



THE RADICAL CATION OF ETHYL FLUOROFORMATE DISSOCIATES THROUGH A SERIES OF ELIMINATION MECHANISMS

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Abstract: The ground-state intramolecular gas-phase dissociation pathways of ethyl fluoroformate radical cation ($\text{FCOOCH}_2\text{CH}_3^+$) are studied using density functional molecular orbital methods. Initial geometries are optimized using the 6-31G* basis set. Electron correlation is incorporated by optimizing the geometries at the B3LYP level using the 6-31G** basis set. Stationary points are characterized by frequency calculation at the same level of theory and basis set. In the first installment of this paper, the existence of so-called enol pathway was reported and the dissociation mechanism was described in detail. In this installment, a new dissociation mechanism, a supposed keto pathway, is proposed. In this reaction channel, the ester linkage is immediately broken in a rate-determining E1 step producing FCOO and C_2H_5^+ which reacts further in a bimolecular elimination mechanism to yield the same intermediates ($\text{FCOOH} + \text{C}_2\text{H}_4^+$) as the enol pathway. In a similar manner as the enol pathway, the keto pathway is terminated by a slow elimination of a proton from C_2H_4^+ by FCOOH which acts as a base in an E2 elimination scheme. The keto pathway is more accessible than the enol pathway explaining the relative heights of the MS peaks in the EI spectrum of ethyl fluoroformate.

1. INTRODUCTION

Fluoroformic acid (FCOOH) in the condensed phase cannot exist long enough for experimental observation because it decays to CO_2 and HF in an autocatalytic fashion [1]. Hence, all attempts to isolate the molecule in solution have failed. In contrast, the hypothetical single molecule of fluorofluoroformic acid is found by Havlas, *et al.* [2] through *ab initio* calculations to be a stable species with an appreciable barrier (50 kcal/mol) for unimolecular decomposition to CO_2 and HF. Weidmann and Wesdemiotis [3] banked on this finding and theorized that by minimizing intermolecular interactions, as in the gas phase, FCOOH should exist long enough to be characterized experimentally. Consequently, they pioneered the generation and characterization of fluorofluoroformic acid and its ionized and protonated forms in the gas phase by neutralization-reionization mass spectroscopy (NRMS) where an isolated neutral species is initially produced by neutralization from the corresponding gaseous ion and subsequently identified by the mass spectrum obtained via reionization.

In an attempt to generate the radical cation of fluoroformic acid $\text{FCOOH}^{\bullet+}$ which will hopefully provide access to the elusive neutral FCOOH , Weidmann and Wesdemiotis [3] used ethyl fluoroformate as a precursor. Such esters are known to undergo McLafferty rearrangement [4] upon ionization and yield the acid ion as one of the fragmentation products (reaction 1, Fig. 1). However, magnetic scan at increased resolution showed that majority of the m/z 64 peak of the electron ionization (EI) mass spectrum of ethyl fluoroformate (Fig. 2) was actually $\text{C}_2\text{H}_5\text{FO}^+$ (reaction 2, Fig. 1) and not $\text{FCOOH}^{\bullet+}$. An alternative route, which consist of generation of protonated fluoroformic acid FC(OH)_2^+ (reaction 4, Fig. 1) via a McLafferty + 1 rearrangement and collisionally activated dissociation (CAD) of the protonated acid (reaction 5, Fig. 1), was proposed. Another proposed dissociation pathway of the radical cation of ethyl fluoroformate, deduced from the abundance of an m/z 28 peak in the EI spectrum, is given by reaction 3 in Fig. 1.

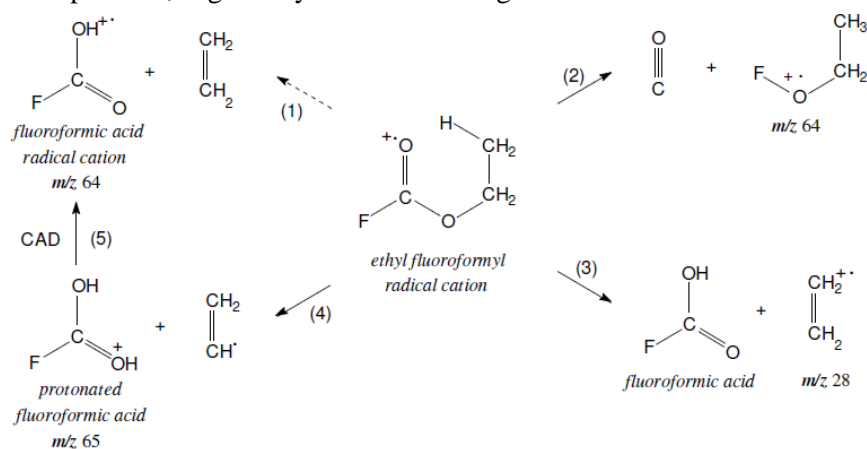


Figure 1. Some of the proposed dissociation pathways of the radical cation of ethyl fluoroformate. Adapted from Weidmann, F.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1994**, *116*, 2481.

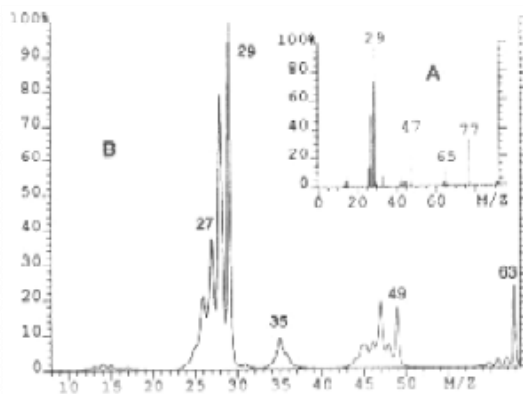


Figure 2. (A) EI spectrum of ethyl fluoroformate. (B) CAD spectrum of the cation at m/z 64 formed by EI of ethyl fluoroformate. Adapted from Weidmann, F.; Wesdemiotis, C. *J. Am. Chem. Soc.* **1994**, *116*, 2481.

The objective of this study is to examine in greater detail the elementary steps involved in the ground-state intramolecular gas-phase dissociation of the radical cation of ethyl fluoroformate $\text{FCOOCH}_2\text{CH}_3^{\bullet+}$.

2. COMPUTATIONAL DETAILS

Geometry optimizations and frequency calculations were done at the Hartree-Fock (HF) level of theory using the standard 6-31G* basis set which requests that a set of d function be included for each atom heavier than hydrogen. Correlation energy correction was incorporated through the Møller-Plesset perturbation theory [5] truncated at the second order with all electrons included [MP2(Full)] using the 6-31G** basis set which includes a set of p function for each hydrogen atom aside from the d function on the heavy ones. Due to limited computational resources, frequency calculation was not done anymore at the MP2 level and HF correction was incorporated instead.

Density functional theory (DFT) geometry optimizations and frequency calculation, utilizing the standard 6-31G** basis set described above were done using the Becke's Three Parameter Hybrid Method (B3) [6] using the correlation functional of Lee, Yang and Parr (LYP) [7] which includes both local and non-local terms.

All calculations were carried out using the Gaussian 94 [8] and GAMESS [9] suite of programs. Zero point energy corrections were scaled as recommended [10]. Unrestricted forms of the wavefunction were used for systems with spin multiplicity higher than singlet. All calculations were done using stable wave functions. Reaction paths were verified by intrinsic path following (IRC).

3. RESULTS AND DISCUSSION

Ab initio and density functional theory calculations reveal that the radical cation of ethyl fluoroformate is α -distonic and has a rather different connectivity compared to its neutral precursor (Fig. 3). Isomerization of radical cations towards a more stable structure where the charge and spin sites are spatially separated have also been reported elsewhere [11]. Contrary to Weidmann's suggestion (Fig. 1), the positive charge on the radical cation of ethyl fluoroformate is never centered on the carbonyl oxygen (compare Figs. 1 & 3b).

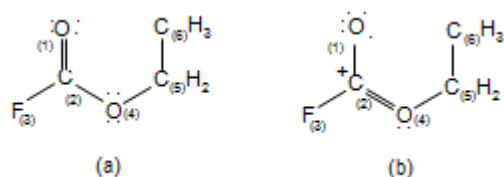


Figure 3. (a) Neutral and (b) radical cationic forms of ethyl fluoroformate.

The precursor ion dissociates in the gas phase in at least two ways. In the enol path, the dissociation starts off with a barrierless exothermic (and probably fast) isomerization to a γ -distonic enol form (Scheme 1) followed by a rate-determining cleavage of the ester linkage (Scheme 2). Succeeding elimination of a β -proton (Scheme 3) appears to be a difficult continuously endothermic process. Figure 4 summarizes the mechanistic details involved in the enol path which follows the previously established Ei + E1 elimination mechanisms.

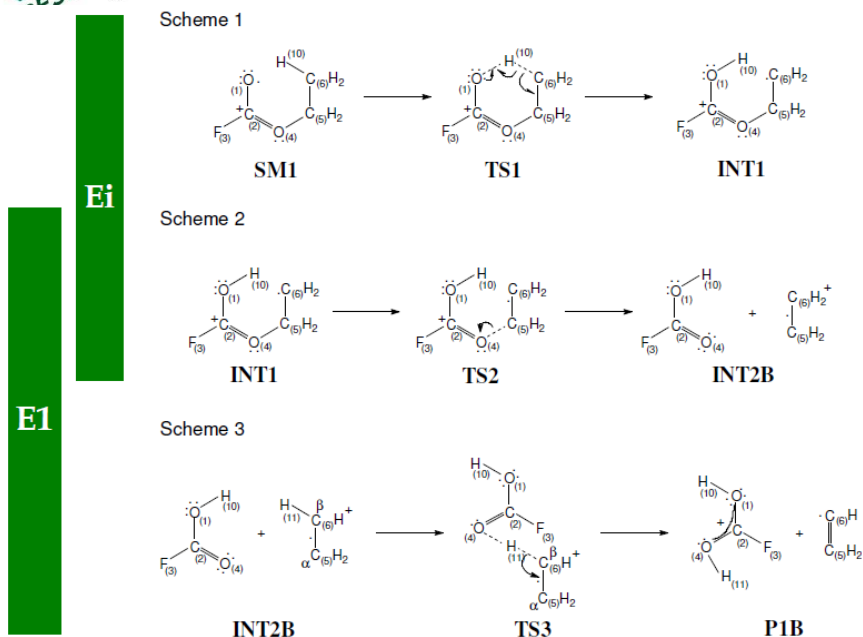


Figure 4. Summary of step-by-step dissociation mechanism for the enol path.

The ester linkage is immediately broken in the keto path (Scheme 4). FCOO^\bullet then eliminates an H^\bullet from C_2H_5^+ in a bimolecular fashion (Scheme 5) to yield the same intermediates FCOOH and C_2H_4^+ as the enol path. Both pathways are terminated by a slow elimination of a proton from C_2H_4^+ by FCOOH which acts as a base (Scheme 6). The keto path follows the $\text{E1} + \text{E2}$ elimination mechanism (Fig. 5).

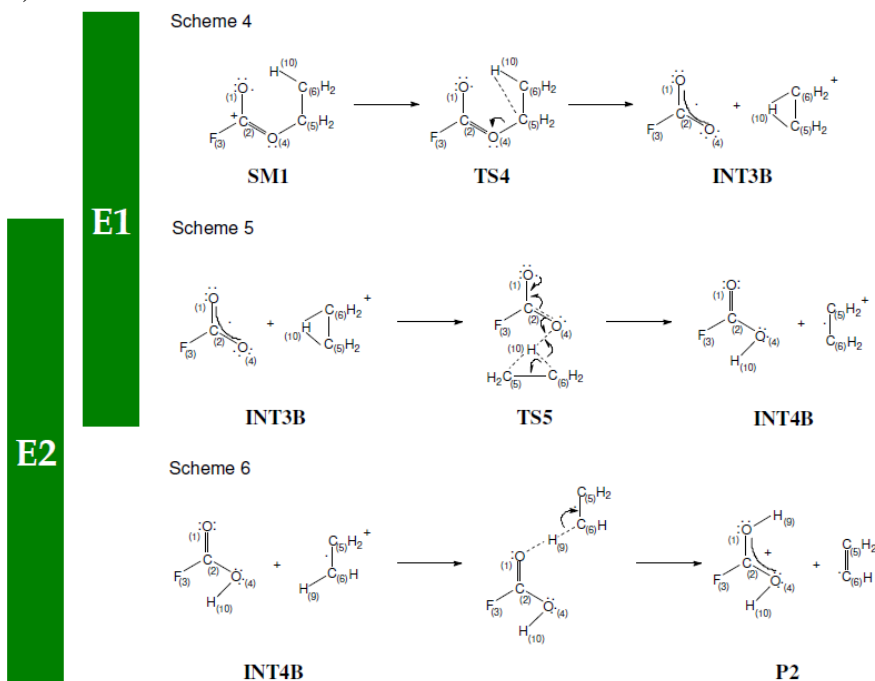


Figure 5. Summary of step-by-step dissociation mechanism for the keto path.

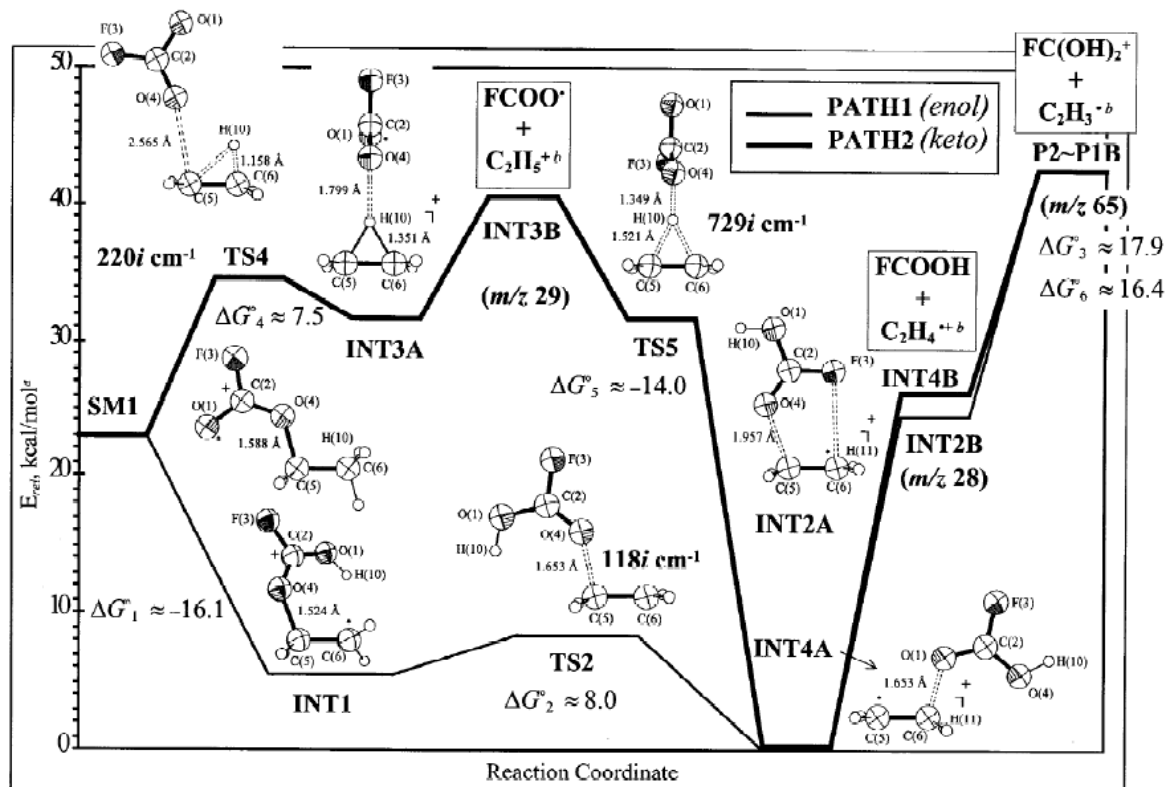


Figure 6. Summary of potential energy profile for the intramolecular dissociation of the radical cation of ethyl fluoroformate calculated at UB3LYP/6-31G**. ^aEnergy relative to lowest-energy intermediate. ^bFormulas (instead of structures) refer to fully dissociated fragments (rather than intermediate complexes).

The calculations also reveal that the conventional *ab initio* techniques (HF and MPPT) gave erroneous energetics due to heavy spin contamination of the wave function. Table 1 summarizes the S^2 eigenvalue of the wave functions.

Table 1. Wave function S^2 eigenvalue of optimized geometries involved in the enol path.

	UHF/6-31G*	UMP2(Full)/6-31G**	UB3LYP/6-31G**
SM1	0.758	0.758	0.754
"TS1"	0.786	0.767	NS ^a
INT1	0.760	0.756	0.753
TS2	0.758	0.756	0.752
INT2A	0.755	NS	0.754
INT2B	0.754	0.754	0.753
"TS3"	0.795	0.781	NS
"P1A"	0.925	0.860	NS
P1B	1.015	0.933	0.761

^aNS=no stationary point found at this level of theory.

4. CONCLUSIONS

Ethyl fluoroformyl radical cation, $\text{FCOOCH}_2\text{CH}_3^{\cdot+}$ (**SM1**), is an α -distonic cation which has a rather different connectivity with the neutral parent molecule, which readily isomerizes to a more stable γ -distonic enol form $\text{FC}^+(\text{OH})\text{OCH}_2\text{CH}_2^{\cdot}$ (**INT1**).

Two distinct reaction paths in the gas-phase intramolecular dissociation of the radical cation of ethyl fluoroformate diverges right at the initial step, but eventually reconverges at the final stage giving a common end product.

In one path (**PATH1**), the radical cation (**SM1**) isomerizes to a more stable γ -distonic enol form (**INT1**, **Scheme 1**) at the initial step of an Ei scheme where the two leaving groups do not necessarily depart simultaneously. In the second step, the Ei mechanism is completed with the rate-determining self-induced departure of the second leaving group yielding a neutral fluorinated acid (FCOOH) and a radical carbocation ($\text{C}_2\text{H}_4^{\cdot+}$; **INT2B**). This second stage of the Ei scheme is the initial step of an E1 mechanism where the substrate (**INT1**) is ionized to yield a carbocation intermediate. The fluorinated acid then acts as a base in eliminating a β -proton to yield the protonated form of the acid $\text{FC}(\text{OH})_2^+$ and an unsaturated hydrocarbon radical $\text{C}_2\text{H}_3^{\cdot}$ (**P1B**).

In another path (**PATH2**), the acid portion in the α -distonic keto form of the ester radical cation (**SM1**) initially departs in what transpires to be the first (and rate-determining) step of an E1 β -elimination scheme (**Scheme 4** + **Scheme 5**) where the intermediates are a deprotonated acid radical FCOO^{\cdot} and a hyperconjugated carbocation $\text{H}(\text{CH}_2)_2^+$. This is immediately followed by a fast hydrogen transfer in the final stage of the E1 step (**Scheme 5**) yielding the same neutral fluorinated acid (FCOOH) and radical carbocation ($\text{C}_2\text{H}_4^{\cdot+}$; **INT4B**) as that of **PATH1** (**INT2B**) except that the acid is of a different stereochemistry. This also appears to be the initial step of an E2 reaction where the deprotonated acid radical acts as a base in successively eliminating two hydrogen atoms from the hyperconjugated carbocation intermediate (**Scheme 5** + **Scheme 6**). Both paths are terminated by a rather difficult proton transfer (**Scheme 3** and **Scheme 6**) owing to high endothermicity (~ 25 kcal/mol) of this process.

The radical cation of fluoroformic acid ($\text{FCOOH}^{\cdot+}$) is not an intermediate in the two reaction channels described here and may only be generated by deprotonation of one of the end products, $(\text{OH})_2^+$. Ironically, neutral fluoroformic acid is readily generated from the radical cation of ethyl fluoroformate as a stable intermediate in at least two distinct reaction channels.

The conventional *ab initio* techniques [UHF/6-31G* and UMP2(Full)/6-31G**] employed in this study failed to give an adequate description of the energetics of the system investigated herein due mainly to severe contamination in the wave function. Meanwhile, the density functional (UB3LYP/6-31G**) wave function suffered tolerable spin contamination ($S^2=0.761$ at most) and offered a good qualitative description of the radical cation potential energy surface.

5. ACKNOWLEDGMENT

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6. REFERENCES

1. Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; John Wiley & Sons: New York, 1980.
2. Havlas, Z.; Kovár, T.; Zahradnik, R. *J. Am. Chem. Soc.* **1985**, *107*, 7243-7246.
3. Weidmann, F.; Wesdemiotis C. *J. Am. Chem. Soc.* **1994**, *116*, 2481-2485.
4. McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra*, 4th ed.; University Science Books: Mill Valley, CA, 1993.
5. (a) Krishnan, R.; Pople, J. A. *Int. J. Quant. Chem.* **1978**, *14*, 91. (b) Krishnan, R.; Frisch, M. J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244-4245.
6. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.
7. (a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789. (b) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H.; *Chem. Phys. Lett.* **1989**, *157*, 200.
8. *Gaussian 94* (Revision D.4), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, C. Y. Peng, P. Y. Ayala, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1995.
9. Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery J. A. *J. Comp. Chem.* **1993**, *14*, 1347-1363.
10. Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502-16513.
11. (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Yates, B. F.; Bouma, W. J.; Radom, L. *Tetrahedron* **1986**, *42*, 6225. (c) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123. (d) Zeller, L.; Farrell, J.; Kenttämaa, H. I.; Vainiotalo, P. *J. Am. Chem. Soc.* **1992**, *114*, 1205. (e) Stirr, K. G.; Kenttämaa, H. I. *J. Am. Chem. Soc.* **1990**, *113*, 5880.