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The Mechanism and Kinetic Studies on Oxidation Reaction of Acetofenate Initiated by HO\textsubscript{x}, NO\textsubscript{3}, O\textsubscript{3}, and Cl Radicals

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

Abstract: Acetofenate (AF) is a widely used pesticide. The mechanism of HO\textsubscript{x}, NO\textsubscript{3}, O\textsubscript{3}, and Cl initiated oxidation reactions of AF was investigated with density functional theory. For each of the OH, NO\textsubscript{3}, and Cl, both addition and hydrogen abstraction were investigated, for each of the HO\textsubscript{3} radicals and O\textsubscript{3}, addition reactions were investigated. The cycloaddition reactions of O\textsubscript{3} were considered, including the exploration of isomerization. Based on the potential energy surface, the rate constants were calculated with the transition state theory method over a temperature range of 200–400 K and fitted with the Arrhenius formulas. The rate constants of AF reaction with OH, HO\textsubscript{x}, NO\textsubscript{3}, O\textsubscript{3}, and Cl, are 4.04×10\textsuperscript{-15}, 7.02×10\textsuperscript{-21}, 6.93×10\textsuperscript{-20}, 1.45×10\textsuperscript{-25}, and 5.07×10\textsuperscript{-12} cm\textsuperscript{molecule}\textsuperscript{-1}s\textsuperscript{-1} at 298.15 K, respectively. The OH-initiated reactions are dominant according to the branching ratio of reaction constants. The atmospheric lifetime of the reaction species was estimated according to rate constants.

Introduction

Acetofenate (AF), also known as benzethazet and plifenate, is used worldwide to control pest. As a commercial organochlorine pesticide, AF was developed as an analogue of DDT since 1970s. Due to its low toxicity, selective insecticidal activity, and high efficacy, AF is considered a good alternative to combat pests, especially health pests. However, its popularity has led to the direct release of pesticide into the environment for a long time.

In the troposphere, radicals have great effects on the removal or transformation of organic compounds through controlling the oxidative capacity of the atmosphere. Once released into the atmosphere, AF could be oxidized by nucleophilic active species, HO\textsubscript{x} radicals, NO\textsubscript{3} radical, O\textsubscript{3}, Cl atom, and other species, and generate a series of oxidation products.

The HO\textsubscript{x} radicals (OH and HO\textsubscript{2} radical), whose photochemical lifetimes are very short, are responsible for the majority of oxidation processes in the troposphere and control concentrations of many species. The degradation pathway of AF initiated by OH is important for the related chemistry features of OH, such as the inherent reactivity. However, the formation of OH mainly takes place in daytime through photolysis, and its concentration decreases rapidly after sunset. As for HO\textsubscript{2}, the principal sources are of photolysis and oxidation of HCHO, and the tropospheric abundances are about 100 times higher than that of OH during the daytime in clean air. On the whole, reactions with HO\textsubscript{x} radicals mainly occur during the day.

It is worth mentioning that not all atmospheric chemistry is initiated in the daytime. In the troposphere, the NO\textsubscript{3} radical is thought to be the main night-time oxidant. During the daytime, the concentration of NO\textsubscript{3} is very low. However, in the night-time atmosphere NO\textsubscript{3} radicals were measured at typical concentrations of 10-100 parts per trillion. Clearly, the reactions of AF with NO\textsubscript{3} pathway during nighttime cannot be ignored. In addition, in polluted environment, NO\textsubscript{3} radical is also an important oxidant and may contribute to the removal of AF.

Ozone is another powerful oxidant that cannot be ignored in atmospheric environment. Its strong oxidizing power and participation in the production of other radicals make ozone a key role in the oxidation of organic matters during both day and night. Most notably, the ozone arises from a variety of sources, and the concentration of O\textsubscript{3} (7.0×10\textsuperscript{11} molecule cm\textsuperscript{-3}) is much higher than that of OH radical (9.7×10\textsuperscript{10} molecule cm\textsuperscript{-3}).

Moreover, in the marine atmosphere where the concentration of Cl atoms can reach a peak value of 10\textsuperscript{5} molecule cm\textsuperscript{-3}, the Cl atom-initiated chemistry can be an important removal process for AF. As for H-abstraction reactions, the rate constant of Cl atom is 10\textsuperscript{2} times more active than that of OH radical. Thus, Cl atom also should be considered for the oxidation of AF in the atmosphere.

In this work, quantum chemistry method was applied to reveal the reaction mechanisms of AF. The initial reactions of HO\textsubscript{x} radicals, NO\textsubscript{3} radical, O\textsubscript{3}, and Cl atom with AF were investigated, and thermodynamic parameters are included too. Based on quantum chemistry information, the rate constants are calculated using the transition state theory method. Arrhenius equations of the rate constants with a temperature range of 200–400 K are fitted, and the lifetimes of the reaction species in troposphere are estimated according to the rate constants.

Computational methods

Mechanism study

It is well known that the density functional theory (DFT) is a calculation tool to deal with atmospheric chemical reaction. In previous studies DFT have successfully applied to medium or even larger scale molecular system. The MPWB1K method...
is a hybrid DFT model with performance for thermochemistry, thermochemical dynamics, weak interactions, and hydrogen bonding. In this paper, all the work is performed using the Gaussian 03 programs and SGI workstation. The geometrical parameters of reactants, transition states (TS), intermediates (IM), and products were fully optimized at the MPWB1K/6-31+G (d, p) level. The vibrational frequencies have been calculated at the same level in order to determine the nature of stationary points. The single point energy is calculated at the basis sets 6-311+G (3df, 2p).

## Kinetic calculation

The transition state theory (TST) is a model based on the interaction potential between reactants and products with a statistical representation of the dynamics to determine rate constants. It has been widely employed to discuss of rate processes in previous explorations. In this paper, the rate constants calculation of all elementary reactions have been carried out with the method over a suitable temperature range. Taking a bimolecular reaction as example:

$$A + BC \rightarrow AB + C$$  \hspace{1cm} (1)

The rate constant is calculated using the following equation:

$$k_{AB} = \frac{k_T Q_a}{h Q_{BC}} \exp\left(\frac{V}{RT}\right) \frac{RT^{10^b}}{P^a N_c}$$  \hspace{1cm} (2)

The definition of each parameter can be referred to literature. The numerical method for linear equation is used to fit the Arrhenius formula of rate constants with temperature.

## Results and discussion

### OH-initiated reaction

Under the atmospheric condition, the chemical reactions of AF can be initiated by the OH radical. Two possible reaction pathways are taken into consideration: OH radical addition and H atom abstraction. For convenience, the atom labels are marked in the structure of AF in Figure 1. The reaction schemes with the potential barriers ($\Delta E_b$) and reaction heats ($\Delta E_r$) are depicted in Figures 1, S1, and S2, respectively.

Because of its molecule asymmetry, AF has two kinds of different addition positions, that is, the same and opposite side of the benzene ring (the cis-addition and the trans-addition) relative to branched chain substituents. This paper mainly presents the cis-addition reactions. It is obvious that all of cis-addition channels can easily happen for their low potential barriers (3.70–9.94 kcal/mol). As for trans-addition reactions, the channels are also easily happen, for the $\Delta E_b$ values are less than 10.00 kcal/mol. All these processes are exothermic (11.81–23.06 kcal/mol), with less than 24.00 kcal/mol of energy released. Taken $\Delta E_b$ values (<9.94 kcal/mol) and $\Delta E_r$ values (<23.06 kcal/mol) into consideration, every OH addition reaction can occur easily. Among these pathways, the C1-cis-addition and C1-trans-addition are thermodynamically favorable since the barriers are low, 3.70 kcal/mol and 2.49 kcal/mol.

Due to its nucleophilicity, OH radical can abstract the H atom from AF. There are five kinds of H atoms in AF molecule, suggesting that there are five possible pathways: three in the aromatic ring, one in the methylene group, and one in the methyl group. All these pathways can easily happen for their low potential barriers (0.59–9.10 kcal/mol). Compared with other three exothermic (1.70–2.84 kcal/mol) processes, pathway A11 (29.05 kcal/mol) and A12 (17.62 kcal/mol) are highly exothermic. Among the abstraction pathways, barriers are lower in the reaction of the H atom abstracted from the methylene group and methyl group than those from the aromatic ring.
As for AF, NO$_3$ can attract C=C or C=O double bond to form two different kinds of NO$_3$-adducts. It can be seen that in each of the pathways NO$_3$ radicals are added to the benzene. There exists an intermediate AF-NO$_3$, whose energy is lower than that of AF + NO$_3$ by 5.89 kcal/mol of the cis-addition and by 4.69 kcal/mol of the trans-addition. Except the processes AF react with NO$_3$ radical in the C$_2$ and C$_7$-trans-site are endothermic, the rest processes are all slightly exothermic with less than 8.67 kcal/mol of energy released. As shown from the cis-addition the calculated potential barriers and reaction heats, NO$_3$ addition to C$_3$ is the most favorable reaction with the lowest barrier (5.18 kcal/mol) and releases the most heat (6.06 kcal/mol). As for the trans-addition reactions, pathway C1’ and C3’ occur more early for the low potential barriers less than 2.26 kcal/mol. Then followed by pathway C4’, the potential barriers is 4.22 kcal/mol, giving out 7.52 kcal/mol of energy.

The hydrogen on the AF can be abstracted by NO$_3$ to produce nitric acid (HNO$_3$). Noticeably, the pathway C11 and C12 are exothermic, while pathway C8, C9, and C10 are endothermic. The potential barrier of pathway C11 (5.68 kcal/mol) is lower than that of other pathways. At the same time, pathway C11 (21.29 kcal/mol) is more exothermic than pathway 12 (9.95 kcal/mol). Thus, the pathway C11, i.e., NO$_3$ abstracts H atom from the methylene group, occurs more easily. What’s more, at 298.15 K the total rate constant of addition reactions (4.59×10$^{-26}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) is larger than that of abstraction reactions (2.34×10$^{-26}$ cm$^3$ molecule$^{-1}$ s$^{-1}$) with NO$_3$ at 298.15 K.

O$_3$-initiated reaction

The ozonolysis reactions are initiated by addition of O$_3$ to the double bond of AF to produce primary ozonide. The reaction channels are provided in Figures 5 and S5, respectively.

The twelve elementary reactions all take place from AF with O$_3$ via TS to form the ozonide. All processes are highly exothermic with released heat of 27.33–35.72 kcal/mol, and the barrier varies over the range of 11.84–21.50 kcal/mol. The smaller energy barrier comes from the trans-addition pathways that O$_3$ addition to C$_2$-C$_3$ products IM2/D. The high reaction energy is retained as the internal energy of the adduct, the excited ozonide subsequently undergoes unimolecular decomposition due to highly exothermic. Then the C$_2$-C$_3$ and O-O of the added O$_3$ bonds break, respectively. In consideration of the large system of reactants and IM2/D is obtained more easily, and only IM2/D is chosen to study the mechanism of isomerization. The reaction scheme is described as follows:

![Diagram of O$_3$-initiated reaction](image)

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**Fig. 3** NO$_3$ initiated addition pathways with the potential barriers $\Delta E_p$ and reaction heats $\Delta E_r$ (kcal/mol)

**Fig. 4** NO$_3$ initiated H atom abstraction pathways with the potential barriers $\Delta E_p$ and reaction heats $\Delta E_r$ (kcal/mol)

**HO$_2$-initiated reaction**

HO$_2$-initiated reaction schemes of AF embedded with the potential barriers and reaction heats are showed in Figures 2 and S3, respectively.

Unlike the OH radical, HO$_2$ radical cannot abstract H atom from AF, and all channels are addition reactions. Clearly, HO$_2$ radicals react with AF via TS to form products. All reactions are endothermic, and the $\Delta E_p$ vary over the range of 3.51–17.43 kcal/mol. The rate constant at 298.15K is 7.02×10$^{-33}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, which is smaller than that of OH-initiated reaction.

**NO$_2$-initiated reaction**

NO$_2$ radical can be added to the double bond and abstract H atom from AF which is similar to the reactions of AF and OH. The diagrams of NO$_2$-initiated degradation mechanism of AF are illustrated in Figures 3, 4, and S4, respectively.
Fig. 5 O₃ initiated pathways with the potential barriers $\Delta E_a$ and reaction heats $\Delta E_r$ (kcal/mol)

Calculations indicate that in the two processes there are apparent potential barriers of 36.30 kcal/mol and 32.25 kcal/mol, absorbing 0.05 kcal/mol and 1.23 kcal/mol of heat.

**Cl-initiated reaction**

Similar to the above reaction pathways, the Cl atom can attack the double bonds of AF, and abstract hydrogen to generate hydrochloric acid (HCl). The probable pathways for the reactions are depicted in Figures 6, 7 and S6, respectively.

The $cis$-addition reactions are analysed in details. When Cl atom is added to the benene ring to react with AF, they first form the intermediate AF-Cl-1, with the energy lower than that of AF + Cl by 0.01 kcal/mol, and then generate IM via TS. The barriers of these processes vary over the range of 0.01–11.27 kcal/mol.

Among the six pathways, the barrierless process comes from pathway E4 (0.01 kcal/mol), and the reaction is slightly exothermic, giving out 2.58 kcal/mol of energy while others are endothermic. When the Cl is added to C=O double bond, this process without the formation of AF-Cl, so the process is endoergic, absorbing 6.91 kcal/mol of heat, and the potential barrier is 8.08 kcal/mol.

The $trans$-addition reactions are similar with the $cis$-addition reactions. When Cl atom is added to the benene ring, there also exists an intermediate AF-Cl-1', and then generate IM via TS. The barriers of these processes vary over the range of 0.16–8.76 kcal/mol. The process of Cl is added to C=O double bond without the formation of AF-Cl, and it is endoergic, absorbing 8.24 kcal/mol of heat, and the potential barrier is 8.76 kcal/mol. Among these reactions, pathway E1', E3', and E4' could easily occur for low potential barriers (<1.18 kcal/mol) and the reaction pathway E2' is slightly endoergic, absorbing 1.39 kcal/mol of energy while others are exothermic.

The H atom abstraction pathways of AF with Cl atoms are all with positive barriers. The potential barriers of pathway E11 and E12 are lower than that of pathway E8, E9, and E10. Compared with other three endothermic (2.78–14.19 kcal/mol) processes, pathway E11 (4.54 kcal/mol) and E12 (1.82 kcal/mol) are slight exothermic. In addition, the rate constants of pathway E11 and E12 are larger than those of other pathways. So taken the thermodynamic and kinetic into consideration, it is obvious that pathway E11 and E12 are favored in H abstraction pathways.

**Subsequent reactions**

In general, the radicals formed from additions and abstractions could further be decomposed in the presence of O₂ and NO/H₂O in the atmosphere. Evidently, the addition reactions in which HO₂, NO₃, and Cl are added to C₃-$cis$ and C₃-$trans$ sites are the most favorable pathways with the lowest barriers in each group, which can further lose the H atom that connected with the C atom and degraded in the atmosphere. In the H atom abstraction pathways, different radicals obtain five similar intermediates. The barrierless and slight exothermic processes where H atom is abstracted from the methylene group and methyl group are more dominant. Some subsequent reactions for this part have been explored by our group.

Fig. 7 Cl initiated H atom abstraction pathways with the potential barriers $\Delta E_a$ and reaction heats $\Delta E_r$ (kcal/mol)
Kinetic analysis

With TST method, the rate constants of OH, HO₂, NO₃, O₃, and Cl initiated reactions of AF at a suitable temperature range of 200–400 K are listed in Tables S1A to S8A, respectively. The Arrhenius equations \( i.e. k(T) = A \exp(-E_a / RT) \) \(^{37}\) for rate constants of element reactions are listed in Tables S1B to S5B, respectively. The total Arrhenius equations and rate constants at 298.15K are shown in Table 1. Obviously, most of the calculated rate constants can be fitted by Arrhenius equations. The correlation coefficient \( R^2 \) is above 0.9. The branching ratios of addition and abstraction reactions among different initiated reaction from 200 to 400 K are shown in Figures S7 to S9.

The rate constants at 298.15 K and 1 atm in the routes have been chosen for discussion. Take OH-initiated reaction for example. The individual rate constants for the addition pathway A1-A7 and A1’-A7’ are noted \( k_{A1} \sim k_{A7} \) and as \( k_{A1} \sim k_{A7} \), respectively, and rate constants for the H atom abstraction pathway 8-12 are noted as \( k_{A8} \sim k_{A12} \). The rate constants of overall OH radical addition reaction and H atom abstraction are defined as \( k_{A1} = k_{A1}^{add} + k_{A1}^{ab} \), \( k_{A8} = k_{A8}^{add} + k_{A8}^{ab} \), and \( k_{OH} = k_{A1} + k_{A8} \). The overall rate constant for the AF with OH reaction is labeled as \( k_{OH} = k_{A1} + k_{A8} + k_{OH} \). At 298.15 K, the overall calculated rate constants for reactions of AF with OH, HO₂, NO₂, O₃, and Cl, are 4.04×10⁻¹³, 7.02×10⁻¹³, 6.93×10⁻¹⁰, 1.45×10⁻⁸, and 5.07×10⁻⁷ cm³ molecule⁻¹ s⁻¹, respectively. The rate branching ratio can be expressed by the formula \( r = k_{add}[X]/[AF] \). Once the concentrations of AF and X radical in atmosphere are determined the degradation rate can be calculated.

The rate branching ratio can be presented by \( R_i = \sum k_{[X]}/[AF] \) (X=OH, HO₂, NO₃, O₃, Cl). In calculations, the 24 h average oxidant concentrations are considered: OH radical concentration of 9.7×10⁸ molecule cm⁻³, HO₂ radical concentration of 1.0×10⁹ molecule cm⁻³, NO₂ concentration of 1.2×10⁷ molecule cm⁻³, O₃ concentration of 7.0×10¹⁰ molecule cm⁻³, and CI concentration of 1×10¹⁰ molecule cm⁻³. Figure S10 indicates the rate branching ratio of different rate constants of initiated reactions to the total rate. It can be observed that the removal of AF in the atmosphere is dominated by its reactions with OH radical (98%), followed by minor reactions with Cl-atom (<2%) in the temperature range of 200–400 K. On the contrary, HO₂, O₃, and NO₂ initiated reactions take little part in this range of temperature. When the temperature below 300K, the rate branching ratio of OH-initiated reactions increases slowly and the rate branching ratio of Cl-initiated reactions decreases as temperature rises. After 300K, the former increases and the later decrease. Generally speaking, the branching ratios change little with the various temperatures. In the whole reactions, OH initiated reactions make more contribution.

Atmospheric lifetime

To assess its impact on the environment, it is critical to know the atmospheric lifetime of AF. The atmospheric lifetimes (τ) of AF, with respect to reactions with OH, HO₂, NO₂, O₃, and Cl, can be calculated and analyzed on the basis of the rate constants in the elementary reaction, using the formula \( \tau = 1/\sum k_{[X]} \). In which \([X]\) term is the concentration of radical and can be taken as a constant in the troposphere. The calculated lifetimes at the range of 200–400 K are listed in Tables S1C to S8C. Overall, the higher the temperature is, the shorter the lifetime.

The total atmospheric lifetime can be calculated with the formula \( \tau_{total} = \sum \tau_i \). Total atmospheric lifetimes of AF with different oxidants are listed in Table SD. According to the results, the \( \tau_{total} \) for all OH, HO₂, NO₂, O₃, and Cl initiated oxidation reactions is 2.14 days. And the τ for the reaction of OH radical is around 2.18 days, and 135 days for Cl. Evidently, AF is more likely to be removed quickly by the reaction with ozone near their emission sources. However, both the concentration of radicals and the rate constant of reactions with radicals determine the atmospheric lifetime of AF. In some places, the abundant OH radicals may play an important role in the degradation of AF. At night or in seriously polluted regions, the 12h averaged NO₂ radical concentration is about 5×10³ cm⁻³ molecule⁻¹ s⁻¹, the reaction with NO₂ may contribute to controlling AF \(^{26}\). Moreover, in some coastal areas where the concentration of CI atoms can reach 1×10⁴ cm⁻³ molecule⁻¹, the reaction of AF with Cl atom may contribute great portion to the removal of AF in the atmosphere.\(^{26}\)

Conclusions

The degradation mechanism of AF initiated by OH radical, HO₂ radical, NO₂ radical, O₃, and Cl were investigated at the MPWB1K/6-31G (d, p) level. The kinetic calculations were carried out with TST method. Some valuable conclusions can be drawn as follows:

The mechanism of OH, HO₂, NO₂, O₃, and Cl initiated reactions of AF includes H abstraction pathways and the addition pathways.

The O₃-adducts can undergo unimolecular decomposition, leading to C-C/C-O bond cleavage. For cis-addition HO₂, NO₂, and Cl added to C₄ are the most favorable reaction pathways with the lowest barrier and release more heat, while they added C₃ are the most favorable reaction pathways among the trans-addition, the adducts can further leave the H atom connect with C₄ or C₅ and be degraded in the atmosphere.

At 298.15 K, the total rate constants of AF with OH, HO₂, NO₂, O₃, and Cl, are 4.04×10⁻¹³, 7.02×10⁻¹³, 6.93×10⁻¹⁰, 1.45×10⁻⁸, and 5.07×10⁻⁷ cm³ molecule⁻¹ s⁻¹, respectively. The rate branching ratio of OH initiated reactions are dominant. The HO₂, NO₂, O₃, and Cl initiated reactions make little contribution to the reaction rate of AF from 200 to 400K compared with the OH initiated reactions.

The τ for all OH HO₂, NO₂, O₃, and Cl initiated oxidation reactions is 2.14 days.

Acknowledgements

This work is supported by National Natural Science Foundation of China (21277082, 21337001), the Promotive Research Fund for Excellent Young and Middle-aged Scientists of Shandong Province (BS2012H3009), Natural Science Foundation of Shandong Province (No. ZR2014BP012), Project for New Century Excellent Talents in University (NCET-13-0349), Marie Curie International Research Staff Exchange Scheme Fellowship within the 7th European Community Framework Program (No. 295132), Project for science and technology development of Shandong province (2014GSF117028), Beijing National Laboratory for Molecular Science (20140160), and the Fundamental Research Funds of Shandong University (2015JC020).

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Notes and references

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Table 1  Arrhenius formulas of rate constants k for elementary reactions at 200–400K (cm³ molecule⁻¹ s⁻¹)

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$k_{\text{react}}$ (T=298.15)</th>
<th>Arrhenius formulas</th>
<th>$R^2$</th>
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<tr>
<td>AF + OH· → IMA</td>
<td>4.04E-13</td>
<td>k=7.71E-12exp(-865.03/T)</td>
<td>0.9941</td>
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<tr>
<td>AF + HO₂· → IMB</td>
<td>7.02E-33</td>
<td>k=2.91E-15exp(-8133.1/T)</td>
<td>0.9999</td>
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<tr>
<td>AF + NO₃ → IMC</td>
<td>6.93E-20</td>
<td>k=8.85E-17exp(-2067.6/T)</td>
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<tr>
<td>AF + O₃ → IMD</td>
<td>1.45E-25</td>
<td>k=5.38E-16exp(-6555.2/T)</td>
<td>0.9999</td>
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<tr>
<td>AF + Cl· → IME</td>
<td>5.07E-12</td>
<td>k=7.84E-10exp(-947.77/T)</td>
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