + CICHCHO), and 2.0 (F + BrCHO) times larger than those at 12 km height above sea level. As the results displayed in Table 4 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 where there are abundant halogen atoms in the atmosphere (for example, MBL). These compounds were slightly soluble and then yield CO$_2$ and HX as final gaseous products. Otherwise, the QCO were degraded to form CO$_2$, X$_2$, and XO in the presence of O$_2$ and halogen atoms. In particular, for the reaction of CICHCHO with Cl atoms, the phosgene and ClO were found during the atmospheric degradation process. Phosgene is well known as a highly toxic colourless 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
Table 4. Calculated CVT/SCT rate constants of H-abstraction and X-addition pathways at different heights* in the earth atmosphere (in \( \text{cm}^3\text{molecule}^{-1}\text{s}^{-1} \)).

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<th>( T ) (K)</th>
<th>( k_{ab} ) ( 10^{-13} )</th>
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![Supplementary material related to this article is available online at http://www.atmos-chem-phys.net/13/11277/2013/acp-13-11277-2013-supplement.pdf.](http://www.atmos-chem-phys.net/13/11277/2013/acp-13-11277-2013-supplement.pdf)

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