

# *Ab initio* calculations on the reaction mechanism for the radical reaction $\text{CH}_3 + \text{ClO}$

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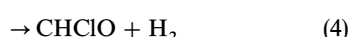
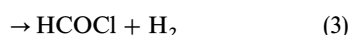
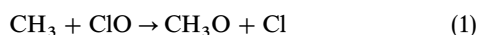
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The probable reaction mechanism for the reaction of methyl and chlorine monoxide radicals has been studied using the G2MP2 method. Among the six possible pathways, the present calculations show that production of methoxyl radical and chlorine atom, and formaldehyde and hydrogen chloride are the two most significant, and their reaction barriers are very close in energy. Simple RRKM calculations have been performed to compare these two main channels in detail. On the basis of detailed comparison with the experimental results, the present theoretical results are generally considered to be good.

## 1. Introduction

It is well known that the methyl radical is one of the most important reactive species in atmospheric chemistry and combustion chemistry.<sup>1</sup> It is also a very common activated intermediate in radical–radical reactions. The chlorine monoxide (ClO) radical is an important species in the field of photochemistry.<sup>2–4</sup> It is believed that the rapid depletion of stratospheric ozone over Antarctica in the austral spring is mainly due to catalytic cycles involving the ClO radical.<sup>5</sup> Hence, it is worth studying the reaction mechanisms and kinetics.

There are six different production pathways that are thermochemically favorable, namely



In 1995, Biggs *et al.*<sup>6</sup> studied the kinetics and mechanisms of the reaction of  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  with ClO and OClO radicals, and obtained the reaction rate constants. They found direct evidence for the production of  $\text{CH}_3\text{O}$  and, by inference, Cl, but did not observe direct production of  $\text{H}_2\text{CO}$  with mass spectrometry. However, as they noted, the background signals at both  $m/z = 29$  and  $30$  were very high, and hence  $\text{H}_2\text{CO}$  production could have been masked. Since HCl was used a source of Cl in these experiments, HCl formed as a product was impossible to detect. Therefore, these authors suggested that the methoxyl radical and the chlorine atom were the main products for the  $\text{CH}_3 + \text{ClO}$  reaction and did not rule out the existence of another channel forming  $\text{H}_2\text{CO}$  and HCl, although there was no direct evidence for it.

In addition, there are other reports, both theoretical and experimental, about analogous reactions, such as the decomposition of  $\text{CH}_3\text{OF}$  radical.<sup>7–11</sup> Compared with these reactions, there are many unclear conclusions for the  $\text{CH}_3 + \text{ClO}$  reaction. Therefore, it is necessary to examine further the  $\text{CH}_3 + \text{ClO}$  reaction through experiment and theory.

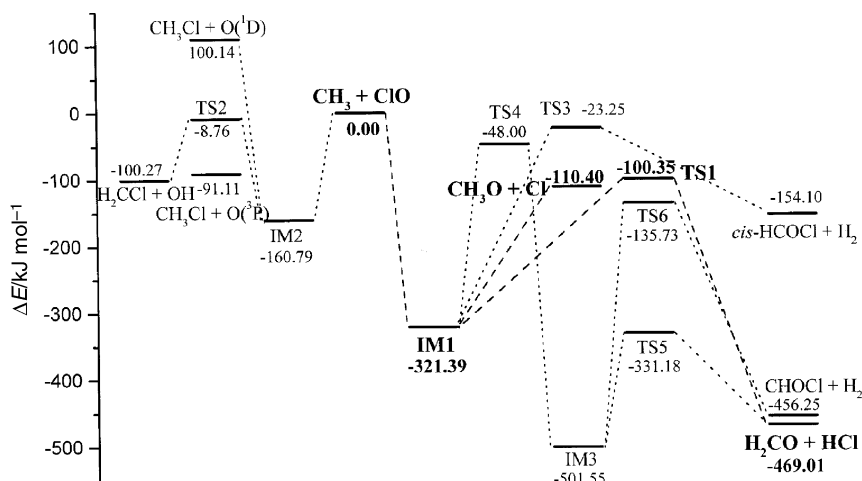
In the present work, we studied the  $\text{CH}_3 + \text{ClO}$  reaction by using *ab initio* molecular orbital calculations, in order to clarify the reaction mechanisms. Two intermediates are found to be first formed, and further thermochemical stability of the intermediates is also explored. Based on the present calculation results, we discuss the most favorable products and relative mechanisms. Furthermore, we also compare our results with experimental ones and discuss the contradiction over the conclusions. Additionally, simple RRKM calculations have been performed to compare the two main production channels in detail, since their reaction barriers are very close in energy.

## 2. Computation methods

All *ab initio* calculations were carried out using the GAUSSIAN 98 program.<sup>12</sup> The lowest singlet extensive potential energy curve for the reaction of  $\text{CH}_3$  and ClO was obtained with G2MP2 theory.<sup>13</sup> The G2MP2 method is the modified version of G2, which uses MP2 instead of MP4 for the basis set extension corrections, and is nearly as accurate as the full G2 method<sup>14</sup> at substantially reduced computational cost. Recent studies<sup>15,16</sup> have shown that the accuracy of the G2MP2 level is sufficient. In this work, geometries of reactants, products, intermediates (denoted as IM) and transition states (denoted as TS) were optimized at the MP2(full) level with 6-31G(d) and 6-311++G(d,p) basis sets respectively. The MP2(full)/6-31G(d) frequency calculations were employed to characterize the stationary points. Furthermore, it is confirmed by using IRC calculations that each transition state links the desired reactants and products. Then, the MP2/6-311G(d,p), MP2/6-311+G(3df,2p) and QCISD(T)/6-311G(d,p) single-point energy calculations were performed with the MP2(full)/6-31G(d) optimized geometries, and hence the barrier heights and reaction heats were obtained at the G2MP2 level.

## 3. Results and discussion

The overall energetic profile based on the G2MP2 energies for the reaction is shown in Fig. 1, and the G2MP2 relative energies are also given. The optimized geometries of the various stationary points (minima and saddle points) on the reaction

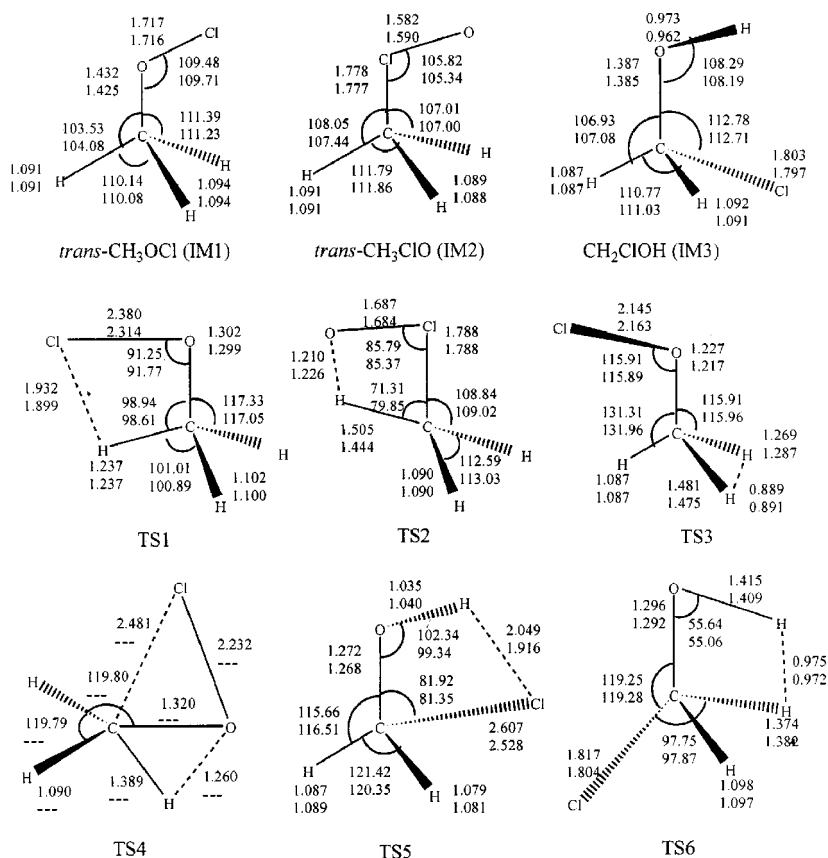


**Fig. 1** Energetic profile for the reaction of  $\text{CH}_3 + \text{ClO}$ . The values are the G2MP2 relative energies in  $\text{kJ mol}^{-1}$ . The dashed lines refer to the most important production pathways.

potential energy surface for the  $\text{CH}_3 + \text{ClO}$  reaction are shown in Fig. 2. The optimized parameters show no major changes with the increasing size of basis set. The harmonic vibrational frequencies for these stationary points are summarized in Table 1. In order to compare with the experimental data,<sup>17</sup> the reaction heats  $\Delta H$  are corrected to 298 K, and are listed in Table 2. The theoretical studies show that many unimolecular decomposition and rearrangement processes with high barriers have to be involved. In the following discussion, the G2MP2 energies and the MP2(full)/6-311++G(d, p) geometries are used unless otherwise noted.

### 3.1 The intermediate formed (IM1 or IM2)

The barrierless, associative reaction between  $\text{CH}_3$  and  $\text{ClO}$  takes place on an attractive potential energy surface. Steric reorientation permits the formation of two intermediates IM1 and IM2. The methyl radical has a planar structure with  $D_{3h}$  symmetry. As the oxygen atom in the  $\text{ClO}$  radical joins to the carbon atom, the intermediate IM1 with  $C_s$  symmetry is formed, in which the nascent C–O bond is 1.425 Å in length. Similarly, the intermediate IM2 with  $C_s$  symmetry is formed where the chlorine atom is adjacent to the carbon atom. The



**Fig. 2** Optimized structures of the intermediates and transition states for the  $\text{CH}_3 + \text{ClO}$  reaction. The upper values are the MP2(full)/6-31G(d) geometric parameters, and the lower values are the MP2(full)/6-311++G(d,p) ones. Bond lengths are in Å, and angles are in degrees.

**Table 1** Harmonic vibrational frequencies of the intermediates and transition states for the CH<sub>3</sub> + ClO reaction

Species	Frequencies/cm <sup>-1</sup> <sup>a</sup>
<i>trans</i> -CH <sub>3</sub> OCl(IM1)	271, 376, 703, 1060, 1201, 1224, 1510, 1533, 1570, 3098, 3191, 3223
<i>cis</i> -CH <sub>3</sub> OCl	266i, 411, 698, 1052, 1172, 1215, 1514, 1545, 1559, 3112, 3209, 3230
<i>trans</i> -CH <sub>2</sub> ClO(IM2)	194, 271, 725, 869, 1072, 1082, 1436, 1501, 1540, 3133, 3256, 3267
<i>cis</i> -CH <sub>2</sub> ClO	200i, 300, 711, 857, 1040, 1040, 1406, 1515, 1523, 3134, 3264, 3264
CH <sub>2</sub> ClOH(IM3)	365, 462, 735, 1006, 1143, 1244, 1411, 1449, 1564, 3147, 3257, 3764
<i>trans</i> -CH <sub>2</sub> ClOH	57i, 399, 785, 1060, 1119, 1261, 1274, 1474, 1581, 3110, 3174, 3758
TS1	2954i, 324, 398, 527, 1032, 1242, 1260, 1312, 1564, 1660, 3021, 3115
TS2	1541i, 384, 518, 666, 841, 1074, 1091, 1238, 1499, 1999, 3167, 3276
TS3	1523i, 248, 340, 426, 860, 937, 1148, 1345, 1513, 1781, 2649, 3260
TS4	2139i, 246, 437, 534, 670, 1070, 1208, 1282, 1557, 1872, 3158, 3291
TS5	646i, 294, 573, 912, 1069, 1195, 1425, 1480, 1649, 2763, 3232, 3387
TS6	2375i, 379, 640, 676, 969, 1048, 1343, 1356, 1551, 2000, 2295, 3108

<sup>a</sup> i represents imaginary frequency.

C–Cl bond formed is 1.777 Å in length. As indicated in Fig. 1, the overall addition pathways are exothermic by 321.39 and 160.79 kJ mol<sup>-1</sup>, respectively. Thus, the intermediates have higher internal energies, so that many production channels would be open. Since IM1 is more stable than IM2, we mostly discuss production pathways of IM1 in the following sections.

### 3.2 Unimolecular decomposition and rearrangement processes of IM1

As shown in Fig. 1, four production pathways have been found and various products are obtained through further decompositions.

The energetically most favorable reaction path (1) is a simple bond fission channel without transition states. Although the dissociation process is endothermic by 210.99 kJ mol<sup>-1</sup>, the total production pathway to yield the methoxyl radical and the chlorine atom is exothermic by 110.40 kJ mol<sup>-1</sup> relative to the initial reactants. As shown in Table 2, the reaction heat  $\Delta H_{298}$  is  $-118.04$  kJ mol<sup>-1</sup>, in good agreement with the experimental values of  $-111$ ,<sup>6</sup> and  $-110$  kJ mol<sup>-1</sup>.<sup>17</sup>

Another important production pathway (2) is IM1 → H<sub>2</sub>CO + HCl. It is analogous to the decomposition process of CH<sub>3</sub>OF to H<sub>2</sub>CO and HF.<sup>11</sup> *Trans*-CH<sub>3</sub>OCl (IM1) transforms first to *cis*-CH<sub>3</sub>OCl, through an internal rotation about the C–O bond. The energy of *cis*-CH<sub>3</sub>OCl is higher than that of IM1 by only 11.81 kJ mol<sup>-1</sup>. Then, the subsequent unimolecular decomposition of *cis*-CH<sub>3</sub>OCl yields H<sub>2</sub>CO and HCl *via* a four-member ring transition state (TS1). The barrier height is 209.23 kJ mol<sup>-1</sup> relative to *cis*-CH<sub>3</sub>OCl. TS1 has C<sub>s</sub> symmetry. The breaking C–H and O–Cl bonds are elongated by about 0.15 and 0.59 Å, respectively. The forming H–Cl bond is 1.899 Å in length, which is far longer than the equilibrium bond length 1.274 Å. This suggests that TS1 is a loose ring structure. The C–O bond length is decreased from 1.425 to 1.299 Å, closing to a multiple bond C=O in the product CH<sub>2</sub>O. The corresponding imaginary frequency of TS1 is 2954

cm<sup>-1</sup>, which suggests that quantum mechanical tunnelling would be very significant for this process. This reaction channel is exothermic by 147.62 kJ mol<sup>-1</sup>, while it is very exothermic, by 469.01 kJ mol<sup>-1</sup>, relative to the initial reactants CH<sub>3</sub> + ClO. As shown in Table 2, the reaction heat  $\Delta H_{298}$  is  $-469.49$  kJ mol<sup>-1</sup>, consistent with the experimental values  $-447$ ,<sup>6</sup> and  $-449$  kJ mol<sup>-1</sup>.<sup>17</sup>

The third decomposition pathway (3), IM1 *cis*-HCOCl + H<sub>2</sub>, could occur *via* a three-center transition state (TS3). TS3 breaks the C<sub>s</sub> symmetry. The two breaking C–H bonds are elongated by about 0.20 and 0.38 Å, respectively. The forming H–H bond length is 0.891 Å, close to the equilibrium value 0.738 Å. It should be noticed that the hybridization of the carbon atom has changed from sp<sup>3</sup> in IM1 to sp<sup>2</sup> in product *cis*-HCOCl. The O–Cl bond length in *cis*-HCOCl is 2.276 Å, which is much longer than that of IM1, by about 0.56 Å. In contrast, the C–O bond length is decreased and is close to the multiple (C=O) bond length in CH<sub>2</sub>O. The corresponding barrier height is 298.14 kJ mol<sup>-1</sup>, which is probably so high due to the strong repulsion of the three-member ring. However, the energy of TS3 is still lower than the initial reactants by about 23.25 kJ mol<sup>-1</sup>. Since there is no available experimental enthalpy of formation for *cis*-HCOCl, it is impossible to compare the theoretical and experimental reaction heat.

There is another energetically favorable channel involving the rearrangement of IM1 to CH<sub>2</sub>ClOH (IM3). The transition state (TS4) is an abnormal four-center structure with C<sub>s</sub> symmetry. The barrier height is 273.39 kJ mol<sup>-1</sup> relative to IM1 and the corresponding imaginary frequency is 2139 cm<sup>-1</sup>. It should be noted that we failed to locate this transition state with the 6-311++G(d,p) basis set. Hence, the structure of TS4 in the present paper is the MP2(full)/6-31G(d) optimized geometry. The C–O bond length is decreased by about 0.11 Å. The breaking C–H and O–Cl bonds are elongated from 1.091 and 1.717 Å in IM1 to 1.389 and 2.232 Å in TS4, respectively. The forming O–H and C–Cl bonds are 1.260 and 2.481 Å, respectively. Thus, *trans*-CH<sub>2</sub>ClOH would be formed at the end of this process, which is an unstable intermediate with one imaginary frequency, as indicated in Table 1. Hence, the O–H bond would rotate around the C–O bond to produce CH<sub>2</sub>ClOH (IM3). IM3 is slightly more stable, by 14.67 kJ mol<sup>-1</sup>, than *trans*-CH<sub>2</sub>ClOH, which is 180.16 kJ mol<sup>-1</sup> lower than IM1. Thus, IM3 has the higher internal energy and is an activated intermediate. Further production pathways will be open. In our calculations, we find two main decomposition channels.

The first is dissociation to H<sub>2</sub>CO + HCl *via* a four-center ring transition state (TS5). TS5 has no symmetry and four atoms of the ring lie in a contorted plane. The dihedral angle D(H,O,C,Cl) is 22.36°.

The other channel (4) is decomposition to CHClO + H<sub>2</sub> *via* a four-member transition state (TS6). Similar to TS5, TS6 has

**Table 2** Calculated reaction heats  $\Delta H_{298}$  and corresponding experimental values (in kJ mol<sup>-1</sup>)

Reaction channels	Reaction heats, $\Delta H_{298}$	
	<i>Ab initio</i> <sup>a</sup>	Experimental
(1) CH <sub>3</sub> + ClO → CH <sub>3</sub> O + Cl	$-118.04$	$-111$ , <sup>b</sup> $-110$ <sup>c</sup>
(2) CH <sub>3</sub> + ClO → H <sub>2</sub> CO + HCl	$-469.49$	$-447$ , <sup>b</sup> $-449$ <sup>c</sup>
(3) CH <sub>3</sub> + ClO → <i>cis</i> -HCOCl + H <sub>2</sub>	$-154.72$	
(4) CH <sub>3</sub> + ClO → CHClO + H <sub>2</sub>	$-457.28$	
(5) CH <sub>3</sub> + ClO → H <sub>2</sub> CCl + OH	$-100.53$	$-87$ <sup>c</sup>
(6) CH <sub>3</sub> + ClO → CH <sub>3</sub> Cl + <sup>1</sup> O	$102.76$	$109$ <sup>c</sup>
CH <sub>3</sub> + ClO → CH <sub>3</sub> Cl + <sup>3</sup> O	$-98.59$	$-81$ <sup>b,c</sup>

<sup>a</sup> This work. <sup>b</sup> From ref. 6. <sup>c</sup> From ref. 17.

no symmetry. Since the C–O and C–Cl bond distances are close to their optimized values in product CHClO, 1.191 and 1.762 Å, respectively, TS6 is a product-like transition state. The corresponding imaginary frequency is 2375 cm<sup>-1</sup>. The barrier height is 365.82 kJ mol<sup>-1</sup>, which is high due to the strong repulsion of the tight four-member ring. Therefore, although the total reaction channel CH<sub>3</sub> + ClO → CHClO + H<sub>2</sub> is very exothermic, by 456.25 kJ mol<sup>-1</sup>, the reaction pathway is impeded due to the higher activation barrier.

As mentioned above, TS1 and TS4 have imaginary frequencies 2954 and 2139 cm<sup>-1</sup>. This suggests that quantum mechanical tunnelling is probably very important for these processes. Thus, the important products H<sub>2</sub>CO and HCl could be formed through two reasonable routes: CH<sub>3</sub> + ClO → IM1 → TS1 → H<sub>2</sub>CO + HCl and CH<sub>3</sub> + ClO → IM1 → TS4 → IM3 → TS5 → H<sub>2</sub>CO + HCl. Obviously, the former should be more feasible.

### 3.3 Unimolecular decomposition and rearrangement processes of IM2

IM2 is also a highly activated complex. It is found that there are probably two production channels.

The first, pathway (5), is decomposition to H<sub>2</sub>CCl + OH. Similar to the dissociation of IM1 to H<sub>2</sub>CO + HCl mentioned above, IM2 must first transform to the *cis*-form. IM2 is just more stable than *cis* CH<sub>3</sub>ClO, by 5.46 kJ mol<sup>-1</sup>. Then, *cis*-CH<sub>3</sub>ClO can decompose to products *via* a transition state (TS2). TS2 is a four-center ring with C<sub>s</sub> symmetry. Four atoms, C, Cl, O and H, lie in one plane. Compared with the geometry of IM2, the breaking Cl–O and C–H bonds are elongated by about 0.09 and 0.35 Å, respectively. The forming O–H bond is 1.226 Å, longer than its equilibrium value 0.968 Å. The others bonds are changed slightly. Obviously, this transition state is reactant-like. The barrier height is 152.03 kJ mol<sup>-1</sup> relative to IM2. The total reaction pathway is exothermic by about 100.27 kJ mol<sup>-1</sup>, while the energy of TS2 is just lower than that of the initial reactants by 8.76 kJ mol<sup>-1</sup>.

The second channel (6) is a simple fission process, IM2 → CH<sub>3</sub>Cl + O without transition states. This process is endothermic by 260.93 kJ mol<sup>-1</sup>. The total reaction pathway is endothermic by 100.14 kJ mol<sup>-1</sup>. Thus, it is impossible to occur due to the high endothermic reaction.

### 3.4 RRKM calculations for two main production channels

As shown in Fig. 1, the barrier heights of two main decomposition channels (1) and (2) are very close. It is difficult to decide which is the most favorable solely based on energies. Therefore, simple RRKM calculations have been performed to compare the two main production channels in detail.

For channel (2), the unimolecular rate constant can be calculated by standard RRKM theory, using the vibrational frequencies at the MP2(full)/6-31G(d) level shown in Table 1 and the G2MP2 energies in Fig. 1. The sum of states for the saddle point and the density of states for the reactant molecules are computed with the Whitten–Rabinovich approximation.<sup>18</sup>

Since we cannot locate any transition state for channel (1), it is classified as simple bond ruptures with a “loose transition state”. In order to estimate the unimolecular rate constants, we used a “loose transition state” model.<sup>19</sup> In this model, the potential energy along with the rupturing bond is represented by the Morse function. The rate constants can be determined by locating the position of the minimum sum of states along with the bond length of the rupturing bond.

We estimate the value of the “looseness parameter”,<sup>20</sup> which is just qualitative and assumed not to influence our conclusion. In the case of total energy 321.39 kJ mol<sup>-1</sup>, the calculated RRKM unimolecular rate constants for channels (1) and (2) are 2.5 × 10<sup>12</sup> and 4.3 × 10<sup>11</sup> s<sup>-1</sup>, respectively.

Hence, channel (1) seems to be the most feasible. These RRKM calculations will be described in detail elsewhere.

### 3.5 Discussion on the experimental and calculated results

Most of the calculated reaction enthalpies Δ*H*<sub>298</sub> are consistent with the experimental values, as indicated in Table 2. It is believed that our theoretical calculation results are reasonable.

Biggs *et al.*<sup>6</sup> assumed four reaction pathways and listed the corresponding reaction enthalpies. Our calculation results are somewhat inconsistent with their conclusion. Owing to the total spin constraint, the product O atom should be the singlet excited state instead of the triplet ground state suggested by Biggs *et al.* Therefore, the CH<sub>3</sub>Cl + O production path is endothermic, not exothermic as predicted by their assumption. The reaction enthalpy at 298 K is 102.76 kJ mol<sup>-1</sup>, which is consistent with the reference value 109 kJ mol<sup>-1</sup>.<sup>17</sup> Moreover, we also calculated the total energy and relative energy of CH<sub>3</sub>Cl + O(<sup>3</sup>P), and the reaction enthalpy at 298 K is –98.59 kJ mol<sup>-1</sup>, which is somewhat larger than the experimental value of –81 kJ mol<sup>-1</sup>.<sup>6,17</sup>

As mentioned above, simple RRKM calculations suggest that channel (1) is the most favorable, which is in good agreement with the previous experiment.<sup>6</sup> However, we believe products H<sub>2</sub>CO and HCl should be also observed as the reaction continues due to the moderate dissociation rate. It is therefore desirable to reinvestigate the experiment, and we make some preliminary brief comments here.

## 4. Conclusions

*Ab initio* calculations have been carried out to explore the possible reaction mechanism for the CH<sub>3</sub> + ClO reaction. The reaction heats and activation barriers are calculated at the G2MP2 level. The present reaction potential energy curve is very similar to that of the unimolecular decomposition of CH<sub>3</sub>OF.<sup>11</sup> The agreement between theoretical and experimental results for the most part is seen to be good.

In the present theoretical studies, it is found that there are two significant production pathways, CH<sub>3</sub>O + Cl and CH<sub>2</sub>O + HCl. Furthermore, quantum mechanical tunnelling seems to be very important for the reaction processes. Simple RRKM calculations indicate that the former pathway is the most favorable, which is in good agreement with the original experiment.<sup>6</sup> Moreover, the latter production pathway, H<sub>2</sub>CO + HCl is believed to be observed as the reaction continues due to the moderate dissociation rate.

## Acknowledgements

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## References

- 1 E. W. Diau, M. C. Lin and C. F. Melius, *J. Chem. Phys.*, 1994, **101**, 3923.
- 2 I. W. M. Smith, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2271.
- 3 P. Biggs, C. E. Canosa-Mas, J. Fracheboud, D. E. Shallcross and R. P. Wayne, *Geophys. Res. Lett.*, 1995, **22**, 1221.
- 4 P. P. Bemand, M. A. A. Clyne and R. T. Watson, *J. Chem. Soc., Faraday. Trans.*, 1973, **69**, 1356.
- 5 *Scientific Assessment of Ozone Depletion: 1991*, WMO Global Ozone Research and Monitoring Project, Report No. 25, 1992, Geneva, Switzerland.
- 6 P. Biggs, C. E. Canosa-Mas, J. Fracheboud, G. Marston, D. E. Shallcross and R. P. Wayne, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 3045.
- 7 M. Kol, S. Rozen and E. Appleman, *J. Am. Chem. Soc.*, 1991, **113**, 2648.

- 8 B. Ruscio, E. Appleman and J. Berkowitz, *J. Chem. Phys.*, 1991, **95**, 7957.
- 9 L. A. Curtiss and J. A. Pople, *J. Chem. Phys.*, 1991, **95**, 7962.
- 10 Y. Apeloig and K. Albrecht, *J. Am. Chem. Soc.*, 1995, **117**, 9564.
- 11 B. Wang, H. Hou and Y. Gu, *Chem. Phys. Lett.*, 1999, **300**, 99.
- 12 M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, *GAUSSIAN 98, Revision A.7*, Gaussian Inc., Pittsburgh, PA, 1998.
- 13 L. A. Curtiss, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 1293.
- 14 L. A. Curtiss, K. Raghavachari, G. W. Trucks and J. A. Pople, *J. Chem. Phys.*, 1991, **94**, 7221.
- 15 X. G. Zhou, J. Li, Z. Wang, S. Q. Yu and X. X. Ma, *Acta Chim. Sin.*, 2001, **59**, 365.
- 16 X. G. Zhou, S. Q. Yu, J. Li, Z. Y. Sheng, L. M. Zhang and X. X. Ma, *Chem. Phys. Lett.*, 2001, **339**, 117.
- 17 M. F. Jacox, *J. Phys. Chem. Ref. Data*, 1997, **26**, 1496.
- 18 S. E. Stein and B. S. Rabinovitch, *J. Chem. Phys.*, 1973, **58**, 2438.
- 19 A. Holbrook, M. J. Pilling and S. H. Robertson, *Unimolecular Reactions*, J. Wiley, Chichester, 1996.
- 20 H. S. Johnston, *Gas-Phase Reaction Rate Theory*, Ronald Press, New York, 1966.