Theoretical Study on the Mechanism of the CH$_2$F + NO$_2$ Reaction

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Abstract: Despite the importance of the Fluoromethyl radicals in combustion chemistry, very little experimental information on their reactions toward stable molecules is available in the literature. Motivated by recent laboratory characterization about the reaction kinetics of Chloromethyl radicals with NO$_2$, we carried out a detailed potential energy survey on the CH$_2$F/H$_2$NO$_2$ reaction at the B3LYP/6-311G(d,p) and MC-QCISD (single-point) levels as an attempt toward understanding the CH$_2$F + NO$_2$ reaction mechanism. It is shown that the CH$_2$F radical can react with NO$_2$ to barrierlessly generate adduct a (H$_2$FCNO$_2$), followed by isomerization to b$_1$ (H$_2$FCONO-trans) which can easily interconvert to b$_2$ (H$_2$FCONO-cis). Subsequently, Starting from b$_1$ (b$_1$, b$_2$), the most feasible pathway is the C—F and N—O1 bonds cleavage along with N—F bond formation of b$_1$ (b$_1$, b$_2$) leading to P$_1$ (CH$_2$O + FNO), or the direct N—O1 weak-bond fission of b$_1$ (b$_1$, b$_2$) to give P$_2$ (CH$_2$O + NO), or the 1,3-H-shift associated with N—O1 bond rupture of b$_1$ to form P$_3$ (CHFO + HNO), all of which may have comparable contribution to the reaction CH$_2$F + NO$_2$. Much less competitively, b$_2$ either take the 1,4-H-shift and O1—N bond cleavage to form product P$_4$ (CHFO + HON) or undergo a concerted H-shift to isomer c$_2$ (HFCONOH), followed by dissociation to P$_4$. Because the rate-determining transition state (TS$_{ab1}$) in the most competitive channels is only 0.3 kcal/mol higher than the reactants in energy, the CH$_2$F + NO$_2$ reaction is expected to be rapid, and may thus be expected to significantly contribute to elimination of nitrogen dioxide pollutants. The similarities and discrepancies among the CH$_2$X/H$_2$NO$_2$ (X = H, F, and Cl) reactions are discussed in terms of the electronegativity of halogen atom. The present article may assist in future experimental identification of the product distributions for the title reaction, and may be helpful for understanding the halogenated methyl chemistry.

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Introduction

The halogenated hydrocarbon species such as CH$_2$F and CH$_3$Cl radicals are important intermediates in combustion processes, especially during incineration of hazardous waste, and can increase soot formation in fuel-rich oxidation. These species can be formed in unimolecular decomposition reactions of stable halogenated hydrocarbon molecules under combustion conditions. Bond-breaking reactions for the stable halogenated compounds occur uniformly at lower temperatures than for the hydrocarbons of similar size. Radical–radical crosscombination reactions constitute an integral part of the overall mechanisms of oxidation and pyrolysis of hydrocarbons. Data on elementary reactions of fluorinated methyl radicals with other radicals are also essential for the description and the prediction of the chemistry of halogenated organic compounds under incomplete combustion as in waste incineration, or pyrolysis, or under poor operating conditions, leading to products of incomplete combustion (PICs). On the
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other hand, it is known that nitrogen oxides (NOx, x = 1, 2) are among the major atmospheric pollutants released by combustion process. To minimize the harmful effects before their release in the atmosphere, one effective way is to chemically reduce them by the reburning of combustion products.7-12 The reaction of the Fluoromethyl radical with NO2 can be expected to be important during the oxidation of fluorinated compounds at low temperatures, because traces of nitrogen oxides are also often present,13 and may then provide an effective means for consummation of the NO2 formed in the combustion processes. Hence, reliable information on the kinetics of this Fluoromethyl reaction is of importance for the modeling of NOx combustion processes.

In the last 2 decades, the studies of the reactives for halocarbons with NOx have been the important topic due to the role of inhibition.14-17 However, the number of the substituted methyl radical reactions with NO2 subjected to direct kinetic studies is few. Up to now, Timonen et al.18 reported for the first time the direct kinetic studies of CH2Cl + NO2 over temperature ranges (220–360 K) using a tubular flow reactor coupled to a photoionization mass spectrometer and derived the rate constant expression as (2.16 ± 0.08) × 10−11 (T/300K)−1.2×0.24 cm3mol−1s−1, which indicate that the reaction of CH2Cl with NO2 is very rapid and may play an important role in the fate of NO2 pollutants during combustion processes. In addition, the reaction of CF3 + NO2 has been the subject of experimental investigation19 and the measured total reaction rate is (1.75 ± 0.26) × 10−11 cm3s−1.

Very recently, we have initiated a series of potential energy surfaces (PES) on CH2X + NO2 (X = H, F, Cl) reactions. The potential energy surfaces of CH2 + NO2,20 and CH2Cl + NO2,21 reactions were calculated at the MC-QCISD//B3LYP/6-311G(d,p) level. The features of the potential energy surfaces of two reactions are almost in parallel. However, some quantitative discrepancy leads to the different product distribution for the two reactions. Then, the question arises: are the mechanisms of the title reactions similar to CH2 + NO2 or to CH2Cl + NO2?

To the best of our knowledge, no experimental and theoretical studies have been reported for the title reaction. Therefore, it is highly desirable to carry out the detailed theoretical study on the PES of the title reaction. The main objectives of the present article are to (1) provide the elaborated isomerization and dissociation channels on the H2FCNO2 PES; (2) investigate the products of CH2F + NO2 reaction to assist in further experimental identification; (3) make comparisons between the CH2X (X = H, F, Cl) reactions with NO2 to deeply understand the halogenated methyl chemistry.

Computational Methods

All calculations are carried out using the GAUSSIAN98 program.22 All structures of the stationary points including reactants, minimum isomers, transition states, and products are calculated using hybrid density functional B3LYP method (the Becke’s three parameter hybrid functional with the nonlocal correlation functional of Lee–Yang–Parr) with the 6-311G(d,p) basis set. The spin-unrestricted B3LYP were applied to doublet of fragment molecules. The stationary nature of structures is confirmed by harmonic vibrational frequency calculations, that is, equilibrium species possess all real frequencies, whereas transition states possess one and only one imaginary frequency. The zero-point energy (ZPE) corrections are obtained at the same level of theory. To yield more accurate energetic information, higher level single-point energy calculations are performed at the multicoefficient correlation method based on quadratic configuration interaction with single and double excitations (MC-QCISD)23 by using the B3LYP/6-311G(d,p) optimized geometries. To conform that the transition states connect designated intermediates, intrinsic reaction coordinate (IRC) calculation is carried out at the B3LYP/6-311G(d,p) level of theory. Moreover, unless otherwise specified, the MC-QCISD single-point energies with zero-point energy (ZPE) corrections are used in the following discussions.

Results and Discussion

The optimized structures of stationary points with the corresponding experimental values24-26 are depicted in Figure 1, as well as the vibrational mode of the imaginary frequencies of the transition states. The electronic states, harmonic vibrational frequencies including available experimental values25,26 are listed in Table 1. Note that the calculated geometries and frequencies are in good agreement with experimental results with the largest deviation of less than 7% at the B3LYP/6-311G(d,p) level. Table 2 displays the relative energies including ZPE corrections of the stationary points. For our discussion easier, the energy of reactants R is set to be zero for reference. For simplicity, only the important products, isomers, and transition states are included in Figure 1 and Tables 1 to 2. The optimized structures of unfavorable isomers for CH2F + NO2 reaction are presented in Figure 2. To clarify the reaction mechanism, the most relevant pathways of the singlet PES for CH2F + NO2 reaction at the MC-QCISD/B3LYP/6-311G(d,p) level are depicted in Figure 3. The unfavorable reaction channels are plotted in Figures 4–5.

Initial Association

Both singlet and triplet CH2FNO2 potential energy surfaces (PES) may be obtained for the radical-molecule reaction of CH2F + NO2. On the singlet PES, the carbon-to-nitrogen approach is rather attractive to form structure a H2FCNO2 without any encounter barrier. To further confirm the nonbarrier of this process, the point-wise potential curve at the B3LYP/6-311G(d,p) level is calculated and the result is shown in Figure 6a. It is obvious that this addition process is a barrierless association. It is noticed that further full optimization of the minimum with a C–N distance of 1.5 Å as presented in Figure 6a leads to the adduct a at the B3LYP/6-311G(d,p) level. From Figure 6a, we know that the adduct a is formed as the C atom of CN approach the N atom of NO2 via an attractive potential energy surface. The association is expected to be fast and will play a significant role in the reaction kinetics. In our calculations, the isomers b1 (trans) and b2 (cis) with formal H2FCO1NO2 structure are located as two energy minima lying 65.9 and 63.6 kcal/mol below the reactants R, respectively. Yet, they has relatively short CO1 and NO2 bond lengths as 1.393 and 1.155 Å for b1, respectively, and 1.398 and
Figure 1. The B3LYP/6-311G(d,p) optimized geometries of reactants, some important products, isomers, and transition states for CH$_2$F$^+$ + NO$_2$ reaction. The values in italics are for the triplet species. Bond distances are in angstroms and angles are in degrees. The values in parentheses are the experimental values (ref. 24. for CH$_2$F, NO$_2$, CH$_2$O; ref. 25. for FNO, HNO, NO). In the transition states the direction of the imaginary frequency is indicated by ""
1.161 Å, for \(b_2\), respectively, and the internal O1N bond is long as 1.484 and 1.481 Å for \(b_1\) and \(b_2\), respectively. Then, isomers \(b_1\) and \(b_2\) are more like the adduct species between H2FCO and NO rather than the ones between H2FC and NO2 at the terminal O end. However, despite their low energy, the initial carbon-to-oxygen approach to form isomers \(b_1\) or \(b_2\) may not be the desired favorable entrance channel because a considerable barrier should be overcome from \(R\) to \(b_1\) or \(b_2\) due to the extensive bond rearrangement (activating the short N==O double bond (1.195 Å) in NO2 to form the long N-O weak bond in \(b\) (1.484 Å in \(b_1\), 1.481 Å in \(b_2\))). Unfortunately, we cannot locate the transition state \(TSR_{b_1}\) or \(TSR_{b_2}\) despite a lot of attempts. Alternatively, we calculate the dissociation curves of isomers \(b_1\) and \(b_2\) at the B3LYP/6-311G(d,p) level via point-wise optimization, as shown in Figure 7a and b. We can clearly see that when the internal C==O bond exceeds 2.3 and 2.7 Å, respectively, the total energy of trans-H2FCONO and cis-H2FCONO starts to get higher than the reactant R CH3F + NO2. Unfortunately, optimization of trans-H2FCONO

Table 1. The Electronic States and Harmonic Vibrational Frequencies (cm\(^{-1}\)) of Reactants, Some Important Relevant Products, Isomers, and Transition States at the B3LYP/6-311G(d,p) Level.

| Species         | State   | Frequencies                              | Expt     |
|-----------------|---------|------------------------------------------|----------|
| CH2F            | \(2^A\) | 514, 1173, 1177, 1472, 3123, 3282         | —, 1163, 1170, 1443, —\(^a\) |
| NO2             | \(2^A\) | 767, 1399, 1707                          | 750, 1318, 1618\(^b\)     |
| CH2O            | \(2^A_2\)| 1202, 1270, 1539, 1827, 2869, 2919       | 1167, 1249, 1500, 1746, 2783, 2843\(^b\) |
| FNO             | \(1^A\) | 526, 799, 1947                           | 520, 766, 1844\(^b\) |
| CH2FO           | \(2^A\) | 553, 767, 1000, 1150, 1158, 1313, 1361, 2871, 2889 |          |
| NO              | \(2^\Pi\)| 1988                                      | 1904\(^b\) |
| CHFO            | \(1^A\) | 667, 1040, 1067, 1376, 1904, 3080         |          |
| HNO             | \(1^A\) | 1576, 1673, 2829                         | 1511, 1569, 2854\(^b\) |
| HON             | \(1^A\) | 1274, 1482, 3055                         |          |
| a               | \(1^A\) | 94, 292, 496, 580, 699, 912, 1096, 1158, 1260, 1385, 1420, 1491, 1680, 3086, 3161 |          |
| b1              |        | 108, 201, 343, 444, 595, 782, 1055, 1095, 1176, 1034, 1450, 1496, 1836, 3050, 3127 |          |
| b2              |        | 97, 244, 356, 491, 546, 859, 1015, 1064, 1153, 1295, 1440, 1490, 1787, 3058, 3133 |          |
| c2              | \(1^A\) | 208, 249, 269, 410, 468, 488, 715, 911, 1037, 1187, 1276, 1344, 1476, 3325, 3837 |          |
| TSab1           | \(1^A\) | 2381, 225, 233, 328, 478, 490, 708, 797, 1195, 1250, 1265, 1467, 1579, 3220, 3438 |          |
| TSRb1           |        | 2171, 119, 258, 426, 524, 765, 1000, 1077, 1138, 1285, 1433, 1499, 1865, 3012, 3095 |          |
| TSRb2           |        | 3711, 158, 271, 336, 421, 465, 539, 796, 1189, 1226, 1450, 1604, 2095, 2983, 3052 |          |
| TSRb3           |        | 9191, 152, 242, 296, 468, 589, 717, 1001, 1184, 1269, 1337, 1453, 1587, 1961, 2962 |          |
| TSRb4           |        | 3751, 144, 252, 332, 437, 459, 553, 814, 1187, 1223, 1442, 1600, 2074, 2954, 3032 |          |
| TSRc2           |        | 4400, 121, 165, 276, 452, 562, 633, 777, 1012, 1195, 1337, 1457, 1757, 1923, 3046 |          |
| TSC2P4          |        | 4741, 292, 339, 525, 574, 823, 987, 1088, 1110, 1168, 1211, 1338, 1413, 1355, 3090 |          |
| TSC2P4          |        | 1471, 207, 239, 337, 468, 646, 716, 757, 953, 1193, 1292, 1306, 1540, 3258, 3659 |          |

\(^a\)Experimental values from ref. 26.  
\(^b\)Experimental values from ref. 25.

Table 2. The Relative Energies (kcal/mol) (with Inclusion of the B3LYP/6-311G(d,p) Zero-Point Energy (ZPE) Corrections) of Reactants, Some Important Products, Isomers, and Transition States at the MCQCISD/B3LYP/6-311G(d,p) Level.

| Species         | MCQCISD/B3LYP | Species         | MCQCISD/B3LYP |
|-----------------|---------------|-----------------|---------------|
| CH2F + NO2      | 0.0           | TSab1           | 0.3           |
| P1 CH2O + FNO   | -49.9         | TSBb2           | -55.9         |
| P1 CH2O + NO    | -29.4         | TSBP1           | -30.7         |
| P1 CHFO + HNO   | -69.5         | TSBP3           | -29.9         |
| P1 CHFO + HON   | -27.5         | TSBP1           | -27.5         |
| a                | -58.1         | TSBP4           | -18.4         |
| b1               | -65.9         | TSRc2           | 1.0           |
| b2               | -63.6         | TSC2P4          | -7.6          |
| c2               | -10.1         | \(^3\)TSRPa     | 24.6          |
| \(^3\)b1         | 8.6           | \(^3\)TSRb2     | 20.3          |
| \(^3\)b2         | -7.3          |                 |               |

The values in italics are for the triplet species.
and cis-H$_2$FCONO with internal C—O bond longer than 4.2 and 4.0 Å, respectively, always meets with energy convergence problems. Because the trans-H$_2$FCONO and cis-H$_2$FCONO complexes with R(CO) = 4.2 and 4.0, respectively, are still 28.5 and 27.6 kcal/mol higher than R, we can conclude that the association between CH$_2$F and NO$_2$ at the O-site is a barrier-consumed process due to the strong repulsion from the lone-pair electrons of O in NO$_2$. Moreover, the single unpaired electron is mainly positioned at the internal N-site of NO$_2$ (N has much more spin density than O, i.e., 0.4489 and 0.2756, respectively, at the B3LYP/6-311G(d,p) level.) Then, the CH$_2$F radical may attack the N-site of NO$_2$ to form isomer a much more favorably than to attack the O-site of NO$_2$ to form isomer b$_1$ or b$_2$. Therefore, it is safe to exclude the entrance way of carbon-to-oxygen attack for the reaction CH$_2$F + NO$_2$ and the carbon-to-nitrogen approach is just the initial adduct step of all of the calculated pathways on the singlet PES in our work. On the other hand, the carbon-to-nitrogen approach on the triplet PES can lead to the triplet branched-isomer 3a (H$_2$FCNO$_2$) (8.6 kcal/mol) via transition state TS$_{Ra}$ with the much higher barrier of 24.6 kcal/mol, and there is a substantial barrier of 20.3 kcal/mol for the carbon-to-oxygen attack to form isomer 3b$_1$ (H$_2$FCONO-trans, −7.3 kcal/mol). In view of the much higher entrance barriers, the triplet pathways may contribute less to the CH$_2$F + NO$_2$ reaction compared with the singlet pathways, and thus will not be further discussed. As a result, this reaction is most likely initiated by the carbon-to-nitrogen approach to form isomer a (H$_2$FCNO$_2$) on the singlet PES. In the following discussions, we mainly discuss the formation pathways of various products proceeding via isomer a (H$_2$FCNO$_2$).

Isomerization and Dissociation Pathways

The initial adduct a (H$_2$FCNO$_2$) is a stable and branched chain-like isomer with C$_s$ symmetry and 1'A' electronic state, 58.1 kcal/mol below the reactants. As shown in Figure 3, the C—O$_1$ bond formation along with C—N bond rupture of isomer a may proceed to a C$_1$-symmetried weak-bound intermediate b$_1$ (H$_2$FCONO-trans) via transition state TS$_{b1}$ with the barrier height 58.4 kcal/mol. As seen in Figure 1, the C$_s$-symmetried TS$_{b1}$ with 'A' state has a loose CNO$_1$ three-membered ring structure, in which the length of forming C—O$_1$ bond is 2.328 Å, while the C—N bond that will be broken is 1.438 Å. The vibrational mode of frequency of TS$_{b1}$ corresponds to C—O and C—N bonds stretch vibration. The conversion from b$_1$ (H$_2$FCONO-trans) $\rightarrow$ b$_2$

Figure 2. The B3LYP/6-311G(d,p) optimized geometries of unfavorable isomers for CH$_2$F + NO$_2$ reaction. Bond distances are in angstroms and angles are in degrees.
(H₂FCONO-cis) can be realized via O₁—N bond rotation transition state TSb₁b₂ with small internal rotation barrier (10 kcal/mol above b₁). Isomer b (b₁, b₂) then can dissociate to give product P₁ (CH₂O + FNO) via C—F and O₁—N bonds cleavage accompanied by N—F bond formation through transition states TSb₁P₁ and TSb₂P₁. Only the 35.2 (for b₁) or 36.1 (for b₂) kcal/mol barrier is needed to overcome for this process. Both TSb₁P₁ and TSb₂P₁ may be viewed as nonplanar FCO₁N four-membered ring species with C₁ symmetry. The forming F—N bonds length are 1.953 and 1.975 Å, respectively, while the breaking C—F and O₁—N distances are 1.865 and 2.084 Å (in TSb₁P₁), 1.847 and 2.087 Å (in TSb₂P₁). The imaginary frequency of respective 371i and 375i mainly involves the simultaneous stretch vibrations of C—F, O₁—N, and F—N bonds. The formation pathway of P₁ is:

Path 1: R → H₂FCNO₂ a → H₂FCONO b₁ (b₂) → P₁ (CH₂O + FNO).

Alternatively, isomer b (H₂FCONO) can directly dissociate to give product P₂ (CH₂FO + NO). Note that we have tried to search for the N—O bond cleavage transition states TSb₁P₂ and TSb₂P₂ at the B3LYP/6-311G(d,p) level, yet with no success. In isomers b₁ and b₂, the O₁—N bond is significantly long as 1.484 and 1.481, respectively, while the N—O₂ bond is very short as 1.155 and 1.161, respectively, which is very close to that of NO equilibrium. So we expect that b₁ and b₂ may easily dissociate to P₂ (CH₂FO + NO) via a simple N—O single weak bond fission without a pronounced barrier. Such process can be described as:

Path 2: R → H₂FCNO₂ a → H₂FCONO b₁ (b₂) → P₂ (CH₂FO + NO).

Furthermore, the isomer b₁ (H₂FCONO-trans) can take a 1,3-H-shift and O₁—N bond rupture leading to P₃ (CHFO + HNO) via TSb₁P₃, while b₂ (H₂FCONO-cis) may undergo a 1,4-H-shift and O₁—N bond cleavage to form product P₄ (CHFO + HON) via TSb₂P₄. The dissociation barriers are 36.0 and 45.2 kcal/mol for b₁ → P₃ and b₂ → P₄, respectively. The loose H2CO₁N four-membered ring, which is slightly nonplanar is found in TSb₁P₃. The migrating Hydrogen is 1.321 Å away from the origin (C atom) and 1.475 Å away from the migrating terminus (N atom), and the O₁—N bond that will be broken is surprisingly long as 2.081 Å. The

Figure 3. Schematic singlet potential energy surface of the most relevant reaction channels for the CH₂F + NO₂ reaction at the MC-QCISD/B3LYP/6-311G(d,p) + ZPE level. E_rel are the relative energies (kcal/mol).
C1 symmetried TSb2P4 presents a nonplanar H2CO1NO2 five-membered ring structure with long O1-O and C-O-H2 distances, but relatively short O2-OH2 distance, that is, r(O1N) = 2.507 Å, r(CH2) = 1.675 Å, and r(O2H2) = 1.131 Å. The large imaginary frequency of respective 919i and 440i are relative to C\&bond;H2, N-O-H2, and O1\&bond;N bonds stretch vibration (in TSb1P3) and C-O-H2, O2-OH2, and O1-O bonds stretch vibration (in TSb2P4). These processes can be described as:

Path 3: R → H2FCNO2 → H2FCONO-trans b1 → P4CHFO + HNO

Path 4: R → H2FCNO2 → H2FCONO-trans b1 → H2FCONO-cis b2 → P4CHFO + HNO.

In addition, b2 can take a concerted H-shift from C to O atom to form c (c1, c2, HFCNOH). We notice that the transition state TSb2c2 lie 5.9 kcal/mol above the reactants R, while TSb2c1 is only 1.0 kcal/mol higher than R. So formation of isomer c1 is more preferable than that of c2. Subsequently, c2 can dissociate to P4 via the O1-N bond rupture transition state TSc2P4 with a very small barrier of 2.5 kcal/mol. The C1 symmetried TSb2c1 and TSb2c2 both have H2CO1NO2 five-membered ring structure. The migrating hydrogen is 1.843 and 1.747 Å away from C atom, respectively, and 1.029 and 1.054 away from O2 atom, respectively. The imaginary frequency of respective 371i and 474i corresponds to the simultaneous stretch vibrations of C-O-H2 and O2-OH2 bonds.

TSc2P4 is characterized by slightly elongated O1-O bond, which indicates that species CHFO and HON are formed. TSc2P4 has C1 symmetry with the O1-N bond stretch vibration for the vibrational mode of imaginary frequency 147i. Such a multistep process can be described as:

Path 5: R → H2FCNO2 → H2FCONO-trans b1 → H2FCONO-cis b2 → HFCNOH-cis c2 → P4CHFO + HON.

As shown in Figure 3, in Paths 1–5, the relative energies of all transition states and isomers are almost lower than the reactants R except for TSab1 and TSb2c2, with much smaller positive values of 0.3 and 1.0 kcal/mol, respectively. As a result, Paths 1–5 are favorable for the total reaction.

Now, we turn our attention to the other isomerization and dissociation channels of the isomer a (H2FCNO2). First, a 1,3-H-shift from C-atom to O-atom associated with a concert twist of a

![Figure 4. Schematic singlet potential energy surface of unfavorable reaction channels for the CH2F + NO2 reaction at the MC-QCISD/B3LYP/6-311G(d,p) + ZPE level. E_{rel} are the relative energies (kcal/mol).](image-url)
can form \( d_1 \) (HFCN(O)OH) or \( d_2, d_3 \), and \( d_3 \) are \( cis-trans \) isomers for the HFCN(O)OH structure in terms of C-bound fluorine or O-bound hydrogen. Isomer \( d_1 \) can readily convert to \( d_2 \) via the N=O single bond rotation transition state \( TSD_{d_1d_2} \), with a small barrier of 0.9 kcal/mol, while no transition states for the conversion of \( d_1 \rightarrow d_3 \) and \( d_2 \rightarrow d_3 \) were found. Because the \( d_1 \rightarrow d_3 \) and \( d_2 \rightarrow d_3 \) conversion both involve the concerted process of C=N double bond rotation, the very high barrier may be faced for them. Subsequently, the ring closure of \( d_1 \) or \( d_2 \) may lead to the three-membered ring isomer \( e \) (HFC(O)NOH), and \( d_3 \) can either take a concerted 1,2-migration of the OH group to form \( h_1 \) (HF(OH)CNO), or dissociate directly to give \( P_5 \) (FCNO + H\textsubscript{2}O) via side-H\textsubscript{2}O cleavage. However, the conversion transition states \( TSD_{d_1e_1}, TSD_{d_2e_1}, TSD_{d_2e_2}, TSD_{d_3e_3}, TSD_{d_3h_1}, \) and \( TSD_{d_3P_5} \) involved in these processes lie 12.0, 4.3, 5.0, 5.4, 9.2, 10.0, 14.0, and 11.2 kcal/mol higher than the reactants \( R \). Clearly, formation of \( d_1 \), \( d_2 \), \( d_3 \), \( e \), \( e_3 \), \( h_1 \), and \( P_5 \) are both thermodynamically and kinetically prohibited for the CH\textsubscript{2}F + NO\textsubscript{2} reaction. As shown in Figures 4–5, although isomer \( e_3 \) can further convert to other isomers or products \( P_4 \) (CHFO + H\textsubscript{2}O), \( P_5 \) (FCNO + H\textsubscript{2}O), \( P_6 \) (HOCNO + HF), \( P_7 \) (FOCN + H\textsubscript{2}O), and \( P_8 \) (FNCO + H\textsubscript{2}O), these processes are kinetically unfavorable and then will not be considered. We also consider the secondary dissociation process of the primary product \( P_1 \) (CH\textsubscript{2}O + FNO) to \( P_6 \) (CH\textsubscript{2}O + F + NO) via the direct N=F single bond rupture. In fact, \( P_6 \) lie 11.6 kcal/mol higher than \( R \). Therefore, formation of \( P_6 \) is energetically inaccessible.

**Reaction Mechanism**

As presented in the preceding sections, there are five important reaction channels (Paths 1–5) that are both thermodynamically and kinetically accessible for the singlet PES of the CH\textsubscript{2}F + NO\textsubscript{2} reaction. The CH\textsubscript{2}F radical can barrierlessly react with NO\textsubscript{2} at the middle-N site to form the low-lying adduct \( a \) (HFCONO\textsubscript{2}). Subsequently, isomer \( a \) most favorably isomerizes to \( b_1 \) (H\textsubscript{2}FCNO\textsubscript{2}). Starting from \( b_1 \), the least competitive pathway should be Path 5, because the rate-determining transition state \( TSB_{b_2e_2} \) (1.0 kcal/mol) lies much higher than \( TSB_{b_1P_1} \) (30.7 kcal/mol) and \( TSB_{b_2P_1} \) (27.5 kcal/mol) in Path 1, \( P_2 \) (29.4 kcal/mol) in Path 2, \( TSB_{b_1P_3} \) (29.9 kcal/mol) in Path 3, and \( TSB_{b_4P_4} \) (18.4 kcal/mol) in Path 4. Furthermore, the relative energy of \( TSB_{b_1P_1} \) in Path 4 is higher than those of \( TSB_{b_1P_4} \) and \( TSB_{b_1P_3} \) in Path 1. \( P_2 \) in Path 2, and \( TSB_{b_1P_3} \) in
Path 3. Thus, we expect that Path 4 cannot compete with Path 1, Path 2, and Path 3. Finally, let us compare the feasibility of Path 1, Path 2, and Path 3. Because from the common intermediate $b_1 (H_2FCONO-trans)$, the overall $b_1 \rightarrow P_1$, $b_1 \rightarrow P_2$, and $b_1 \rightarrow P_3$ barriers are very close within 3 kcal/mol, these three pathways may have comparable contribution to the CH$_2$F + NO$_2$ reaction. On the other hand, products $P_1$, $P_2$, and $P_3$ lie at $-49.9$, $-29.4$, and $-69.5$ kcal/mol, respectively. So the formation of $P_3$ is the most thermodynamically favorable followed by that of $P_1$, and the formation of $P_2$ is the least favorable. Thus, the actual yields of these three products may depend on the reaction condition in the experiment. Up to now, no product for the CH$_2$F + NO$_2$ reaction has been detected in the experiment, although based on our present calculations, we predict that (1) the four products $P_1$, $P_3$ (CHFO + HNO), and $P_4$ (CHFO + HON) may be observed. (2) $P_1$, $P_2$, and $P_3$ are the most favorable products with comparable yields. (3) $P_4$ is the least competitive product. Because all the involved intermediates and transition states in Path 1, Path 2, Path 3, and Path 4 lie almost below the reactants R, the CH$_2$F + NO$_2$ reaction is expected to be fast. Thus, the reaction between CH$_2$F and NO$_2$ may represent a very effective route in NO$_2$-reduction in atmospheric and combustion chemistry, and may thus be considered as an important process, referred to as “reburning.”

Comparison with the CH$_3$ + NO$_2$ and CH$_2$Cl + NO$_2$ Reactions

It is of interest to compare the potential energy surface feature of the CH$_3$F + NO$_2$ reaction with those of the analogous ones CH$_3$ + NO$_2$ and CH$_2$Cl + NO$_2$. Recently, we studied in detail the singlet PES of the CH$_3$ + NO$_2$ and CH$_2$Cl + NO$_2$ reactions. By comparison, it is readily found that the features of potential energy surfaces on the CH$_2$X + NO$_2$ (X = H, F, and Cl) reactions are almost in parallel. The reaction pathways leading to the feasible products (including the secondary dissociation pathways) can be summarized as

Path 1: CH$_3$X + NO$_2$ $\rightarrow$ H$_2$XCNO$_2$ $\rightarrow$ H$_2$XCONO $\rightarrow$ CH$_3$O + NO (for X = H, F) or CH$_2$O + XNO (for X = F, Cl)

Path 2: CH$_3$X + NO$_2$ $\rightarrow$ H$_2$XCNO$_2$ $\rightarrow$ trans-H$_2$XCONO $\rightarrow$ CHXO + HNO

Path 3: CH$_3$X + NO$_2$ $\rightarrow$ H$_2$XCNO$_2$ $\rightarrow$ trans-H$_2$XCONO $\rightarrow$ CHXO + HON

Path 4: CH$_2$F + NO$_2$ $\rightarrow$ H$_2$FCNO$_2$ $\rightarrow$ trans-H$_2$FCONO $\rightarrow$ cis-H$_2$FCONO $\rightarrow$ trans-HFCONOH $\rightarrow$ CHFO + HON.
Figure 7. (a) Dissociation curve of the isomer trans-$\text{H}_2\text{FCONO}$ ($b_1$) at the B3LYP/6-311G(d,p) level. (b) Dissociation curve of the isomer cis-$\text{H}_2\text{FCONO}$ ($b_2$) at the B3LYP/6-311G(d,p) level. The calculations are performed by point-wise optimization of the other varied geometric parameters for every fixed internal C–O distance. The dotted line denotes the relative energy of the reactants $R\left(\text{CH}_2\text{F} + \text{NO}_2\right)$. 

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However, some quantitative discrepancy leads to the different product distribution for the three reactions. For the CH$_3$ + NO$_2$ reaction, CH$_3$O + NO (via Path 1) and CH$_3$O + HNO (via Path 2) are the most favorable products with a comparable yield, followed by CH$_3$O + HON is the least competitive product. For the CH$_3$Cl + NO$_2$ reaction, the most feasible product is CH$_3$O + ClNO (via Path 1) and the second feasible product is CHClO + HNO (via Path 2). For the present CH$_2$F + NO$_2$ reaction, four products can be formed, that is, CH$_3$O + FNO and CH$_3$FO + NO (via Path 1), CHFO + HNO (via Path 2), and CHFO + HON (via Path 3 and Path 4). The order of their feasibility should be CH$_3$O + FNO ∼ CH$_3$FO + NO ∼ CHFO + HNO ∼ CHFO + HON. In addition, the major product CH$_3$O + ClNO in CH$_3$Cl + NO$_2$ reaction can further dissociate to give species CH$_2$O + Cl + NO, while in CH$_2$F + NO$_2$ reaction, the similar process CH$_3$O + FNO → CH$_2$O + F + NO is thermodynamically prohibited.

To avoid as much as possible for these pathways involve the same middle-N association process CH$_2$X + NO$_2$ → H$_2$XCONO (X = H, F, Cl), followed by isomerization to trans-H$_2$XCONO. However, it is worthwhile to note that for the rate-determining step, that is, CH$_2$X + NO$_2$ → trans-H$_2$XCONO, the barriers of reactants R as reference of three reactions lie in the distinct difference, that is, −6.6-barrier for CH$_3$ + NO$_2$, −4.7-barrier for CH$_2$Cl + NO$_2$, and 0.3-barrier for CH$_2$F + NO$_2$ at the MC-QCISD/B3LYP/6-311G(d,p) + ZPE level. Because the barrier heights increase from CH$_3$ + NO$_2$, CH$_2$Cl + NO$_2$, to CH$_2$F + NO$_2$, the opposite reactivity trend is obtained theoretically, that is, $k(CH_3) > k(CH_2Cl) > k(CH_2F)$.

Also, the reactivity of the three CH$_2$X + NO$_2$ reactions can be discussed in terms of the Allnä–Rochow electronegativity of H (2.20), Cl (3.00), and F (3.91). Because electronegativity increase from H, Cl to F, the electron density on the carbon atom is reduced in sequence, thus leading to the decreasing of the Methyl reactivity towards NO$_2$ from CH$_3$, CH$_2$Cl, to CH$_2$F. The predicted order for CH$_3$ + NO$_2$ and CH$_2$Cl + NO$_2$ is in line with the experimental results, that is, the measured total rate constant (298 K) of CHX with NO$_2$ are (2.5 ± 0.5) × 10$^{-11}$ and (2.16 ± 0.08) × 10$^{-11}$ cm$^3$ mol$^{-1}$ s$^{-1}$ for X = H and Cl, respectively.$^{18,28}$ Usually, several kcal/mol difference of the barrier height will lead to several orders of difference of rate constants. Hence, it may be significant to give a quantitative comparison of the rate constants $k$ of the three reactions CH$_2$X + NO$_2$ (X = H, F, and Cl). By means of our calculated potential energy surfaces, we roughly estimate the theoretical rate constants of the rate-determining step, that is, CH$_2$X + NO$_2$ R → H$_2$XCONO, a → trans-H$_2$XCONO $b_1$ based on the simple transition state theory. The rate constant formula $k(\text{TH/} e^{\Delta S^o e^{\Delta F^o}})$ is used, where $k$, ∆S, and ∆F denote the rate constant, entropy difference, and barrier height, respectively. On the basis of the calculated values ∆S = −0.035346, −0.041841, −0.041776 kcal/mol, ∆F = −6.6, −4.7, 0.3 kcal/mol for the three reactions CH$_3$, CH$_2$Cl, and CH$_2$F with NO$_2$, we can obtain the rate constants 1.16 × 10$^{-8}$, 2.16 × 10$^{-11}$, and 4.1 × 10$^{-15}$ cm$^3$ mol$^{-1}$ s$^{-1}$ at T = 298 K, respectively. Thus, based on our theoretical prediction, the CH$_3$ + NO$_2$ reaction is much faster than CH$_2$Cl + NO$_2$, but the experimental rate constants of CH$_3$ + NO$_2$ [(2.5 ± 0.5) × 10$^{-11}$$]_{28}$ and CH$_2$Cl + NO$_2$ [(2.16 ± 0.08) × 10$^{-11}$$]_{18}$ are very close. Clearly, such an experimental measurement cannot be consistent with our calculated result. On other hand, the calculated rate constant 4.1 × 10$^{-15}$ cm$^3$ mol$^{-1}$ s$^{-1}$ can represent roughly the low reactivity of the CH$_2$F + NO$_2$ reaction. However, the experimental and theoretical rate constants of this reaction are not obtained as yet. It is therefore highly desirable to perform further kinetic investigations to measure the total rate constant and identify the product distributions so as to give a deep insight into the mechanism of the CH$_2$X + NO$_2$ reaction.

As an extrapolation, we would like to discuss the other two potentially important reactions of CH$_3$Br + NO$_2$ and CH$_3$I + NO$_2$ that have not been previously studied both experimentally and theoretically. According to the difference of electronegativity of halogen atom (F > Cl > Br > I), we predict that the mechanism of the CHBr and CHI reactions with NO$_2$ should be more related to the reaction CH$_2$Cl + NO$_2$ than to CH$_2$F + NO$_2$. Path 1 and Path 2 may play significant roles. Moreover, the Allnä–Rochow electronegativities of I (2.56) and Br (2.76) are smaller than those of CH$_2$Cl and CH$_2$F, and still lower than that of CH$_3$. Accordingly, the total rate constants of CH$_3$Br + NO$_2$ and CH$_3$I + NO$_2$ reactions are expected to be between that of CH$_3$ + NO$_2$ and those of CH$_2$Cl + NO$_2$ and CH$_2$F + NO$_2$. Moreover, we hope that such reactivity versus electronegativity relation may be useful for other CH$_2$X reactions.

Conclusions

In light of the important role that the CH$_2$F radical played in the incineration of fluorine-containing wastes and in the combustion inhibition mechanism of a fluorine-containing flame, the mechanistic study of the CH$_3$F + NO$_2$ reaction system was carried out theoretically as an attempt to understand the halogenated methyl chemistry. A detailed potential energy surface including 41 isomers and 51 transition states was established at the B3LYP and MC-QCISD (single-point) levels. The mechanism can generally be summarized as association, isomerization, and dissociation processes.

1. The C atom of CH$_2$F radical can barrierlessly attack the N atom of NO$_2$ to form the initial radical–molecule adduct a (H$_2$FCNO$_2$) followed by isomerization to b$_1$ (H$_2$FCONO-trans). Starting from b$_1$, four kinds of products $P_1$ (CH$_2$O + FNO), $P_2$ (CH$_2$FO + NO), $P_3$ (CHFO + HNO), and $P_4$ (CHFO + HON) should be observed, in which $P_1$, $P_2$, and $P_3$ are the most favorable products with comparable yields, while $P_4$ is the least competitive product. Because the rate-determining transition state $TS_{ab1}$ in the kinetically feasible pathways Paths 1–4 is only 0.3 kcal/mol higher than the reactants R in energy, the radical–molecule reaction of CH$_2$F with NO$_2$ is expected to be fast, and may play an important part in combustion processes, which are related to the prompt NO$_2$ formation and NO$_2$-burning mechanism.$^{29}$

2. Further comparisons were made on the PES of the CH$_3$F + NO$_2$ reaction with those of the analogous CH$_3$ + NO$_2$ and CH$_2$Cl + NO$_2$. For the CH$_3$X + NO$_2$ reactions, the total rate constants may increase along $X = F$, Cl, and H with the decreased electronegativity. The calculated results presented
here may assist in future experimental identification of products of the title reaction that could be related to the NO₂ combustion processes and are expected to be useful for gaining insight into the systematic understanding of the halogenated methyl chemistry. Further laboratory investigations on the title reaction are strongly desirable.

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