Kinetics of Hydroxyl Radical Reaction with $CF_2ClOCHO$: A Theoretical Investigation

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The rate constant for the hydrogen abstraction reaction between $CF_2ClOCHO$ and OH radical has been calculated for the first time by using the modified ab initio G2(MP2) and standard transition state theories. The Arrhenius equation for the rate constant, k_{total}, within the temperature range of 250 K to 450 K is estimated to be $7.1 \times 10^{-13} \exp(-845/T)\,cm^3\,molecule^{-1}\,s^{-1}$.

Recent works[1,2] have shown formates as a major product resulting from the oxidation of halogenated ether compounds in the atmosphere. The atmospheric impact of the resulting formates should, therefore, be included while considering the global warming potential of haloethers. Since hydrogen abstraction reaction with OH radical is likely to be one of the major degradation channels for halogenated formates in the atmosphere,[3] it is important to understand the reaction of formates with OH radical. The kinetic data on hydrogen abstraction from formates is very limited. The purpose of the present study is to investigate for the first time the kinetics and mechanism of the hydrogen abstraction reaction: $CF_2ClOCHO + OH \rightarrow CF_2ClOCO + H_2O$ using ab initio theory and to evaluate the rate constant over a temperature range which covers the tropospheric temperatures (i.e., $T < 298$ K). The result provides indication how the reactivity for hydrogen abstraction changes with the change in halogen substitution.

In our previous work on the reaction between CF_3OCHO and OH radical,[4] we employed a modified G2(MP2) procedure. The geometry optimizations and vibrational frequency calculations were carried out at the MP2(full)/6-311G(d,p) level, whereas in the usual G2(MP2) method[5] the MP2(full)/6-31G(d)-optimized geometries and HF/6-31G(d) frequencies are employed. The MP2 frequencies were scaled by a factor of 0.9496.[6] This modified G2(MP2) procedure produced very good results for hydrogen abstraction from CF_3OCHO.[4] We also calculated the hydrogen abstraction rate constant for the reaction between CH_3OCHO and OH by applying this procedure and the calculated value of $1.8 \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$ is found to be in good agreement with the experimental value of $(1.73 \pm 0.21) \times 10^{-13}\,cm^3\,molecule^{-1}\,s^{-1}$.[7] Thus, we employed the same modification of the G2(MP2) procedure in the present study. Figure 1 shows the MP2(full)/6-311G(d,p)-optimized transition state (TS) structures of the title reaction. The reactant molecule $CF_2ClOCHO$, as well as the product radical CF_2ClOCO, has two stable conformers, *syn* (C3-O1-C2-O4 = 0 °) and *anti* (C3-O1-C2- O4 = 180 °) (see Figure 1). Correspondingly, we were able to locate the *syn* and *anti* transition states (TSs) for hydrogen abstraction from $CF_2ClOCHO$: the normal mode of the imaginary frequency for each TS corresponds to the C-H bond breaking and O-H bond forming.

Table 1 presents the calculated values for the energetics for the hydrogen abstraction. We estimated the C-H bond dissociation enthalpy, BDE(C-H), from the calculated value for the heat of the reaction for $CH_3 + CF_2ClOCHO \rightarrow CH_4 + CF_2ClOCO$ and the experimental C-H bond dissociation enthalpy of CH_4, 438.9 kJ/mol.[8] Significant difference in BDE(C-H) value between the *syn* and *anti* conformer is noteworthy: the BDE(C-H) value for the *syn* conformer is larger by 15.9 $kJ\,mol^{-1}$ than for the *anti* conformer. This is due to the reversal in stability order of the *syn* and *anti* conformers for the reactant molecule and for the product radical. For reactant $CF_2ClOCHO$ molecule, the modified G2(MP2) procedure indicated that the *syn* conformer is 4.6 $kJ\,mol^{-1}$ lower in energy than the *anti* conformer. Meanwhile, the *anti* conformer of CF_2ClOCO radical is 10.9 $kJ\,mol^{-1}$ lower in energy than the corresponding *syn* conformer.

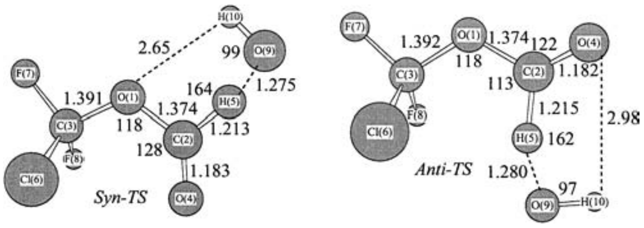

Figure 1. Optimized structures of the transition states for the reactions of *syn*- and *anti*-$CF_2ClOCHO$ with OH radical. Bond lengths and angles are given in Å and degrees, respectively.

Table 1. The C-H bond dissociation enthalpy (BDE(C-H)), barrier heights ($\Delta E_0^{\#}$, including the zero-point energy), and heats of reaction ($\Delta_r H$(298 K)) for *syn*- and *anti*-$CF_2ClOCHO$. Data are given in $kJ\,mol^{-1}$

conformer	BDE	$\Delta E_0^{\#}$	$\Delta_r H$(298 K)
syn	423.4	13.8	−73.6
anti	407.5	11.2	−89.5

The calculated values for the heats of reaction [$\Delta_r H$(298 K)] indicate that the hydrogen abstraction from $CF_2ClOCHO$ is exothermic regardless its conformer. Correspondingly, we find early TSs for both the *syn* and *anti* conformers, as expected from the Hammond's postulate.[9] For both the *syn* and *anti* TSs, the breaking C-H bonds are elongated by only 11% from C-H bond length of 1.09 Å in the isolated $CF_2ClOCHO$ molecule, while the forming O-H bonds are longer by around 33% than the O-H bond in H_2O molecule, indicating a reactant-like TS. In spite of differences in the C-H bond strength, no significant difference in the breaking and forming bond lengths can be seen between the *syn* and *anti* TSs . This might be related with the hydrogen bonding interaction in the *syn* TS. The distance between the bridging oxygen atom (C-$\underline{O}$-C) and the hydroxyl hydrogen atom in the *syn* TS is 2.65 Å, which is slightly shorter that the sum of the van der Waals radii of oxygen and hydrogen atoms (2.72 Å).[10] Thus, weak hydrogen bonding interaction may exist in the *syn* TS. Such interaction is not seen in the *anti* TS.

Owing to stronger C-H bond in the *syn* conformer, *syn*-$CF_2ClOCHO$ is less reactive than *anti*-$CF_2ClOCHO$. The calculated barrier height values for the hydrogen abstraction are 13.8 and 11.2 kJ mol^{-1} for the *syn* and *anti* conformer, respectively (see Table 1). We calculated the rate constant for the hydrogen abstraction reaction by using the standard transition-state theory (TST) expression:[11]

$$k_{TST} = \Gamma \frac{k_B T}{h} \frac{Q_{TS}}{Q_A Q_B} e^{-\Delta E_o^{\#}/RT} \tag{1}$$

The k_B, T, h, and Q's represent the Boltzmann constant, temperature, the Planck constant, and partition functions, respectively. The tunneling factor, Γ, was calculated by using Eckart's method for unsymmetrical one-dimensional potential barrier.[12] Since the barriers for interconversion between the *syn* and *anti* conformers are higher, *i.e.* 28.9 kJ mol^{-1} from *syn* to *anti* and 24.3 kJ mol^{-1} from *anti* to *syn*, than those for the hydrogen abstraction, we calculated separately the rates of hydrogen abstraction from the *syn* and *anti* conformers. Moreover, the total hydrogen abstraction rate constant (k_{total}) was calculated from the weighted sum of the two individual rate constants for *syn*- (k_{syn}) and *anti*-$CF_2ClOCHO$ (k_{anti}):

$$k_{\text{total}} = \mathrm{w}_{syn} k_{syn} + \mathrm{w}_{anti} k_{anti} \tag{2}$$

where w_{syn} and w_{anti} are weight factors of the equilibrium distribution of the *syn* and *anti* conformers of $CF_2ClOCHO$.

The calculated rate constants in the temperature region from 250 K to 450 K are given in Table 2. The free energy gap between the *syn*-and *anti*-$CF_2ClOCHO$ amounts to only 3.3 kJ mol^{-1} at 298 K. Thus, both the conformers contribute to the total rate constant for the hydrogen abstraction. The rate constant for the *anti*-$CF_2ClOCHO$ is larger than that for the *syn*-$CF_2ClOCHO$. However, the population of the *anti* conformer is much lower than that for the *syn* conformer. As a consequence of the balance of these two factors, the Arrhenius plots of the rate constants indicate that the contribution of *anti* conformer to the total rate constant is always much less than the contribution from the *syn* conformer in the temperature region from 250 K to 450 K (see Figure 2). Arrhenius equation of the total rate constant for the hydrogen abstraction from $CF_2ClOCHO$ in the temperature region from 250 K to 450 K is estimated to be $7.1 \times 10^{-13} \exp(-845/T)$.

To the best of our knowledge, no experimental value for the hydrogen abstraction from $CF_2ClOCHO$ by OH radical is available. Our estimate in the present work for the total rate constant of the hydrogen abstraction from $CF_2ClOCHO$ is 4.0×10^{-14} cm^3 $molecule^{-1}$ s^{-1} at 298 K. The atmospheric lifetime τ_{OH} of a molecule due to degradation via the reaction with OH radical can be determined from the expression, $\tau_{OH} = 1/(k_{OH} \times [OH])$, and using $[OH] = 9.7 \times 10^5$ molecule cm^{-3}.[13] Using the rate constant value at 298 K, the τ_{OH} value for $CF_2ClOCHO$ is found to be 0.8 year. Since our estimate for the hydrogen abstraction rate for $CF_2ClOCHO$ is double to the calculated value for CF_3OCHO molecule (2.0×10^{-14} cm^3 $molecule^{-1}$ s^{-1}),[4] the τ_{OH} value for $CF_2ClOCHO$ is likely to be shorter than that for CF_3OCHO. The lower barrier height and larger pre-exponential factor are the reason behind the larger rate constant value for $CF_2ClOCHO$ than CF_3OCHO. In addition to the hydrogen abstraction by OH radical, degradation channel via hydrolysis in the atmosphere should not be negligible for halogenated formates, which will probably make the atmospheric lifetime of halogenated formates still shorter. Further investigation on this point is now being carried out in our laboratory.

Table 2. The rate constants (in cm^3 $molecule^{-1}$ s^{-1}) for hydrogen abstraction from the *syn*- and *anti*-$CF_2ClOCHO$

T	k_{syn}	k_{anti}	k_{total}
250	2.5×10^{-14}	3.5×10^{-14}	2.6×10^{-14}
298	3.7×10^{-14}	5.0×10^{-14}	4.0×10^{-14}
350	5.6×10^{-14}	7.1×10^{-14}	5.9×10^{-14}
450	1.1×10^{-13}	1.3×10^{-13}	1.2×10^{-13}

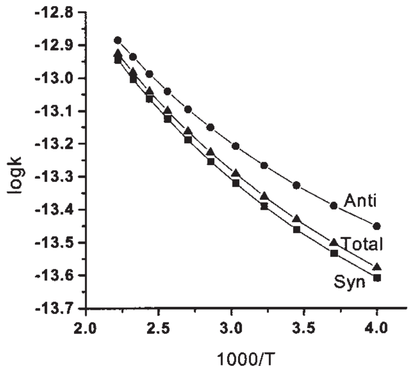

Figure 2. Arrhenius plots of the rate constants for the reaction: $CF_2ClOCHO + OH \rightarrow CF_2ClOCO + H_2O$.

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