

Thermal decomposition of CF₃CFCIO radical – A computational study

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A theoretical study on the decomposition pathways of haloalkoxy radical formed from 2-chloro-1,1,1,2-tetrafluoroethane has been reported. Structures of all the reactants, products and transition states involved in the decomposition pathways have been optimized and characterized at MP2(full)/6-31G(d,p) level of theory. Single point energy calculations have been performed using MP4, QCISD(T) and CCSD(T) levels of theory. Critical energy barriers have been calculated for C-C bond scission and Cl elimination, the two prominent decomposition channels considered in the present investigation, and found to be 8.4 and 1.5 kcal mol⁻¹ respectively. Results show that Cl elimination is the dominant path involving a lower barrier height. Using transition state theory, rate constants for the decomposition pathways, viz., Cl-elimination and C-C bond scission, calculated at 298 K and 1 atm pressure are found to be 4.6×10⁵ and 5.1×10⁴ s⁻¹, respectively. The existence of transition states on the corresponding potential energy surface has been ascertained by performing Intrinsic Reaction Coordinate calculations.

Keywords: Theoretical chemistry, Chlorofluorocarbons, Haloalkoxy radicals, Decompositions, Transition state theory

It has been globally recognized that the release of man-made chlorofluorocarbons (CFCs) has a deleterious effect on the earth's atmosphere¹⁻³. CFCs possess strong chemical stability and it is this property that originally made these compounds attractive for a wide range of industrial applications. On the other hand, it is this property which also makes it environmental unfriendly. In particular, their strong resilience towards OH radical attack implies their unusually long lifetimes in the atmosphere⁴⁻⁶. Consequently, they reach the stratospheric region of the earth's atmosphere in amounts virtually undiminished, without being removed through any action. Once in the stratosphere they are broken down by UV light releasing chlorine atoms that initiate chain processes destroying ozone. In addition to their ability to destroy stratospheric ozone, the long

atmospheric lifetime of the CFCs, makes these as potential "greenhouse gases"⁵⁻⁷.

To protect the earth's atmosphere from the deleterious effects of chlorofluorocarbons, serious efforts have been made during the recent past to search for suitable replacements. Such efforts focused on hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs). These compounds have been found to possess physico-chemical properties similar to those of CFCs and widely accepted as an alternative to CFCs in industrial applications. The inclusion of at least one hydrogen atom in the structures of HCFCs makes them prone to attack by OH radicals, leading to their breakdown in the troposphere. This leads to a significant reduction in the atmospheric lifetimes of HCFCs as compared to that of the CFCs, providing a partial solution to protect the earth atmosphere from the greenhouse effect.

Based on the physical properties and low ozone-depleting potential⁷ of 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), it is regarded as the most suitable replacement for dichlorotetrafluoroethane (CFC-114), one of the most widely used CFCs in the industry, as refrigerant and fire extinguishing agent. In order to access the full impact of its potential, knowledge of the detailed atmospheric chemistry of HCFC-124 is needed. HCFC-124 possesses H atom and is prone to be attacked by OH radicals present abundantly in the troposphere⁸ and is considered to be the most important degradation pathway. Like most HCFCs, HCFC-124 also breaks down by OH radical attack in the atmosphere as given by reaction (1),



The haloalkyl radical (CF₃CFCI) thus formed adds atmospheric molecular oxygen to give the peroxy radical (CF₃CFCIO₂) as follows:



Peroxy radicals formed via reaction (2) react further with NO in the atmosphere leading to the formation of the haloalkoxy radical CF₃CFCIO⁹ as given by reaction (3).



The chemistry of haloalkoxy radicals has been a subject of extensive experimental and theoretical investigations as these species are interesting intermediates in the atmospheric oxidation of halogenated hydrocarbons¹⁰⁻¹³. Two important pathways for the decomposition of haloalkoxy radicals are proposed to be Cl atom elimination and C-C bond fission as given by reactions (4) and (5).



To the best of our knowledge no theoretical study has been reported to elucidate the dissociative pathways of the CF_3CFCIO radical. The details of the reactions kinetics are still unknown for this haloalkoxy radical which is formed in abundant and plays an important role in the atmospheric chemistry. In the present work we have carried out a systematic study of the thermal decomposition of CF_3CFCIO using computational methods. The structures of all the species are optimized and their characteristic parameters are determined. Transition states of two decomposition channels (reactions 4 and 5) are determined and characterized on their potential energy surfaces. Energy barriers involved during the decomposition reactions are also determined.

Computational method

Ab initio calculations¹⁴ were performed in the present investigation using the GAUSSIAN 03 series of program¹⁵. The geometries of all species involved have been optimized at MP2 (full)¹⁶ level of theory using 6-31G(d,p)¹⁷ basis set. On these optimized geometries, single point energy calculations were performed using Fourth order Møller-Plesset (MP4)¹⁶, QCISD(T)¹⁸ and CCSD(T)¹⁹ levels of theory. Standard and extended basis sets incorporating diffused and polarized functions were also used for energy calculation in order to see the effect of the basis sets. Total energies are corrected for zero-point energy and the latter was calculated using HF/6-31G(d)²⁰⁻²¹ method. In order to characterize the stationary points, vibrational frequencies were calculated on the optimized geometries obtained by MP2(full)/6-31G(d,p) method. Absence of any imaginary frequency during the frequency calculation

shows that the stationary points obtained on the corresponding potential energy surface were the minima corresponding to the optimized structures. Transition states were identified by the presence of only one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were also performed to ascertain that each transition state is linked to the desired reactant and products²².

The rate constants of reactions (4) and (5) have been calculated using conventional transition state theory (TST)^{23,24}. The thermo-chemical formulation of TST leads to the determination of rate constant k as given by Eq. (6).

$$k = \frac{k_b T}{h} e^{\frac{-\Delta G^\ddagger}{RT}} \quad \dots(6)$$

where $\Delta G^\ddagger$ is the standard Gibbs free energy change for the conversion of reactants into transition state and all other terms have their usual meaning. Gibbs free energy change needed to calculate rate constant using Eq. (6) is determined from the thermal data obtained from the frequency calculation on the optimized geometries of the species involved.

Results and discussion

The haloalkoxy radical considered for detailed study during the course of the present investigation (CF_3CFCIO) does not have any H-atom and therefore, its reaction with O_2 is not expected to be significant. Thus, the most plausible fate of this radical in the atmosphere is predominantly its thermal decomposition. Two dominant decomposition pathways to be considered are the Cl elimination and C-C bond scission involving transition states TS1 and TS2 respectively as given by reactions (4) and (5). Optimized geometries of reactant (CF_3CFCIO), products (CF_3CFO , Cl , CF_3 and C(O)FCl) and transition states (TS1 and TS2) obtained at MP2(full)/6-31G(d,p) level are shown in Fig. 1. Using the Gaussview visualization program²⁵, structural parameters were obtained from optimized geometries of various species involved (Table 1). Frequency calculation for reactant, products and transition states made at MP2(full)/6-31G(d,p) level are given in Table 2. These results show that the reactant and products have stable structures characterized by valid vibrational frequencies. Vibrational frequency calculation performed on each of the transition states,

shows the occurrence of only one imaginary frequency at 908 and 970 cm^{-1} for TS1 and TS2 respectively. These frequencies were analyzed using the Gaussview program, which showed the vibrations corresponding to well defined transition state geometries connecting reactant and products. In order to ascertain the existence of transition state on the potential energy surface, reaction path calculations (IRC) were also performed for each transition states. IRC results for TS1 and TS2 are shown in Figs 2 and 3 respectively. The IRC calculation shows that each transition state connects smoothly the reactant and products on the potential energy surface. Visualization of the optimized structure of TS1 reveals the elongation of C—Cl bond length from 1.76 Å to 2.05 Å with a simultaneous shrinkage of the C—O distance from 1.34 Å to 1.19 Å and forming a carbon-oxygen double bond. Similarly, visualizing the structure of TS2 reveals the elongation of C—C bond length from 1.53 Å to 1.88 Å.

Single point energy calculations of various species involved in the decomposition pathways were performed using MP2, MP4, QCISD(T) and CCSD(T) levels of theory using MP2(full)/6-31G(d,p) optimized geometries. In order to refine the values, these calculations were also performed using larger basis sets incorporating polarized and diffused basis sets. Calculated total energies are corrected for

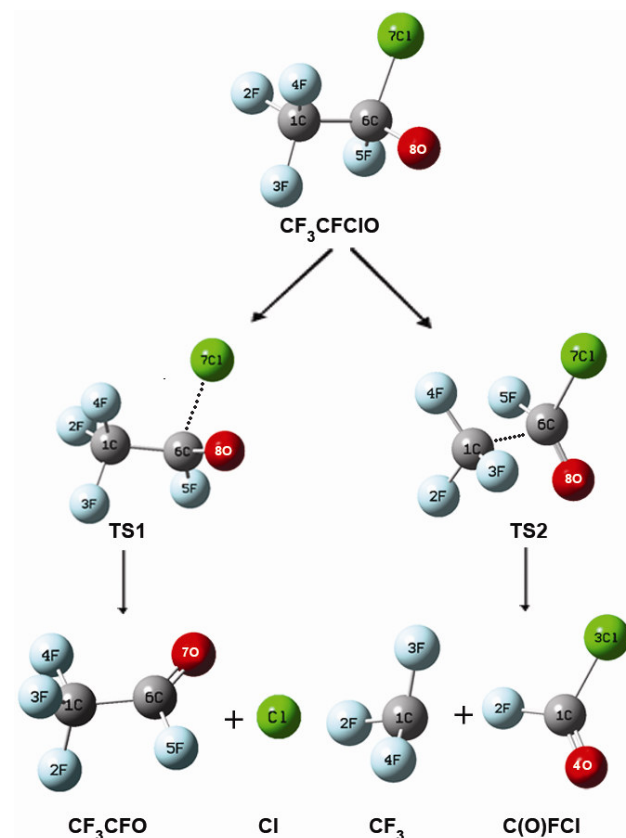


Fig. 1—Optimized geometries of reactant, products and transition states involved in the decomposition of CF_3CFCIO using MP2 (full)/6-31G(d,p) method.

Table 1 – Structural parameters of reactant, products and transition states involved in CF_3CFCIO decomposition via Cl elimination (TS1) and C-C bond scission (TS2) at MP2(full)/6-31G (d, p) level

	CF_3CFCIO	TS1	TS2	CF_3	C(O)FCl	CF_3CFO
<i>Bond lengths (Å)</i>						
R (C1-C6)	1.537	1.537	1.884			1.527
R (C6-O8)	1.348	1.234	1.205			
R (C6-O7)						1.192
R (C1-F2)	1.336	1.335	1.312	1.327	1.338	1.342
R (C1-F3)	1.342	1.344	1.312	1.327		1.333
R (C1-F4)	1.336	1.331	1.318	1.327		1.342
R (C6-F5)	1.362	1.339	1.364			1.345
R (C6-Cl7)	1.766	2.051	1.772			
R (C1-Cl3)					1.728	
R (C1-O4)					1.189	
<i>Bond angles (deg.)</i>						
A (F2-C1-F4)	109.278	109.721	111.353	111.191		109.248
A (F2-C1-F3)	109.077	108.872	112.593	111.191		108.788
A (C1-C6-F5)	106.608	108.717	96.812			108.676
A (F5-C6-Cl7)	109.751	105.561	107.933			
A (F5-C6-O8)	113.050	121.349	122.300			
A (F5-C6-O7)						124.474
A (F2-C1-Cl3)					109.389	
A (O4-C1-Cl3)					126.406	
A (O4-C1-F2)					124.206	

zero-point energy, the latter being calculated at HF/6-31G(d) and corrected with a scale factor of 0.8929 (ref. 26). Zero-point corrected total energies using standard and extended basis sets are recorded in Table 3 for species and the transition state involved in the decomposition via Cl-elimination and in Table 4 for C—C bond scission. Zero-point energy corrected barrier heights for both the channels were also calculated (Tables 3 and 4). The barrier heights calculated in this work tend to decrease with increasing basis set size and with the treatment of electron correlation. Results show that energy barrier for C-C bond scission is in the range of 8-12 kcal mol⁻¹ whereas for Cl elimination it is in the range of 1-7 kcal mol⁻¹. The computed data shows that energetically most favorable decomposition channel for CF₃CFCIO is the C-Cl bond cleavage involving an energy barrier of 1.5 kcal mol⁻¹. Literature survey reveals that there is no experimental data available for

Table 2—Unscaled vibrational frequencies of species calculated at MP2 (full)/6-31G (d, p) level

	Vibrational frequencies (cm ⁻¹)
CF ₃ CFCIO	74, 179, 226, 273, 313, 371, 426, 448, 557, 596, 651, 766, 938, 1118, 1228, 1285, 1309, 1373
TS1	908i, 73, 156, 227, 264, 307, 384, 424, 439, 565, 600, 680, 809, 1138, 1273, 1323, 1362, 1523
TS2	970i, 67, 161, 201, 257, 293, 345, 434, 476, 540, 552, 714, 749, 989, 1065, 1355, 1386, 1603
CF ₃ CFO	46, 226, 236, 389, 424, 511, 595, 684, 763, 815, 1136, 1259, 1310, 1402, 1935
C(O)FCI	418, 507, 669, 769, 1142, 1919
CF ₃	504, 505, 704, 1126, 1317, 1318

the comparison of these energy barriers for the corresponding decomposition pathways of CF₃CFCIO radical. In order to ascertain the reliability of the calculated values using CCSD(T)//MP2(full)/6-31G(d,p), we tried to compare our results with the calculated energy values for a similar compound, CF₃CFHO, made by Wu and Carr²⁷ at a level using CCSD(T)/TZ2P//MP2(full)/6-31G(d,p) method. Wu and Carr²⁷ have reported the energy barrier for C-C bond scission to be 10.7 kcal mol⁻¹. Our calculated value for C-C bond scission of CF₃CFCIO is 8.4 kcal mol⁻¹, which is slightly lower than the value calculated by Wu and Carr²⁷ for CF₃CFHO radical. Our calculated barrier heights for C-C bond scission at different level of theory are found to be slightly lower than that reported by Wu and Carr²⁷ for CF₃CFHO radical. This is expected due to the presence of a more electronegative Cl atom instead of H in the CF₃CFCIO radical. This gives us a confidence to use single point energies obtained with CCSD(T)/6-311++G(d,p) method on the geometries optimized at MP2(full)/6-31G(d,p) level to calculate energy barriers for two decomposition channels taken into consideration during the present study. The constructed energy diagram shows values of 8.4 and 1.5 kcal mol⁻¹ as barrier heights for C-C and Cl elimination pathways respectively (Fig. 4). This diagram is constructed with the zero-point corrected energies data relative to the ground state energy of CF₃CFCIO arbitrarily taken as zero. The barrier height of 1.5 kcal mol⁻¹ for Cl elimination is considerably lower than that corresponding to C-C bond scission process. This shows that Cl-elimination

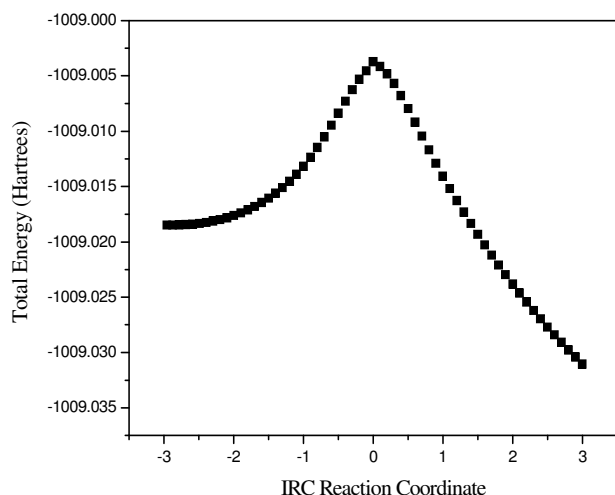


Fig. 2—IRC plot for the transition state TS1 for Cl elimination in CF₃CFCIO decomposition.

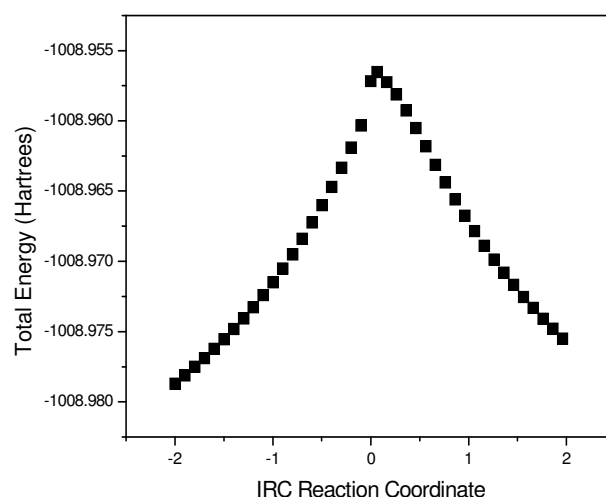


Fig. 3—IRC plot for the transition state TS2 for C-C bond scission in decomposition of CF₃CFCIO.

Table 3—ZPE-corrected total energies for species involved in Cl elimination from CF₃CFCIO decomposition and the energy barrier, ΔE . [Geometries optimized at MP2(full)/6-31G(d, p)]

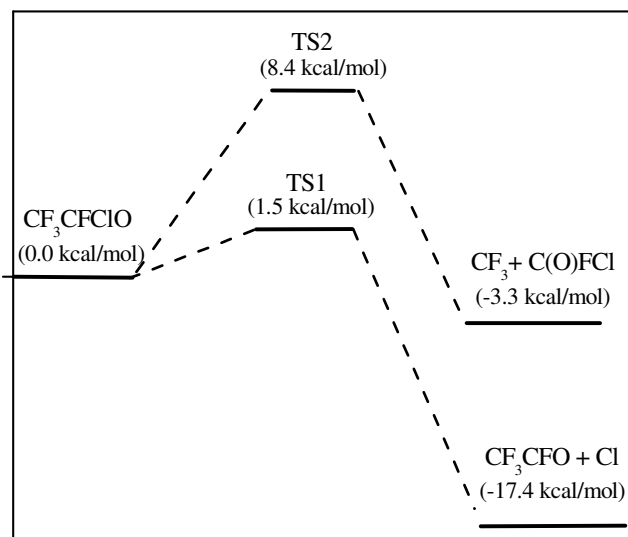
	Total energy (hartree)				ΔE (kJ/mol)
	CF ₃ CFCIO	TS1	CF ₃ C (O)F	Cl	
MP2/6-311G (d,p)	-1009.296561	-1009.284616	-549.749055	-459.601319	7.5
MP4/6-311G (d,p)	-1009.369597	-1009.361030	-549.795630	-459.602633	5.3
MP4/6-311++G (d,p)	-1009.402428	-1009.394626	-550.822966	-459.601311	4.8
MP4/6-311++G(2df,p)	-1009.743689	-1009.736199	-550.107474	-459.657666	4.7
QCISD(T)/6-311G(d,p)	-1009.366488	-1009.362116	-549.746932	-459.633378	2.7
CCSD(T)/6-311++G(d,p)	-1009.395788	-1009.393362	-549.809149	-459.604426	1.5
ZPE HF/6-31G (d)	0.030204	0.028111	0.029563	0.0000	----

Table 4—ZPE-corrected total energies for species involved in C-C bond scission from CF₃CFCIO decomposition and the energy barrier ΔE . [Geometries optimized at MP2(full)/6-31G(d, p)]

	Total energy (hartree)				ΔE (kJ/mol).
	CF ₃ CFCIO	TS2	CF ₃	C (O)FCl	
MP2/6-311G (d, p)	-1009.296561	-1009.276395	-336.936995	-672.394407	12.6
MP4/6-311G (d, p)	-1009.369597	-1009.351425	-336.958306	-672.422236	11.4
MP4/6-311++G (d,p)	-1009.402428	-1009.385806	-336.975634	-672.438119	10.4
MP4/6-311++G (2df, p)	-1009.743689	-1009.727504	-337.147186	-672.606403	10.1
QCISD(T)/6-311G (d, p)	-1009.366488	-1009.352061	-336.955271	-672.416369	9.0
CCSD(T)/6-311++G (d, p)	-1009.395788	-1009.382336	-336.970760	-672.430384	8.4
ZPE HF/6-31G(d)	0.030204	0.026838	0.013565	0.013746	----

from CF₃CFCIO dominates C-C bond scission, which is in agreement with the experimental findings²⁸.

Modeling of the rate constants of reactions 4 and 5 was attempted with the transition state theory using Eq. (6). Gibbs free energy change required to calculate rate constant was determined from the thermal data output of frequency calculation on the optimized geometries of reactant and transition states. The calculated free energy for CF₃CFCIO is -1009.013314 h, whereas for TS1 and TS2 these are -1008.98702 and -1008.995753 h respectively at MP2/6-31G (d,p) level of theory. Thus, $\Delta G^\ddagger$ for TS1 and TS2 are calculated to be 11.0 and 9.7 kcal mol⁻¹ respectively. Using these data, rate constant for Cl elimination taking TS1 as the transition state is found to be 4.6×10^5 s⁻¹ at 298 K and 1 atm pressure. Literature survey reveals that no experimental data is available for the decomposition pathways of CF₃CFCIO radical. Based on an analogy with the decomposition of other oxy-radicals by Cl elimination process Bhatnagar and Carr²⁸ estimated a rate constant of the order of 10^5 s⁻¹ for the decomposition of CF₃CFCIO. Our calculated value is of the same order of magnitude. The rate constant for C-C bond scission is calculated taking TS2 as the transition state. This gives a modeled rate constant as 5.1×10^4 s⁻¹ at 298 K and 1 atm pressure. Our result for

Fig. 4—Relative energy diagram for the thermal decomposition of CF₃CFCIO at CCSD(T)/6-311++G(d,p) level.

C-C bond scission is also found to be in the same order of magnitude as obtained during several recent computational studies²⁹⁻³¹.

In the present study, the most important stationary points on the potential energy surface for the thermal decomposition of CF₃CFCIO radical have been investigated using *ab initio* quantum mechanical method with the initial optimization of reactant,

products and transition states carried out at the MP2(full)/6-31G(d,p) level of theory. The most dominant decomposition pathways for CF₃CFCIO is the Cl elimination via C-Cl bond breaking using a barrier height of 1.5 kcal mol⁻¹ in comparison to the other channel occurring via C-C bond breaking, which utilizes 8.4 kcal mol⁻¹. The rate constant evaluated for both the decomposition pathways occurring via Cl elimination and C-C bond scission are found to be 4.6×10⁵ and 5.1×10⁴ s⁻¹ at 298 K and 1 atm pressure, respectively.

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