Theoretical studies on mechanism for the reaction of the excited nitrogen atom and chloromethane

Xiaoguo Zhou, Linsen Pei, Limin Zhang, Jinghua Dai, Yang Chen,
Shuqin Yu*, Xingxiao Ma

*Open Laboratory of Bond-selective Chemistry, Department of Chemical Physics, University of Science and Technology of China,
Hefei 230026, PR China*

Abstract

The probable reaction mechanism for the reaction of excited nitrogen atom and chloromethane has been studied using the G2MP2 method. Based on the calculated reaction processes, the excited nitrogen atom will insert into the C—Cl bond firstly to form the intermediate *trans*-CH_3NCl, which can subsequently decompose and isomerize to further products. The present result suggests that CH_2NCl is the most feasible among all possible products. The reaction mechanisms for the $N(^2D) + CH_3X$ (X = H, F, Cl) system are contrasted in detail. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

An electronically excited metastable nitrogen atom, $N(^2D)$, is known to be very important in reaction systems of various fields such as atmospheric chemistry and combustion chemistry. Methane derivative is believed to be one of the most important species in atmosphere chemistry. Several studies on the reaction systems of $N(^2D) + CH_3X$ (X = H, F, Cl) have been reported recently [1–5]. The overall rate constants for the reaction of $N(^2D)$ with some hydrocarbon molecules have been measured [1,2]. Umemoto et al. [3] studied t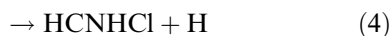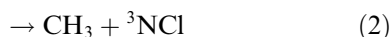he nascent rotational and vibrational distributions of $NH(X^3\Sigma)$ produced in the $N(^2D) + CH_4$ reaction using a laser-induced fluorescence technique. It is the first report about the detected initial reaction product. Their results implied the insertional mechanism that $N(^2D)$ inserts into the C—H bond. Takayanagi and co-workers [4] calculated this reaction using a high-quality ab initio MO method and obtained information on possible reaction products. The insertional process was confirmed and the reaction pathways to product $CH_2NH + H$ and $CH_3 + NH$ were found to be important. As far as we know, there are few reports about the reaction of $N(^2D)$ and methane derivative. Very recently, we have investigated the reaction process for the $N(^2D) + CH_3F$ reaction system [5]. The calculated reaction pathways are very similar to those of the $N(^2D) + CH_4$ reaction [4]. Both are very similar to

* Corresponding author.
E-mail address: sqyu@ustc.edu.cn (S. Yu).

the occurring insertional process and further decomposition or isomerization. However, there are no studies on the reaction of nitrogen atom and chloromethane, including experimental and theoretical investigations. Therefore, the aim of this work is to do a fundamental theoretical study in order to compare the reactions of $N(^2D)$ and methane derivative, and to give some useful information for future experiments.

Analogous to the former study on the $N(^2D) + CH_3F$ reaction, the probable pathways in the present reaction processes are suspected as follows:

$$N(^2D) + CH_3Cl \rightarrow CH_2NCl + H \tag{1}$$
$$\rightarrow CH_3 + {}^3NCl \tag{2}$$
$$\rightarrow CH_2 + HNCl \tag{3}$$
$$\rightarrow HCNHCl + H \tag{4}$$

In this paper, the reactions of $N(^2D)$ and CH_3Cl are studied by ab initio molecular orbital calculations. The most possible reaction mechanism is studied by using high-level G2MP2 theory. Several possible production channels involved in the reaction are examined.

2. Computation methods

All ab initio calculations were carried out using the Gaussian 98 suite of programs [6]. The lowest doublet extensive potential energy curve for the reaction of $N(^2D)$ and CH_3Cl was explored with the G2MP2 theory [7]. The MP2(full) optimized structures of reactants, products, intermediate (denoted as IM) and transition states (denoted as TS) were obtained with the 6-31G(d) and 6-311+G(d,p) basis sets, respectively. The vibrational frequency calculations were used to determine the nature of stationary points and estimate the zero-point-energy (ZPE). For each transition state, the internal reaction coordinate (denoted as IRC option) calculations were also employed to confirm that it linked 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) optimized geometries, and hence the

barrier heights and reaction heats were obtained at the G2MP2 level.

In the present open-shell reaction PES, the calculated $\langle S^2 \rangle$ values of the UHF wavefunctions in the present calculation were 0.76–0.98, indicating that there existed moderately large spin contamination in standard G2MP2 calculations. Thus, spin contamination probably led to somewhat errors in relative energies. In this case, projected UMP2 [8–10] calculations were expected to provide more accurate results. Therefore, we used the projected MP2(full) energies instead of the default UMP2(full) energies in standard G2MP2 method. According to that the eigenvalues after annihilation of the $\langle S^2 \rangle$ operator were very close to the theoretical value 0.75 in general, and the present calculated results seem to be reliable. Furthermore, the harmonic frequencies and ZPEs should be obtained at the HF level in standard G2MP2 theory. Unfortunately, there are somewhat large differences between the MP2(full) and HF optimized geometries in the present study, so that we used the MP2(full)/6-31G(d) frequencies to estimate ZPEs instead of the default HF level.

3. Results and discussion

The overall energetic profile based on the G2MP2 energies for this reaction is shown in Fig. 1, and the G2MP2 relative energies are also given. The optimized structures of main stationary points (minima and saddle points) on the reaction potential energy surface are shown in Fig. 2. In fact, there are no major changes with the increasing size of basis set on the optimized geometries. The harmonic vibrational frequencies for main reactants, products, and stationary points are summarized in Table 1. There are available experimental vibrational frequencies [11,12] for CH_2, CH_3, NCl, etc. The agreement between the calculated and experimental results is generally seen to be good, although the former are somewhat larger, which suggests our calculations to be accurate enough. Eigenvalues of the $\langle S^2 \rangle$ operator are also included in Table 1. Our theoretical studies show that many unimolecular decomposition and rearrangement processes have to be involved. In the
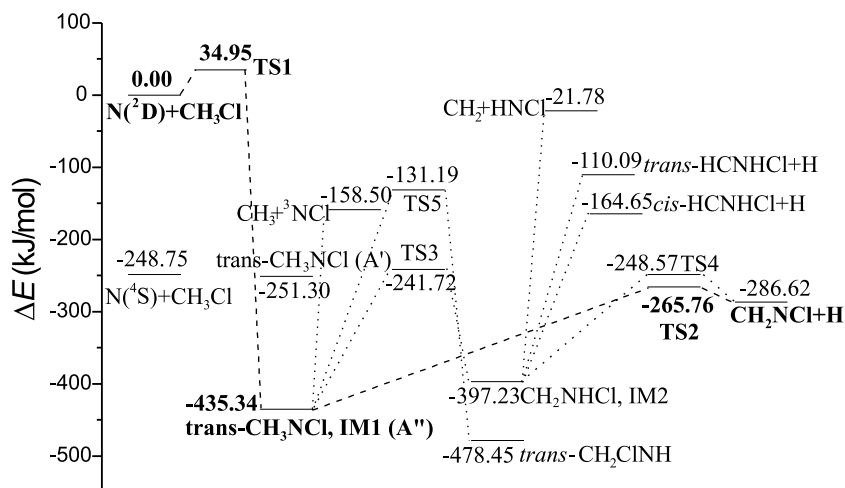
Fig. 1. Energetic profile for the reaction of N(^{2}D) and CH$_3$Cl. The values are the G2MP2 relative energies in kJ mol^{-1}. The dashed line refers to the most important production pathway.

following sections, the G2MP2 energies and the MP2(full)/6-311+G(d,p) geometries are used unless otherwise noted.

3.1. The insertional reaction mechanism

The interaction between N(^{2}D) and chloromethane takes place as they are approaching each other along the doublet potential energy surface. The reaction potential energy surface should have C$_s$ symmetry due to C$_{3v}$ structure of chloromethane. Therefore, this reaction process should have occurred along two possible doublet potential energy surfaces with A$'$ and A$''$ symmetries, respectively. As shown in Fig. 1, the product, trans-CH$_3$NCl (IM1) with A$''$ symmetry is 435.34 kJ/mol more stable than the reactant N(^{2}D) + CH$_3$Cl, while trans-CH$_3$NCl with A$'$ symmetry is 184.04 kJ/mol higher than that of A$''$ symmetry. Hence, that of A$'$ symmetry is an excited state of transform product. In IM1, the C—N bond is 1.449 Å and N—Cl bond is 1.700 Å, whilst these two bonds are 1.423 and 1.633 Å in A$'$ one, respectively. It is interesting that the C—N—Cl bond angle is changed from 109.22° in IM1 to 133.34° in that of A$'$ symmetry. Based on population analysis using the MP2 density, atomic spin density of nitrogen atom is slightly decreased from 0.90 in IM1 to 0.78 in A$'$ one. It shows that lone electron pair of nitrogen

participates in forming σ bond in the A$'$ excited state more than the ground state, which is consistent with changes of bond length and bond angle. Moreover, the structure of the methyl moiety in both of transform products is almost the same as that of chloromethane.

For the A$'$ and A$''$ symmetry doublet reaction potential energy surface, we have tried to locate the transition state, respectively. Similar to the analogous insertional mechanism for the N(^{2}D) + CH$_3$X (X = H or F) reaction, we only obtained a transition state for the A$''$ symmetry PES. As indicated in Fig. 1, trans-CH$_3$NF (IM1) can be formed via a three-member ring barrier TS1 (A$''$ symmetry). The barrier height is 34.95 kJ/mol relative to the reactants, N(^{2}D) + CH$_3$Cl. The TS1 has an imaginary frequency of 1175 cm^{-1}, and the corresponding vibrational mode is shown in Fig. 2. This vibrational mode shows that the mechanism is really the insertional process. The breaking C—Cl bond is elongated by about 0.43 Å, while the C—H bonds are shortened slightly. The forming C—N bond is 2.373 Å and N—Cl bond is 1.762 Å, which are longer than those of the product IM1 of about 0.92 and 0.06 Å, respectively. Additionally, as shown in Table 1, the corresponding harmonic frequencies of TS1 are nearly the same as those of chloromethane. Therefore, the TS1 is a loose
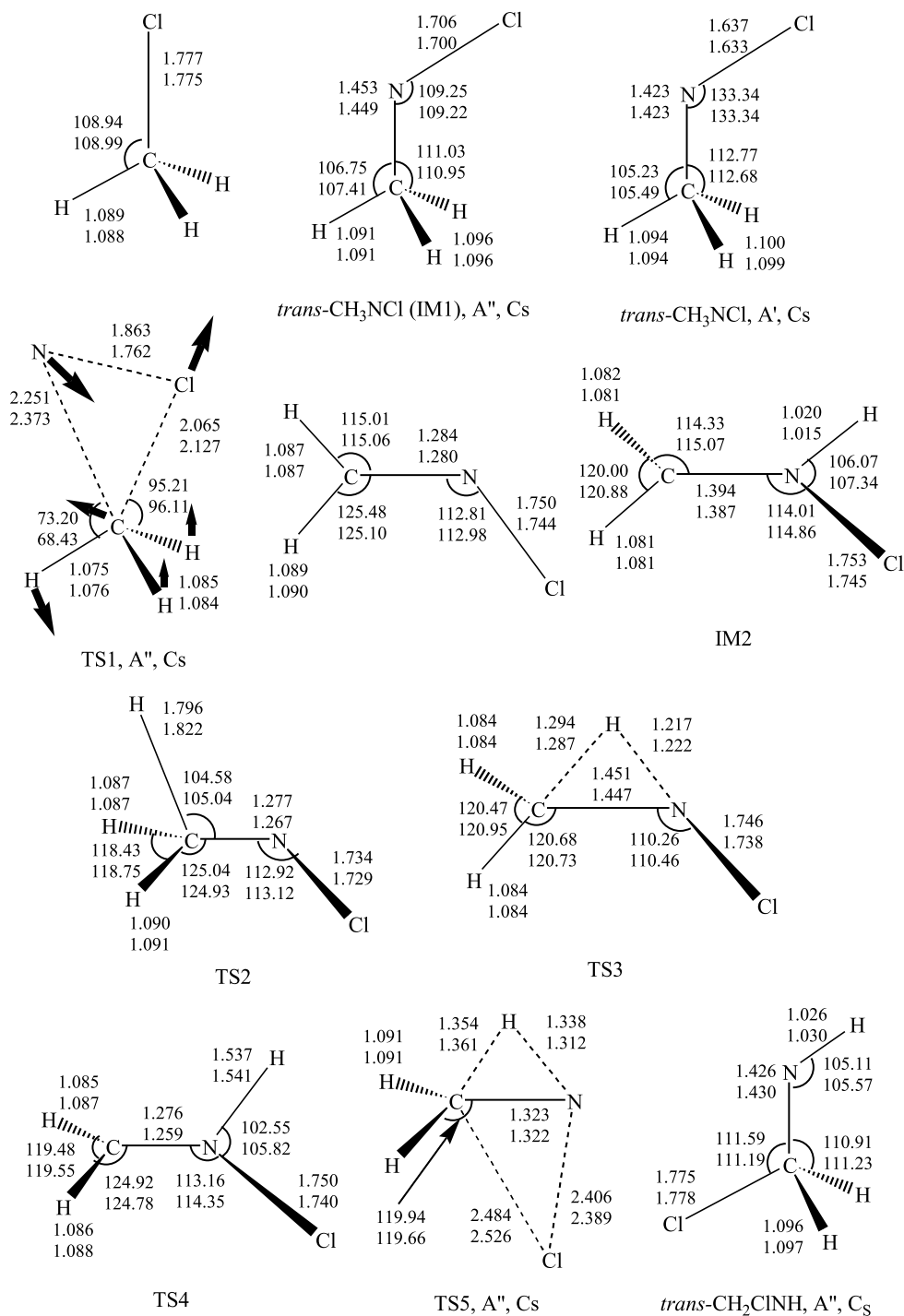
Fig. 2. Optimized geometries of main reactant, product, intermediates and transition states. The upper values are the MP2(full)/6-31G(d) geometric parameters, and the lower are the MP2(full)/6-311+G(d,p) ones. Bond lengths are in Ångströms, and bond angles are in degrees.

Table 1
MP2(full)/6-31G(d) harmonic vibrational frequencies of main reactant, product, intermediates and transition states in the present reaction[a]

	Frequencies (cm^{-1})	$\langle S^2 \rangle$
trans-CH$_3$NCl (IM1)	184, 406, 728, 1029, 1069, 1182, 1471, 1531, 1534, 3084, 3166, 3219	0.766
trans-CH$_3$NCl (A')	207, 320, 717, 1136, 1254, 1325, 1471, 1508, 1578, 3037, 3106, 3180	0.763
CH$_2$NHCl (IM2)	279, 376, 650, 718, 847, 1137, 1246, 1455, 1525, 3236, 3366, 3550	0.772
trans-CH$_2$ClNH	367, 407, 755, 867, 1089, 1211, 1214, 1426, 1495, 3086, 3144, 3437	0.760
TS1	1175i, 151, 506, 645, 889, 1021, 1345, 1500, 1562, 3191, 3325, 3395	0.765
CH$_3$Cl	786, 1087, 1087, 1470, 1547, 1547, 3148, 3260, 3260	0.0
TS2	1347i, 337, 470, 548, 705, 946, 1184, 1216, 1468, 1643, 3174, 3293	0.981
CH$_2$NCl	450, 661,743, 1043, 1199, 1477, 1666, 3173, 3289	0.0
TS3	2337i, 389, 404, 688, 880, 1106, 1140, 1234, 1473, 2524, 3209, 3344	0.805
TS4	2139i, 450, 518, 633, 715, 722, 1061, 1206, 1474, 1667, 3203, 3320	0.963
TS5	1805i, 175, 322, 358, 944, 1069, 1091, 1379, 1488, 1881, 3146, 3267	0.776

Eigenvalues of the $\langle S^2 \rangle$ operator are also listed.

[a] i represents imaginary frequency.

transition state. It will be discussed in detail in the following section.

As a result of the insertional process, the *trans* form IM1 is formed with high internal energy, so that it can further decompose or isomerize to various products. There are four production channels discussed in the present calculation, which will be discussed, respectively, in Sections 3.2 and 3.3.

3.2. Decomposition channels of IM1

As indicated in Fig. 1, there are two possible decomposition channels of IM1 in our results. The energetically most favorable path is to produce CH$_2$NCl and hydrogen atom, via a barrier TS2 of 169.58 kJ/mol height. The C—H bond cleavage barrier TS2 has no symmetry. As shown in Fig. 2, the breaking C—H bond is elongated from 1.096 Å in IM1 to 1.822 Å. The C—N bond length is decreased from 1.449 to 1.267 Å, closing to a multiple bond C=N in the product CH$_2$NCl. And the other bond lengths are changed slightly. Contrasted with the IM1 structure, one C—H bond turns around the C—N bond, so that those five atoms (besides the decomposing H atom) almost lie in a plane. Moreover, the corresponding harmonic frequencies of TS2 are very close to those of CH$_2$NCl, as shown in Table 1. Thus, the TS2 is a product-like barrier. The total reaction pathway, N(^{2}D) + CH$_3$Cl → CH$_2$NCl + H, is exothermic by 286.62 kJ/mol.

The other is a simple C—N bond scission channel to form methyl and triplet NCl. This pathway is endothermic by 276.84 kJ/mol, while the total pathway from N(^{2}D) and chloromethane to methyl and NCl is exothermic by 158.50 kJ/mol.

3.3. Isomerization channels of IM1

The present ab initio calculation implies two energetically favorable isomerization pathways. The first possible channel is isomerization from IM1 to CH$_2$NHCl (IM2), via a three-member ring barrier TS3 with 193.62 kJ/mol height. The transition state has a large imaginary frequency of 2337 cm^{-1} without symmetry. It suggests that the TS3 is a tight transition state and the tunneling effect probably is very important for this process. Compared to the optimized structures of the IM1, IM2 and TS3, H atom is transferred from the carbon atom to nitrogen atom. The breaking C—H bond is elongated by about 0.19 Å and the forming N—H bond is 1.222 Å. Moreover, the HCN bond angles are increased to close those in IM2, which suggests that hybridization of the carbon atom will be changed from sp^3 to sp^2 in product IM2. Although this process is endothermic by 38.11 kJ/mol, the product IM2 is still a highly activated intermediate, 397.23 kJ/mol stable relative to the initial reactants N(^{2}D) + CH$_3$Cl. Therefore, further decompositions will be easy to occur.

Four probable production channels are examined in our calculations. Firstly, $CH_2NCl + H$ can be produced from dissociation of the IM2, via a cleavage barrier TS4 with 148.66 kJ/mol height. The TS4 has a large imaginary frequency 2139 cm^{-1}, so that any effects due to quantum mechanical tunneling should be much noticeable. As shown in Fig. 2, the TS4 structure is very close to product CH_2NCl, especially the C—N bond length closing to a multiple bond C=N. And hence the TS4 is a product-like state.

The IM2 can also decompose to *cis*- or *trans*-HCNHCl and hydrogen atom. Although we have located the transition states for these C—H bond cleavage processes at the HF level, the G2MP2 energies show that energies of the transition states are lower than those of products. The overall dissociation channels from IM2 to *cis*- or *trans*-HCNHCl and hydrogen atom are endothermic by 232.58 and 287.14 kJ/mol, respectively.

Eventually, there is one simple C—N bond scission process to form the triplet methylene and HNCl without any transition state. It is very endothermic by 375.45 kJ/mol, while total energy of products is very close to that of the initial reactants $N(^2D) + CH_3Cl$.

The IM1 can also isomerize to product *trans*-CH_2ClNH, via an abnormal four-center ring barrier TS5. As shown in Fig. 2, the breaking C—H and N—Cl bonds are elongated by 0.27 Å and 0.69 Å, whilst the forming N—H and C—Cl bonds are 1.312 and 2.526 Å, respectively. It is abnormal that the C—N bond is shorter than that of IM1 and *trans*-CH_2ClNH. This process is exothermic by 43.11 kJ/mol with a very high barrier 304.15 kJ/mol. This high barrier suggests the strong repulsion of the abnormal four-member ring and it is difficult to be over. According to a 1805 cm^{-1} imaginary frequency, the quantum mechanical tunneling effect may be significant for this isomerization process.

3.4. Discussion on the present calculation

Analogous to discussion on the reaction mechanism of nitrogen atom and fluoride methane before [5], the H_2 and HCl elimination pathways are not included in the present calculations due to too high dissociation barriers.

For the reaction system of nitrogen atom and methane derivative, the initial reaction is assumed to be an insertion process. It has been confirmed by the original studies, such as $N(^2D) + CH_4$ [4], and $N(^2D) + CH_3F$ [5]. The present results are similar to those conclusions. We could not locate any transition state for the directly insertional process to form *trans*-CH_2ClNH and to only obtain an insertional transition state to produce IM1. The corresponding barrier height is 34.95 kJ/mol, which is larger than that of the $N(^2D) + CH_4$ reaction, 23.0 kJ/mol [4] and much lower than that of the $N(^2D) + CH_3F$ reaction, 123.5 kJ/mol [5]. In this case, reaction rate for the present reaction is probably far slower than the $N(^2D) + CH_4$ reaction rate.

Moreover, the most feasible production pathways of $N(^2D)$ and CH_3X (X = H, F, Cl) reactions are very similar as hydrogen atom and CH_2NX.

4. Conclusion

Ab initio calculations have been carried out to study the possible production pathways for the $N(^2D) + CH_3Cl$ reaction. It has been confirmed that in the present reaction, $N(^2D)$ firstly inserts into the C—Cl bond to produce the intermediate *trans*-CH_3NCl (IM1), which will further decompose or isomerize to various products. Among the probable processes considered, the reaction pathway to product $CH_2NCl + H$ is most feasible.

Acknowledgements

References

[1] K. Schofield, J. Phys. Chem. Ref. Data 8 (1979) 723.
[2] B. Fell, I.V. Rivas, D.L. McFadden, J. Phys. Chem. 85 (1981) 224.

[3] H. Umemoto, Y. Kimura, T. Asai, Chem. Phys. Lett. 264 (1997) 215.

[4] Y. Kurosaki, T. Takayanagi, K. Sato, S. Tsunashima, J. Phys. Chem. A 102 (1998) 254.

[5] X.G. Zhou, S.Q. Yu, J. Li, Z.Y. Sheng, L.M. Zhang, X.X. Ma, Chem. Phys. Lett. 339 (2001) 117.

[6] M.J. Frisch et al., Gaussian 98, Revision A.7, Gaussian Inc., Pittsburgh, PA, 1998.

[7] L.A. Curtiss, K. Raghavachari, J.A. Pople, J. Chem. Phys. 98 (1993) 1293.

[8] H.B. Schlegel, J. Chem. Phys. 84 (1986) 4530.

[9] C. Sosa, H.B. Schlegel, Int. J. Quantum Chem. 29 (1986) 1001.

[10] C. Sosa, H.B. Schlegel, Int. J. Quantum Chem. 30 (1986) 155.

[11] M.F. Jacox, J. Phys. Chem. Ref. Data 17 (1988) 279.

[12] M.F. Jacox, J. Phys. Chem. Ref. Data 19 (1990) 1437.