

Theoretical study of HF elimination kinetics of ethane fluorides and derivatives [C₂H_{6-n}F_n (n = 1- 4)]

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A theoretical study of the thermal decomposition kinetics of ethane fluorides, viz., ethyl fluoride, 1,1-difluoroethane, 1,1,1-trifluoroethane and 1,1,2,2-tetrafluoroethane, has been carried out at the B3LYP/6-31++G**, B3PW91/6-31++G** and MP2/6-31++G** levels of theory. Among these methods, data for activation parameters obtained with the B3PW91/6-31++G** method is in good agreement with the experimental data. The calculated data demonstrate that in the HF elimination reaction of the studied compounds, the polarization of the C₁-F₃ bond is rate determining. Analysis of bond order, NBO charges, bond indexes and synchronicity parameters suggest the HF elimination occurs through a concerted and asynchronous four-membered cyclic transition state type of mechanism.

Keywords: Theoretical chemistry, Ab initio calculations, Elimination, Molecular modeling, Thermal decomposition, EBEO method, NBO analysis, Bond energy, Bond order, Ethane fluorides

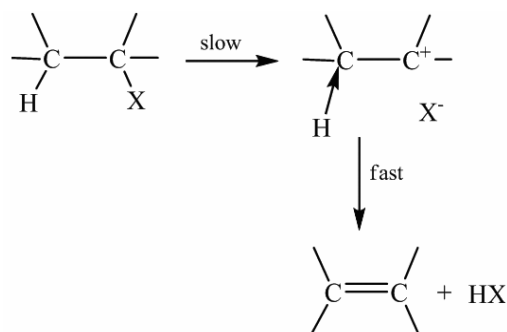
The elimination of hydrogen halides from alkyl halides to yield the corresponding olefins has been extensively studied^{1,2}. The nature of the reaction which occurs upon pyrolysis of an alkyl halide, i.e., whether unimolecular or free radical, homogenous or heterogeneous, depends upon the halogen involved and upon the structure of the compound concerned. In many cases it is possible to isolate a unimolecular homogenous mode of pyrolysis which is now widely accepted^{1,2} (Scheme 1), although a semi-ion-pair rather than an ion-pair transition state has also been suggested³.

The alkyl fluorides appear to be particularly studied for such investigations because of noncomplicated kinetics derived principally from the strength of the carbon-fluorine bond which is neither attacked by radicals nor involved in isomerizations. In particular, a number of studies have dealt with the fluoro derivatives of ethane and ethylene. Sianesi, Nelli, and Fontanelli⁴ were the first to report the pyrolysis of the series.

These investigations have shown that, at the temperatures at which first product formation occurs, the principal mode of decomposition is via molecular elimination of hydrogen fluorides. Furthermore, contrary to the results of Sianesi *et al.*⁴, the shock-tube studies provide clear evidence that the activation energy for the dehydrofluorination reaction increases with additional fluoro substitution, while the

pre-exponential factors change only in a minor way. Therefore, for any given temperature the values of the rate constants decrease with increasing *n* in the series C₂H_{6-n}F_n (n=1-4). If this trend of increasing activation energy with increasing fluorination continues, then, in relation to the HF elimination, the parallel reaction involving the C-C bond scission should become progressively more important at the elevated temperatures used in shock-tube studies⁵. The log *A* and *E*_a of the gas-phase decomposition of ethane fluorides and derivatives [C₂H_{6-n}F_n (n=1-4)] have been experimentally studied⁶⁻⁹. From experimental values of log *A* and *E*_a, and the rate coefficients can be calculated.

In the present work, theoretical studies of the thermal decomposition kinetics of ethyl fluoride (1),



Scheme 1

1,1-difluoroethane (**2**), 1,1,1-trifluoroethane (**3**), and 1,1,2,2-tetrafluoroethane (**4**) have been carried out at the MP2 and DFT levels in order to obtain the kinetic and thermodynamic parameters for understanding the HF elimination in ethane fluorides.

Computational Method

The *ab initio* molecular orbital calculations have been performed at B3LYP/6-31++G**, B3PW91/6-31++G**, and MP2/6-31++G** levels of theory with GAUSSIAN 98 package of programs¹⁰. Full geometry optimizations were performed on each species without any symmetry constraint at each particular basis set. Each optimized structure was characterized by frequency calculations to be a minimum without any imaginary vibrational frequency. Comparison with experimental values showed the best agreement at B3PW91/6-31++G** level of theory. Hence, the B3PW91/6-31++G** level, was used for calculation of thermodynamics and kinetics parameters. Initial estimates of the geometries of compounds **1-4** and related products were obtained by a molecular-mechanics program PC-MODEL (88.0)¹¹ followed by full minimization using semi-empirical PM3 in the MOPAC 6.0 computer program^{12,13}.

Energy minimum molecular geometries were located by minimizing the energy, with respect to all geometrical coordinates, without imposing any symmetrical constraints. The structures of the transition state geometries were obtained using the optimized geometries of the equilibrium structures according to the procedure of Dewar *et al.*¹⁴ (keyword SADDLE). The nature of the stationary points for compounds **1-4** has been fixed by means of the number of imaginary frequencies. For minimum state structure only real frequency values, and in the transition states, only single imaginary frequency value (with negative sign) was accepted^{15,16}. NBO analysis were also performed using B3PW91/6-31++G** level of theory by the NBO 3.1 program included in GAUSSIAN 98 package of programs¹⁷.

The unimolecular rate coefficient $k(T)$ was computed using the transition state theory (TST)^{18,19} and assuming that the transmission coefficient is equal to 1, as expressed in the following relationship,

$$k(T) = \left(\frac{k_B T}{h} \right) \exp \left(- \frac{\Delta G^\ddagger}{RT} \right) \quad \dots (1)$$

where ΔG^\ddagger is the Gibbs free energy change between the reactant and its corresponding transition

state, and k and h are the Boltzmann and Planck constants, respectively. ΔG^\ddagger was calculated as follows: $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$, and, $\Delta H^\ddagger = V^\ddagger + \Delta ZPVE + \Delta E(T)$, where V^\ddagger is the potential energy barrier and $\Delta ZPVE$ and $\Delta E(T)$ are the difference of ZPVE and temperature corrections between the TS and the corresponding reactant, respectively²⁰.

Results and Discussion

The zero-point vibrational energies (ZPVE), total electronic (E_{el}) energies and total internal energies at 0 K ($E_0 = E_{el} + ZPVE$) of compounds **1-4**, as calculated by B3LYP/6-31++G**, B3PW91/6-31++G**, and MP2/6-31++G** levels of theory, are summarized in Table 1. The B3PW91/6-31++G** results are in good agreement with the experimental data^{7,8,21,22} and show that the barrier height of the decomposition of compounds **1-4** is 54.97, 59.82, 66.08 and 73.43 kcal/mol, respectively. The comparative kinetic and thermodynamic parameters, i.e., Gibbs free energies (ΔG_r), enthalpies of activation (ΔH^\ddagger), Gibbs activation free energies (ΔG^\ddagger), activation entropies (ΔS^\ddagger), pre-exponential factor (A) and the unimolecular rate coefficients (k) of the thermal decomposition of compounds **1-4** are listed in Table 2.

The parameters were calculated using the relationship $\Delta H^\ddagger = E_a - RT$, the Arrhenius equation, $k = A \cdot \exp(-E_a/RT)$, and the Eyring equation, $k = (k_B T/h) \cdot \exp(-\Delta G^\ddagger/RT)$, $\Delta S^\ddagger = R[\ln A - \ln(ek_B T/h)]$ (ref. 23). The kinetic and thermodynamic parameters of compounds **1-4** were found to be constant within the experimental temperature range. As can be seen, ΔS^\ddagger has small values, either positive or negative numbers, so that the calculated ΔH^\ddagger and ΔG^\ddagger parameters are close to the ΔE_0 values.

For compound **1**, the rate constant, k_1 , can be represented as $k_1 = 6.44 \times 10^{13} \exp(-27669/T) \text{ s}^{-1}$, while k_2 for compound **2** is $8.41 \times 10^{13} \exp(-30108/T) \text{ s}^{-1}$, k_3 for compound **3** is $1.03 \times 10^{14} \exp(-33258/T) \text{ s}^{-1}$ and k_4 for compound **4** is $9.59 \times 10^{13} \exp(-36956/T) \text{ s}^{-1}$. The activation energy in compound **4** is higher than that of compounds **1-3**. This indicates again that k_1 is much higher than k_2 , k_3 and k_4 . According to the experimental data, the decomposition rate at 1200 K for compounds **1-4** are 6236.794, 1067.304, 30.848 and 4.047 s^{-1} , respectively; while the computed values for compounds **1-4** at the B3PW91/6-31++G** level of theory are slightly less than the lower values of their in experimental data (336.061, 424.198, 30.848 and 4.5894 s^{-1} , respectively).

The transition state (TS) geometrical parameters optimized at B3PW91/6-31++G** theoretical level compared to the reactants are given in Table 3. The log *A* has been used to suggest the type of transition state according to Benson^{18,24,25}. The TS for the thermal decomposition of compounds **1-4** is a cyclic four-membered cyclic structure, as suggested by log *A* values from 13.8 – 14.01. Atoms involved in the TS are fluorine, hydrogen, adjacent carbon and the carbon

atom bearing the fluorine group. Atom numbering is shown in Fig. 1 for clarity. The most significant change is observed for the C₁-F₃ bond, which is elongated in the TSs (at 1.759-1.973 Å), when compared to that in the reactant (1.352-1.407 Å). The C₂-H₄ bond distances increases (1.092-1.114 to 1.304-1.476 Å) showing breaking of this bond in the TSs. The H₄-F₃ bond is formed as the distance between these atoms decreases in the TS (1.246-1.335 Å), while the C₁-C₂

Table 1— Calculated total electronic energies (E_{el}), zero-point energies (ZPE) and relative energies (ΔE_o) for the reactant (**R**) and transition state (**TS**) of ethyl fluoride (**1**), 1,1-difluoroethane (**2**), 1,1,1-trifluoroethane (**3**) and 1,1,2,2-tetrafluoroethane (**4**) at various levels of theory

	1		2	
E_a (kcal/mol) ^a	59.8		61.9	
	(R)	(TS)	(R)	(TS)
<i>B3LYP/6-31++G**</i>				
ZPE (kcal/mol)	42.578436	37.869600	37.854540	33.301328
E_{el} (kcal/mol)	-112374.5893	112315.6874	174656.0693	-174592.3112
E_o (kcal/mol)	-112332.0115	-112277.8184	-174618.2148	-174559.0105
ΔE_o^b (kcal/mol)	0.000000	54.193019	0.000000	59.204313
<i>B3PW91/6-31++G**</i>				
ZPE (kcal/mol)	42.710213	38.015183	37.998240	33.451930
E_{el} (kcal/mol)	-112331.8207	112272.1464	-174590.2379	-174525.8673
E_o (kcal/mol)	-112289.1111	-112234.1318	-174552.2403	-174492.4154
ΔE_o^b (kcal/mol)	0.000000	54.979288	0.000000	59.824921
<i>MP2/6-31++G**</i>				
ZPE (kcal/mol)	43.864831	39.039279	0.062092	0.054472
E_{el} (kcal/mol)	-112052.3698	-111989.1689	-277.6015	-277.49116
E_o (kcal/mol)	-112008.5056	-111950.1296	-277.5394	-277.4366
ΔE_o^b (kcal/mol)	0.000000	58.376000	0.000000	(64.489830) ^b
	3		4	
E_a (kcal/mol) ^a	68.7		69.4	
	(R)	(TS)	(R)	(TS)
<i>B3LYP/6-31++G**</i>				
ZPE (kcal/mol)	32.708331	28.480168	28.624496	23.415535
E_{el} (kcal/mol)	-236939.9929	-236870.0300	-299198.3022	-299120.2318
E_o (kcal/mol)	-236907.2852	-236841.5498	-299169.6783	-299096.8163
ΔE_o^b (kcal/mol)	0.000000	65.735437	0.000000	72.862069
<i>B3PW91/6-31++G**</i>				
ZPE (kcal/mol)	32.872738	28.628261	28.793923	23.637674
E_{el} (kcal/mol)	-236851.7462	-236781.4187	-299085.9353	-299007.3484
E_o (kcal/mol)	-236818.8741	-236752.7904	-299057.1413	-298983.7107
ΔE_o^b (kcal/mol)	0.000000	66.083705	0.000000	73.430593
<i>MP2/6-31++G**</i>				
ZPE (kcal/mol)	33.642066	29.102658	29.377508	23.922563
E_{el} (kcal/mol)	-236346.1896	-236269.9553	-297857.6986	-298378.5520
E_o (kcal/mol)	-236312.5482	-236240.8533	-298436.8759	-298354.6301
ΔE_o^b (kcal/mol)	0.000000	71.694900	0.000000	82.245853

^a Expt values from refs 7, 8, 21, 22.

^b Relative to the best configuration.

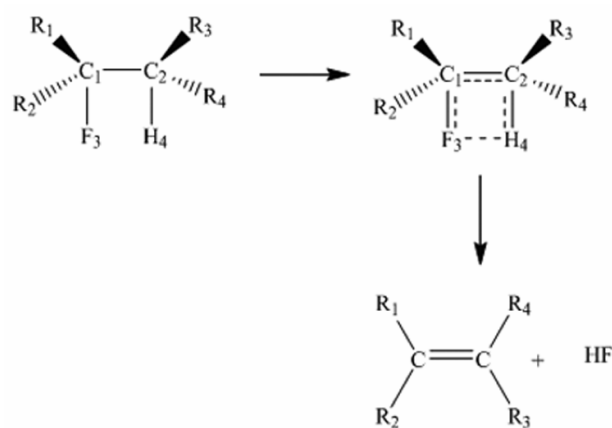
Table 2 — Kinetic and thermodynamic parameters for the thermal decomposition of ethyl fluoride (1), 1,1-difluoroethane (2), 1,1,1-trifluoroethane (3), and 1,1,2,2-tetrafluoroethane (4) at B3PW91/6-31++G** level of theory

Substrate	k^a (s ⁻¹)	log A^a (s ⁻¹)	ΔH^\ddagger (kcal/mol)	ΔS^\ddagger (cal/mol/K)	ΔG^\ddagger (kcal/mol)	ΔH_r (kcal/mol)	ΔG_r (kcal/mol)
(1)	6236.794 (336.061)	13.80 (13.41)	54.932852	-0.106	54.964228	16.466489	6.469000
(2)	1067.304 (424.198)	13.92 (13.90)	59.863198	0.423	59.737069	23.578060	13.289406
(3)	94.701 (30.848)	14.01 (14.0)	66.179087	0.836	65.929338	31.838602	21.244978
(4)	4.047 (4.589)	13.98 (13.3)	73.617590	0.684	73.413649	25.559109	15.222765

^a Expt. values from refs 7,8, 21, 22 are shown in parentheses.

Table 3 — Structural parameters for the reactant (R) and transition state (TS) of the thermal decomposition of ethyl fluoride (1), 1,1-difluoroethane (2), 1,1,1-trifluoroethane (3), and, 1,1,2,2-tetrafluoroethane (4) at B3PW91/6-31++G** level of theory

	1		2		3		4	
	R	TS	R	TS	R	TS	R	TS
<i>Bond lengths (Å)</i>								
C ₁ -C ₂	1.510	1.416	1.512	1.400	1.512	1.400	1.504	1.400
C ₁ -F ₃	1.352	1.759	1.407	1.972	1.407	1.973	1.396	1.973
C ₂ -H ₄	1.114	1.476	1.092	1.305	1.092	1.304	1.094	1.304
H ₄ -F ₃	2.651	1.246	2.669	1.335	2.668	1.335	3.320	1.335
<i>Dihedral angles (°)</i>								
F ₃ -C ₁ -C ₂ -H ₄	-60.351	-0.031	-58.860	-1.710	-59.978	-0.004	-171.670	-2.356
C ₁ -C ₂ -H ₄ -F ₃	28.685	0.068	27.864	3.670	27.362	0.008	7.480	5.241
C ₂ -H ₄ -F ₃ -C ₁	-36.835	-0.056	-36.290	-2.993	-36.805	-0.007	-162.001	-4.202
H ₄ -F ₃ -C ₁ -C ₂	24.402	0.036	24.453	1.982	24.898	0.004	5.766	2.898
Imaginary frequency (cm ⁻¹)	1695		1677		1681		1880	



(1): R₁=R₂=R₃=R₄=H, (2): R₁=F, R₂=R₃=R₄=H

(3): R₁=R₂=F, R₃=R₄=H, (4): R₂=R₃=R₄=F, R₁=H

Fig. 1 — HF elimination reaction in the studied compounds 1-4. [Numbering system shown for clarity].

bond distances reveal changes from single to double bond character (1.504-1.512 to 1.4-1.416 Å) in TS. According to geometrical parameters, dihedral angles in the TS are small (-4.202° to 5.241°), suggesting that the TS geometry is almost planer. Imaginary frequencies characterized for the TS found for ethyl fluoride, 1,1-difluoroethane, 1,1,1-trifluoroethane and 1,1,2,2-tetrafluoroethane are 1695, 1677, 1681 and 1880 cm⁻¹, respectively.

A more balanced measure of the extent of bond formation or bond breaking along a reaction pathway is provided by the concept of bond order (*B*). This theoretical technique has been used to investigate the molecular mechanism of chemical reactions²⁶. To follow the nature of the decomposition process, the Wiberg bond indices have been computed by using the NBO^{27,28} analysis as implemented in GAUSSIAN 98. There are several breaking/forming bond processes

along the fragmentation process and the global nature of the decomposition reaction can be monitored by means of the synchronicity (S_y) concept²⁹, defined by the following expression (Eq. 2).

$$S_y = 1 - \frac{\left[\sum_{i=1}^n \frac{|\delta B_i - \delta B_{av}|}{\delta B_{av}} \right]}{2n - 2} \quad \dots (2)$$

In Eq. (2), n is the number of bonds directly involved in the reaction and the relative variation of the bond index (δB_i) for a bond i at the TS is given as a percentage by Eq. (3),

$$\delta B_i = \frac{B_i^{TS} - B_i^R}{B_i^P - B_i^R} \quad \dots (3)$$

where the superscripts R, TS, and P, refer to the reactant, transition state and product, respectively. The evolution in bond change is calculated as Eq. (4).

$$\%EV = \delta B_i \times 100 \quad \dots (4)$$

The average value is calculated by Eq. (5).

$$\delta B_{av} = \frac{1}{n} \sum_{i=1}^n \delta B_i \quad \dots (5)$$

Bonds indexes were calculated for those bonds which changed in the reaction pathway, i.e., C₁-C₂, C₁-F₃, C₂-H₄ and H₄-F₃ bonds (Fig. 1); all other bonds remain practically unaltered during the processes. The calculated Wiberg indexes B_i for reactants, transition states and products for compounds **1-4**, enable us to examine the progress of the reactions and position of the transition states between reactant and products (Table 4). For compounds **1-4**, the most advanced reaction coordinate is C₁-F₃ bond breaking (57.50-67.28 %). Also important is the progress in C₂-H₄ bond breaking (50.32-52.89 %). Less progress is observed in C₁-C₂ double bond formation (33.68-34.76 %) in compounds **2-4**. Interestingly, for ethyl fluoride, the H₄-F₃ bond breaking shows less progress than C₁-C₂ reaction coordinate. The synchronicity values of the decomposition compounds **1-4** are 0.867, 0.851, 0.843 and 0.858, respectively, indicating that the reaction pathways can be described as concerted and asynchronous.

Table 4 — Bond order analysis for the thermal decomposition of ethyl fluoride (**1**), 1,1-difluoroethane (**2**), 1,1,1-trifluoroethane (**3**), and, 1,1,2,2-tetrafluoroethane (**4**) at the B3PW91/6-31++G** level of theory using NBO analysis

Comp.		C ₁ -C ₂	C ₁ -F ₃	C ₂ -H ₄	H ₄ -F ₃	δB_{av}	S_y
(1)	B_i (R)	1.0363	0.8310	0.9240	0.0020	0.4601	0.867
	B_i (TS)	1.4092	0.3532	0.4353	0.2459		
	B_i (P)	2.0406	0.0000	0.0000	0.6696		
	% EV	37.1303	57.4970	52.8896	36.5339		
(2)	B_i (R)	1.0292	0.8504	0.9159	0.0019	0.4638	0.851
	B_i (TS)	1.3525	0.3138	0.4540	0.2507		
	B_i (P)	1.9592	0.0000	0.0000	0.6696		
	% EV	34.7634	63.0997	50.4313	37.2622		
(3)	B_i (R)	1.0191	0.8708	0.9105	0.0011	0.4761	0.843
	B_i (TS)	1.3139	0.2849	0.4523	0.2587		
	B_i (P)	1.8785	0.0000	0.0000	0.6696		
	% EV	34.3030	67.2830	50.3240	38.5340		
(4)	B_i (R)	0.9578	0.8824	0.9065	0.0085	0.4760	0.858
	B_i (TS)	1.2390	0.3137	0.4434	0.2809		
	B_i (P)	1.7926	0.0000	0.0000	0.6696		
	% EV	33.6847	64.4492	51.0866	41.2041		

Table 5 — NBO charges of reactant (**R**) and transition state (**TS**) for the thermal decomposition of ethyl fluoride (**1**), 1,1-difluoroethane (**2**), 1,1,1-trifluoroethane (**3**), 1,1,2,2-tetrafluoroethane (**4**) at the B3PW91/6-31++G** level of theory

	1			2		
	R	TS	P	R	TS	P
C1	0.00338	-0.10866	-0.43826	0.57685	0.51315	0.22377
C2	-0.72617	-0.78445	-0.43826	-0.75228	-0.84670	-0.54804
F3	-0.40472	-0.58990	-0.57635	-0.38718	-0.60521	-0.57635
H4	0.24365	0.45555	0.57635	0.25880	0.45148	0.57635
	3			4		
	R	TS	P	R	TS	P
C1	1.08167	1.04287	0.78886	0.52718	0.43684	0.70102
C2	-0.76653	-0.88202	-0.63139	0.52718	0.42731	0.05096
F3	-0.36830	-0.60939	-0.57635	-0.35932	-0.57464	-0.57635
H4	0.26322	0.45446	0.57635	0.20087	0.41214	0.57635

NBO charges analysis demonstrate that H₄-F₃ bond is polarized in all the reactants (H₄ charge is 0.20 to 0.26 and F₃ is -0.35 to -0.40, charge separation $\Delta q=0.55-0.66$) in the sense H₄^{δ+}-F₃^{δ-}. As the reaction proceeds from reactant to TS, the following changes in partial charges occur: the increase in positive charges δ+ in hydrogen H₄ (0.20087-0.26322 in the reactants compared to 0.41214-0.45555 in TS), an increase in negative charge δ- in fluorine F₃ (-0.35932 to -0.40472 in the reactants compared to -0.57464 to -0.60939 in TS) are presented in Table 5.

Hammond's postulate can be interpreted in terms of the position of the transition state along the reaction coordinate, n_T , as defined by Agmon²⁰:

$$n_T = \frac{1}{2 - (\Delta G_r / \Delta G^\ddagger)} \quad \dots (6)$$

The magnitude of n_T indicates the degree of similarity between the transition state and the product. According to this equation, the position of the transition state along the reaction coordinate is determined solely by ΔG_r° (a thermodynamic quantity) and ΔG^\ddagger (a kinetic quantity). The value of n_T for the thermal decomposition compounds **1-4**, are 0.5312, 0.5625, 0.596 and 0.5578, respectively. In fact, the similarity between transition states and products increase with respect to reactions in the order of: $R_3 > R_2 > R_4 > R_1$.

In the present work, the thermal decomposition of the ethyl fluoride (**1**), 1,1-difluoroethane (**2**), 1,1,1-trifluoroethane (**3**) and 1,1,2,2-tetrafluoroethane (**4**)

has been studied at various levels of theory. The B3PW91/6-31++G** level of theory gives values of activation energies very close to the experimental values. The decomposition barrier heights increase from compounds **1** to **4**. The TS in the rate determining step for the studied reactions is a four-membered cyclic transition state. The TS shows more progress in C₁-F₃ bond breaking compared to the other reaction changes. Also, NBO charges analysis demonstrate that the increase in negative charge in fluorine F₃ and hydrogen H₄ becomes more positively charged in the TSs. The synchronicity values of the compounds **1-4** are 0.84-0.88. The above results show that the mechanism for the HF elimination in these reactions is concerted and asynchronous.

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