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Ab initio potential energy surface for the reaction of $O(^{3}P)$ with $CH_{2}F$

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Abstract

The potential energy surface (PES) for the reaction of an oxygen atom with a fluorinated methyl radical has been studied using the G2MP2 level of theory. The calculations reveal an association–elimination mechanism. The addition reaction of $O({}^{3}P)$ to $CH_{2}F$ produces an energy-rich intermediate $OCH_{2}F^{*}$ which subsequently decomposes irreversibly. Five production channels of $OCH_{2}F^{*}$ are found: H + CHFO, HF + HCO, CHFOH, F + CH₂O and H₂ + FCO. CHFOH can decompose through six production channels: H + CHFO, HF + HCO, H + HCOF, H₂ + FCO, F + HCOH and OH + CHF. Based on the present ab initio PES, the kinetic characteristics of the $O({}^{3}P) + CH_{2}F$ reaction are estimated. The energy-specific rate constants for the unimolecular decomposition of $OCH_{2}F$ are calculated by RRKM theory. H + CHFO are predicted to be the major products. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Incineration is an effective technique for the management of hazardous polyhalogenated hydrocarbon waste. At typical fuel-lean combustion conditions, the reactions of halogenated alkyls with oxygen atoms are important in the oxidation process of polyhalogenated hydrocarbons [1].

Halogenated alkanes also can undergo photodecomposition to halogenated alkyl radicals. The reaction of halogenated alkyl radicals with $O({}^{3}P)$ atoms is known to produce halogenated alkoxy radicals, which play an important role in stratospheric ozone depletion [2]. In contrast with the extensive studies of the reaction of methyl with $O({}^{3}P)$, there are only a few reports on the reactions of halogenated alkyl radicals with oxygen atoms [3,4]. To date, no direct experimental or theoretical studies of the reaction of $O({}^{3}P)$ with the simplest halogenated alkyl radical, $CH_{2}F$, have been reported.

In this Letter, the reaction of $O({}^{3}P)$ with $CH_{2}F$ is studied by ab initio molecular orbital theory calculations. Several features of our theoretical investigation are: (1) an extensive potential energy surface (PES) for the reaction of $O({}^{3}P)$ with $CH_{2}F$ was calculated using high-level G2MP2 theory; (2) various possible production channels involved in the reaction of $O({}^{3}P) + CH_{2}F$ are examined; (3) overall kinetic characteristics are estimated based on the calculated PES; (4) relative yields of various products are predicted by RRKM theory.

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2. Computation methods

Ab initio calculations are carried out using the Gaussian 94 programs [5]. An inexpensive and reli-

able G2MP2 theory [6] is used to explore the lowest doublet potential energy surface for the reaction of $O(^{3}P)$ with $CH_{2}F(^{2}A')$. The geometries of reactants, products, intermediates and transition states were



Fig. 1. The optimized geometries of various stationary points at the UMP2(full)/6-31G(d, p) level. Bond lengths are in ångström and bond angles are in degrees.

optimized at the UMP2(full)/6-31G(d, p) level. The vibrational frequencies were obtained at the same level in order to determine the nature of different stationary points and the zero-point-energy (ZPE) corrections (scaled by a factor of 0.95). The number of the imaginary frequency (0 or 1) confirms whether a bound minimum or a transition state has been located. Then, a series of single-point energies are calculated at the UMP2/6-311G(d, p), QCISD(T)/6-311G(d, p) and UMP2/6-311+G(3df, 2p) levels with frozen-core approximation, respectively. Finally, the G2MP2 energy is given as:

$$E(G2MP2) = E[QCISD(T)/6 - 311G(d, p)] + E[UMP2/6 - 311 + G(3df, 2p)] - E[UMP2/6 - 311G(d, p)] + HLC + ZPE,$$

where HLC is a high-level correction, HLC = $-0.00019n_{\alpha} - 0.00481n_{\beta}$. n_{α} and n_{β} are the number of α and β valence electrons, respectively.

3. Results and discussion

The optimized geometries of various stationary points are shown in Fig. 1. The corresponding frequencies and the energies are listed in Tables 1 and 2, respectively. The overall energetic profile based on the G2MP2 energies for the reaction of $O(^{3}P) + CH_{2}F$ is shown in Fig. 2.

3.1. Reaction mechanism

As indicated in Fig. 2, a typical addition–elimination mechanism [7] for the reaction of $O({}^{3}P)$ with $CH_{2}F$ is revealed. The reaction between two openshell species, $O({}^{3}P)$ and $CH_{2}F({}^{2}A')$, takes place as they are approaching one another to interact on an attractive potential surface. An intermediate $OCH_{2}F$ (denoted as IM1) is formed when the $O({}^{3}P)$ atom combines with the carbon radical center of the $CH_{2}F$ radical. As this process involves a bond formation between radical centers, it is found to be a barrierless

Table 1

Scaled UMP2(full)/6-31G(d, p) harmonic vibrational frequencies of the reactants, products, adducts and transition states in the reaction of $O(^{3}P)$ with CH₂F

Species	Frequenc	ZPE (kcal/mol)								
	(chi)									
CH_2F	727	1154	1158	1477	3084	3234				15.48
CH ₂ O	1159	1233	1509	1707	2878	2952				16.35
CHFO	630	1004	1066	1360	1794	3050				12.73
HCO	1081	1923	2660							8.10
FCO	598	1042	1906							5.07
CHF	1115	1243	3111							7.82
HCOH	1086	1164	1303	1469	2825	3610				16.38
FCOH	612	790	973	1258	1332	3476				12.07
HF	3982									5.69
OH	3652									5.22
H ₂	4378									6.26
IM1	522	806	1024	1105	1165	1370	1405	2920	2984	19.01
IM2	346	526	971	1056	1160	1262	1368	3103	3687	19.27
TS1	1756i ^a	582	627	686	1043	1167	1335	1741	2956	14.49
TS2	683i	469	833	885	1029	1246	1775	1965	2983	15.99
TS3	2130i	523	700	1017	1084	1231	1336	2503	3046	16.36
TS4	757i	582	585	606	718	1014	1663	1955	3783	15.59
TS5	2843i	328	622	742	1008	1108	1356	1747	3097	14.26
TS6	1677i	648	708	837	998	1094	1529	1934	2951	15.30
TS7	711i	208	257	621	794	978	1269	1340	3480	12.79
TS8	1866i	525	600	732	1030	1102	1483	1922	2290	13.84

^ai represents imaginary frequency.

 Table 2

 Total energies and relative energies of various species

Species	UMP2/ 6-311G (d, p)	UMP2/ 6-311 + G (3df, 2p)	UQCISD(T)/ 6-311G(d, p)	G2MP2	ΔE
$\overline{O(^{3}P) + CH_{2}F}$	-213.69108	-213.80886	-213.73328	-213.86694	0.00
H + CHFO	-213.84156	-213.96969	-213.86506	-214.02388	-95.21
HF + HCO	-213.86070	-213.99007	-213.89041	-214.04300	-110.48
$F + CH_2O$	-213.78919	-213.90831	-213.82677	-213.96502	-61.55
$H_2 + FCO$	-213.83854	-213.96516	-213.87011	-214.02388	-98.48
H + FCOH	-213.76354	-213.89175	-213.79500	-213.94917	-51.60
F + HCOH	-213.70072	-213.81865	-213.74469	-213.88170	-9.26
$OH + {}^{3}CHF$	-213.67359	-213.79681	-213.71290	-213.85592	6.92
IM1	-213.84474	-213.97411	-213.88389	-214.02815	-101.16
IM2	-213.86131	-213.99307	-213.89227	-214.03851	-107.66
TS1	-213.80792	-213.93960	-213.84822	-214.00200	-84.75
TS2	-213.78674	-213.91965	-213.82732	-213.97994	-70.91
TS3	-213.79193	-213.92493	-213.82731	-213.97943	-70.58
TS4	-213.71238	-213.84397	-213.74749	-213.89942	-20.38
TS5	-213.79664	-213.92844	-213.83643	-213.99070	-77.66
TS6	-213.78841	-213.91979	-213.81862	-213.97082	-65.18
TS7	-213.75694	-213.88550	-213.79390	-213.94727	-50.40
TS8	-213.73153	-213.86634	-213.76230	-213.92024	- 33.44

^aTotal energies are in hartree, relative energies are in kcal/mol.

association. The adduct IM1 has C_s symmetry and a ²A" electronic ground state. C–F and C–H bonds in IM1 are somewhat longer than those in the reactant CH₂F.

As can be seen from Fig. 2, the association reaction of $O(^{3}P) + CH_{2}F$ is exothermic by 101.16 kcal/mol at the G2MP2 level. The intermediate IM1

should be an energy-rich, and thus short-lived, activated complex. Once IM1 is formed, it can undergo various possible production channels immediately by isomerization or decomposition. Five production channels of IM1 have been found.

The energetically most favorable reaction path is $IM1 \rightarrow H + CHFO$ via a C-H bond cleavage transi-



Fig. 2. The overall profile of the potential energy surface for the reaction of $O(^{3}P)$ with CH₂F, calculated at the G2MP2 level.

tion state (TS1). The barrier height for this channel is 16.41 kcal/mol relative to IM1 at the G2MP2 level. TS1 has C₁ symmetry. The breaking C–H bond is elongated by 0.432 Å. The C–O bond is shortened by 0.143 Å, which is close to the equilibrium length of the C–O bond, 1.194 Å, in the final product CHFO. It shows that the transition state TS1 is a product-like barrier. The corresponding imaginary frequency is 1756 cm⁻¹.

The second production channel is 1,1-HF elimination of IM1 forming HF + HCO via a three-centered transition state (TS2). As shown in Fig. 1, the breaking C–H and C–F bonds are elongated simultaneously by 0.133 and 0.263 Å, respectively. The forming H–F bond is 1.440 Å, which is 0.519 Å longer than that of the HF molecule. The geometry of forming HCO is close to the final product HCO molecule. The barrier height for this channel is 30.25 kcal/mol, which is 13.84 kcal/mol higher than that for the C–H bond fission path. It is noted that the production of HF + HCO is the most exothermic channel in the reaction of $O(^{3}P)$ with CH₂F. The heat of reaction is as high as 110.48 kcal/mol at the G2MP2 level.

The third pathway involves the isomerization of IM1 to CHFOH (IM2) via a three-member-ring transition state (TS3). The corresponding barrier height, 30.58 kcal/mol, is approximately equal to that for the HF elimination path of IM1. The transition state TS3 has C_1 symmetry. One of the hydrogen atoms migrates from the C atom to the O atom with a large imaginary frequency 2130 cm⁻¹. The breaking C–H bond is 1.243 Å and the forming O–H bond is 1.204 Å. The isomer IM2 has C_1 symmetry. It is predicted to be 6.50 kcal/mol more stable than IM1. Therefore, IM2 has higher internal energy. Many production channels of IM2 would be open.

The fourth production channel of IM1 is the formation of $F + CH_2O$. This process is found to be a simple C–F bond fission without a pronounced barrier at the UMP2(full)/6-31G(d, p) level. We have noted that the extrusion of a fluorine atom from an OCH₂F radical was studied by Rayez et al. [8] using MNDO/CI and SCF/CI methods. A transition state with ²A' symmetry was located at the MNDO level. The corresponding barrier height was found to be 76.2 kcal/mol. But this value is reduced to 38.6 kcal/mol, which is close to the enthalpy of the

products $F + CH_2O$, 32.3 kcal/mol, at the SCF level. It is confirmed that the electron correlation effect is important in this bond fission process. At the higher UMP2(full)/6-31G(d, p) level, we found that the energy rises smoothly to the total energy of the products $F + CH_2O$ with stretching of the C–F bond. No transition state can be located for this path. The enthalpy of $F + CH_2O$ is 39.68 kcal/mol at the G2MP2 level.

The last examined production channel of IM1 is the three-center decomposition of IM1 to $H_2 + FCO$ via the transition state TS4. The transition state TS4 has C_s symmetry and an ²A" electronic state. Two C–H bonds are elongated simultaneously from 1.095 to 1.776 Å. The forming H–H bond is 0.766 Å which approaches the bond length of the final product, H_2 (0.734 Å). The barrier height for this process is as high as 80.85 kcal/mol due to the strong repulsion of the three-member ring. But the energy of TS4 is still 20.38 kcal/mol lower than that of the reactants O(³P) + CH₂F.

As mentioned above, the highly activated isomer IM2 can further decompose to various products. Six production channels of IM2 are investigated as follows.

Similar to IM1, the most feasible decomposition channel of IM2 is the formation of H + HCOF via a O-H bond cleavage transition state (TS5). The breaking O-H bond is elongated from 0.966 Å in IM2 to 1.350 Å in TS5. The barrier height is calculated to be 30.00 kcal/mol. The large imaginary frequency (2843 cm⁻¹) reflects that this path should have a large tunneling effect.

The next pathway is the 1,2-HF elimination of IM2 forming HF + HCO via a four-member-ring transition state (TS6). In TS6, H–O–C–F is almost planar and another H atom is out of the plane. The breaking C–F and O–H bonds are 1.681 and 1.253 Å, respectively. The forming H–F bond is 0.254 Å longer than the equilibrium bond length of HF molecule. The reaction activation energy is 42.48 kcal/mol.

The third reaction channel is the C–H bond fission to the products H + cis-HOCF. The transition state TS7 for this channel has C₁ symmetry. The breaking C–H bond is elongated by 1.05 Å. The structure of the forming 'HOCF' is very similar to that of the final product HOCF molecule. Thus, the

transition state TS7 is very loose. As a result, the energy of TS7 is only 1.20 kcal/mol higher than that of the products H + HCOF. The barrier height is 57.26 kcal/mol.

The fourth decomposition path of IM2 involves a four-member-ring transition state TS8. The final products are H₂ and FCO. The breaking C-H and O-H bonds are stretched by 0.222 and 0.455 Å, respectively. The forming H-H bond (0.964 Å) is 0.23 Å longer than the bond length of H_2 molecule. The barrier height for this channel is 74.22 kcal/mol.

The last two reaction channels of IM2 are simple bond fission processes without transition states. One is the C-F bond fission forming an F atom and trans-HCOH. The other is the C-O bond fission forming $OH + {}^{3}HCF$. As shown in Fig. 2, these two channels have the highest barriers. In addition, the overall reaction path $O + CH_2F \rightarrow OH + {}^{3}HCF$ is endothermic by 6.92 kcal/mol.

3.2. RRKM rate constants

Because there are no experimental measurements on the reaction of $O(^{3}P) + CH_{2}F$, some theoretical predictions may be very useful. It is worth noting that the potential energy surface for the reaction of $O(^{3}P) + CH_{2}F$ has similar characteristics to that of

the $O(^{3}P) + CH_{2}Cl$ reaction [9]. This implies that these two reactions have similar kinetic features. The association of O(³P) with CH₂F takes place on an long-range attractive potential surface via a 'loose transition state' [7]. Once the initial adduct $OCH_{2}F^{*}$ is formed, the reaction proceeds forward irreversibly. Therefore, the addition of $O(^{3}P)$ with $CH_{2}F$ acts as a rate limiting step. The $O(^{3}P) + CH_{2}F$ reaction should have the near gas collision number rate, $\sim 10^{-10}$ cm^3 molecule⁻¹ s⁻¹. Furthermore, the rate constant should be negative temperature dependent and pressure independent because the energy-rich intermediate OCH₂F^{*} has a relatively short lifetime. The relative vields of various products are determined by the unimolecular decomposition rates of OCH₂F* [7]. Five production channels of OCH₂F^{*} are considered, namely.

$$OCH_2F \to H + CHFO$$
 (1)

$$\rightarrow$$
 HF + HCO (2)

$$\rightarrow$$
 CHFOH (3)

$$\rightarrow$$
 F + CH₂O (4)

 \rightarrow H₂ + FCO. (5)

The energy-specific rate constants for unimolecular decomposition of OCH₂F^{*} can be calculated by





RRKM theory [10] using a simple treatment of adiabatic rotations as [11]

$$k_i(E) = l_i (I_a^{\neq} I_b^{\neq} I_c^{\neq} / I_a I_b I_c)^{1/2}$$
$$\times G_i (E - E_i^{\neq}) / hN(E),$$

where l_i is the reaction path degeneracy for channel *i*. *h* is Planck's constant. N(E) is the density of vibrational states of OCH_2F at internal energy E and $G_i(E-E_i^{\neq})$ is the sum of accessible vibrational states of the transition states for channel *i* at energy $E - E_i^{\neq}$, E_i^{\neq} is the barrier height. $(I_a^{\neq} I_b^{\neq} I_c^{\neq})$ and $(I_{a}I_{b}I_{c})$ are the products of the three overall moments of inertia of the transition state for channel *i* and the adduct OCH₂F, respectively. N(E) is deduced by the steepest-decent method [12] and $G_i(E)$ $-E_i^{\neq}$) is calculated using the Bever–Swinehart algorithm [13]. For the sake of simplicity, the 'transition state' for channel (4) is assumed to be 'tight'. The vibrational frequencies including those of the product CH₂O and two of 200 cm⁻¹ are used in the calculation.

The RRKM rate constants for the five dissociation channels (1)–(5) as a function of the internal energy E are depicted in Fig. 3. The reaction rate for channel (1), k_1 , is the fastest one within the range of the internal energy considered in this study. At E =101.16 kcal/mol (enthalpy of the addition step) [14]. the ratio of rates for the five channels is 1.0:0.087:0.14:0.18:0.00013. It is obvious that channel (1) is the dominate decomposition pathway of OCH₂F^{*}, mainly resulting from the lowest barrier of channel (1). Moreover, considering that the decomposition of the isomer CHFOH to H + CHFO also has the lowest barrier among the six production channels of CHFOH, we can predict that the formation of H + CHFO is the major production channel in the $O(^{3}P) + CH_{2}F$ reaction. The products H + CHFO account for an 80% branching ratio, approximately. k_2 , k_3 and k_4 have similar rates. So channels (2)-(4) may be competitive. The rate for channel (5), k_5 , is much smaller than those of k_1 , k_2 , k_3 and k_4 due to the high activation energy of channel (5). Thus, channel (5) plays a negligible role in the overall reaction.

4. Conclusions

G2MP2 theory is used to investigate the potential energy surface (PES) for the reaction of $O({}^{3}P)$ with $CH_{2}F$. The calculations reveal an addition–elimination mechanism. The association of $O({}^{3}P)$ with $CH_{2}F$ is found to be a barrierless process forming an energy-rich intermediate $OCH_{2}F^{*}$. Various decomposition and isomerization reaction channels of $OCH_{2}F^{*}$ have been examined in detail. The overall kinetic characteristics of the $O({}^{3}P) + CH_{2}F$ reaction are estimated based on the G2MP2 PES. The energy-specific rate constants calculated by RRKM theory predict that the formation of H + CHFO is the major production channel.

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