

Ab initio, DFT and transition state theory calculations on 1,2-HF, HCl and ClF elimination reactions from CH₂F–CH₂Cl†

B. Rajakumar and E. Arunan*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560 012, India. E-mail: arunan@ipc.iisc.ernet.in

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This paper reports *ab initio*, DFT and transition state theory (TST) calculations on HF, HCl and ClF elimination reactions from CH₂Cl–CH₂F molecule. Both the ground state and the transition state for HX elimination reactions have been optimized at HF, MP2 and DFT calculations with 6-31G*, 6-31G** and 6-311++G** basis sets. In addition, CCSD(T) single point calculations were carried out with MP2/6-311++G** optimized geometry for more accurate determination of the energies of the minima and transition state, compared to the other methods employed here. Classical barriers are converted to Arrhenius activation energy by TST calculations for comparisons with experimental results. The pre-exponential factors, *A*, calculated at all levels of theory are significantly larger than the experimental values. For activation energy, *E_a*, DFT gives good results for HF elimination, within 4–8 kJ mol⁻¹ from experimental values. None of the methods employed, including CCSD(T), give comparable results for HCl elimination reactions. However, rate constants calculated by CCSD(T) method are in very good agreement with experiment for HCl elimination and they are in reasonable agreement for HF elimination reactions. Due to the strong correlation between *A* and *E_a*, the rate constants could be fit to a lower *A* and *E_a* (as given by experimental fitting, corresponding to a *tight* TS) or to larger *A* and *E_a* (as given by high level *ab initio* calculations, corresponding to a *loose* TS). The barrier for ClF elimination is determined to be 607 kJ mol⁻¹ at HF level and it is unlikely to be important for CH₂FCH₂Cl. Results for other CH₂X–CH₂Y (X,Y = F/Cl) are included for comparison.

I. Introduction

The HX elimination reactions from haloethanes have continued to attract both experimental^{1–6} and theoretical efforts.^{6–10} One of the main reasons for this interest is the fact that these reactions offer an excellent example for a truly unimolecular reaction involving complicated motions along at least 4 bonds. It is ideal for discussing the intricacies of ‘the reaction coordinate’ in a classroom. These reactions have served as benchmarks for testing the canonical (TST) -and microcanonical (RRKM) unimolecular reaction rate theories.^{11,12}

The main focus in this paper is on the HF/HCl elimination from CH₂F–CH₂Cl (CFE) and comparisons to the other chloro/fluoroethanes: CH₃CH₂Cl (CE), CH₂ClCH₂Cl (DCE), CH₂FCH₂F (DFE) and CH₃CH₂F (FE). Our interest in this molecule arose due to two different reasons. Recently, we reported a detailed account of the HCl elimination reaction of DCE using a single pulse shock tube.⁶ Moreover, *ab initio* and DFT calculations on the transition state for HCl elimination from DCE and CE were reported. The CE was included for calibration of both experimental and theoretical results. The experimental activation energy (*E_a*) determined for the HCl elimination for DCE was close to that of CE (*ca.* 243 kJ mol⁻¹) within an uncertainty of 8 kJ mol⁻¹. Earlier chemical activation studies inferred a difference in critical energy (*E₀*) of at least 21 kJ mol⁻¹ for these two reactions.¹³ It was noted that similar difference existed between the thermal and chemical activation results for HF and HCl elimination both from

CFE.¹⁴ Thermal studies resulted in activation energies of 251 and 264 kJ mol⁻¹ for HF and HCl elimination, respectively. On the other hand, chemical activation studies inferred critical energies of 259 and 285 kJ mol⁻¹ for the same reactions, suggesting that *E_a* would be even larger, *vide infra*. Thermal studies reported the pre-exponential factors for the two reactions as well and they differed by a factor of 4.4. *Ab initio* and DFT calculations can be useful in not only resolving the difference in activation energy but also for interpreting the pre-exponential factors. To the best of our knowledge, such results for CFE are not available.

Another reason for our interest in this molecule is to look at the F substitution effect on HCl elimination barriers, especially from the theoretical point of view. Previously, we have reported MP2/6-311++G** results on the HCl elimination reaction from CH₃COCl and FCH₂COCl.¹⁵ These results predicted an increase of 50 kJ mol⁻¹ in HCl elimination barrier on β-F substitution of CH₃COCl. This appeared rather large compared to the 21 kJ mol⁻¹ increase in the experimental activation energy for HCl elimination on β-F substitution of CE. Experimental results on these barriers for CH₃COCl and FCH₂COCl are still not available and it was not clear if the increase predicted at the MP2 level was real. Safont and co-workers had reported theoretical study on HCl elimination from 2-chloropropionic acid and concluded that MP2/6-31G** level was necessary to obtain a reasonably accurate result for kinetic parameters.¹⁶ Both HF and HCl elimination are possible for CFE and experimental results are available. Together with the results on CE and FE, the effect of β-Cl/F substitution on the HF/HCl elimination barriers could be calculated and compared with experimental results. Hence, theoretical results on CFE would be valuable and they are presented here.

† Electronic supplementary information (ESI) available: Structural details and vibrational frequencies for the ground and transition states for HX elimination from CFE, FE and DFE (Tables 1S–20S). See <http://www.rsc.org/suppdata/cp/b3/b306833a/>

Zhu and Bozzelli reported theoretical calculations on Cl₂ elimination from DCE,¹⁷ and they concluded that it is not an important channel. It is well known that C–C dissociation dominates decomposition of C₂H₆ but HF elimination dominates C₂H₅F decomposition, *i.e.* the barrier for HF elimination is smaller than C–C dissociation but it is not true for H₂ elimination. Would the ClF elimination have a smaller barrier than Cl₂ elimination? This led us to explore the possibility of ClF elimination from CFE and the results are included here. Recently, McGrath and Rowland¹⁸ have discussed the importance of tunneling in the HCl elimination reaction from CE. They have reported results using CCSD(T) method for CE. The same method is employed for CFE in this work and together these results would be useful to address the β-F substitution effect. Chuang and Truhlar¹⁹ have discussed the statistical thermodynamics of bond torsional modes and provided partition functions for the torsional mode in CE, CFE and DCE. Results from both of these papers have important consequences in interpreting thermal rate parameters, *i.e.* pre-exponential factor and activation energy. A detailed discussion on these consequences is presented at the end as well. Throughout this manuscript, HF is used to denote hydrogen fluoride and Hartree–Fock and what is meant should be obvious from the context.

II. Computational details

All calculations have been performed with the GAUSSIAN-94 program suite.²⁰ Both ground and transition state geometries were fully optimized at HF, MP2(FULL) and DFT(B3LYP) levels with 6-31G*, 6-31G** and 6-311++G** basis sets, internally available in the Gaussian package. For CFE only, single point CCSD(T) level calculations were also done with 6-311++G** basis set. Frequency calculations were carried out for both ground and transition state geometries, with the latter having one imaginary frequency corresponding to the reaction coordinate. The structure and normal mode vibrations were viewed with Molden²¹ and the normal mode corresponding to the reaction coordinate is consistent with the reaction of interest. The TST rate constant at a given *T* was calculated using the *ab initio* results as follows:²²

$$k(T) = l \frac{k_B T}{h} \frac{Q_{\ddagger}}{Q_R} \exp\left[-\frac{E_0}{RT}\right] \quad (1)$$

where k_B is the Boltzmann constant, Q_{\ddagger} and Q_R are partition functions for the TS and reactant, respectively, and E_0 is the zero-point barrier for the reaction. There has been a lot of discussion on reaction path degeneracy^{11,12,22–24} and we follow the recommendation by Pollak and Pechukas²³ as summarized by Gilbert and Smith.¹²

$$l = \frac{m^{\ddagger} \sigma}{m \sigma^{\ddagger}} \quad (2)$$

Here, σ is the symmetry number and m is the number of optical isomers and \ddagger represents the transition state. The thermodynamic formulation of TST is then used to estimate E_a and A for comparison with experimental results:²²

$$k = l e^{\frac{k_B T}{h}} \exp\left[\frac{\Delta S_{\ddagger}}{R}\right] \exp\left[-\frac{E_a}{RT}\right] \quad (3)$$

Here, ΔS_{\ddagger} is the entropy of activation calculated using the partition functions for the reactant and TS. Rigid rotor and harmonic oscillator partition functions are used for the rotational and vibrational degrees of freedom, except for the torsional degree of freedom. For the latter, partition functions are calculated assuming harmonic oscillator and free rotor models, independently and results from both models are included. The A and E_a were calculated at every 25 K within the *T* range

of interest and the average values are reported. The rate constants calculated using eqn. (1) could be independently fitted to Arrhenius expression as well and it yielded results in close agreement with the average values of A and E_a from eqn. (3). Moreover, these fits had correlation coefficients close to 1 suggesting that the Arrhenius form for the rate expression is consistent with theory within this temperature range. For the di-substituted ethanes, both *trans* and *gauche* forms exist and the total rate constant was calculated as the sum of the values for the two conformers weighted by the Boltzmann factor, *i.e.* $k = w_t k_t + w_g k_g$ where w stands for the Boltzmann factor and the subscripts refer to *trans* and *gauche*.

III Results and discussion

III.1.A. Structure and vibrational frequencies of the reactants and TS for HX elimination

There have been numerous reports on the structure and vibrational frequencies of CFE.^{25,26} The calculated geometries of the *trans*- and *gauche*- forms of CFE and the TS for HF, HCl and ClF elimination reactions are shown in Fig. 1. Our results on CE and DCE have already been published.⁶ During the course of this investigation, similar calculations were performed for FE and DFE for comparisons. Our results are in complete agreement for the *trans*- and *gauche*- conformers

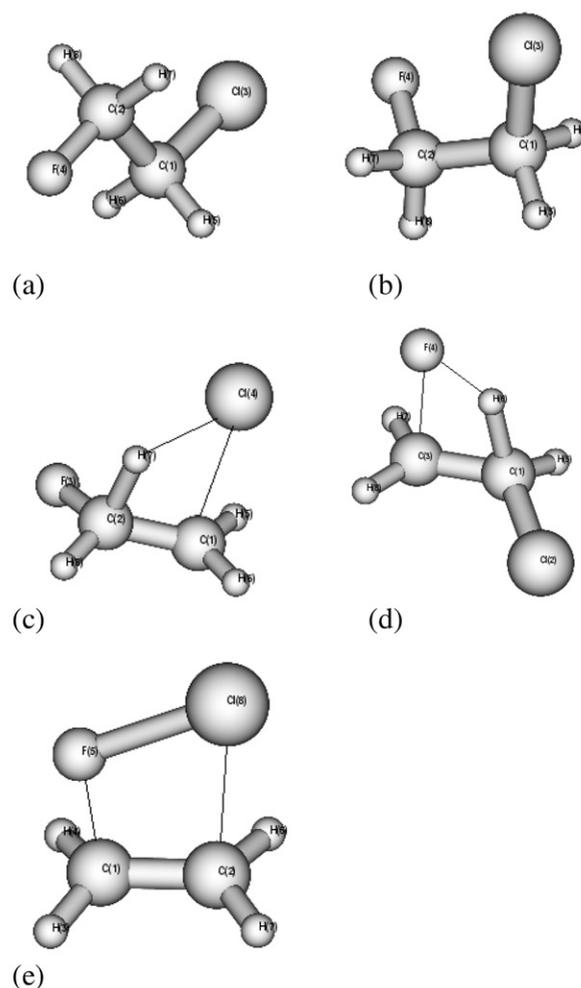


Fig. 1 Optimized structures for *trans* (a) and *gauche* (b) CFE and TS for HF(d) HCl(c) and ClF(e) elimination reactions. The complete structural parameters are given in supporting information and some relevant details are given in Tables 1 and 2.

with earlier published results at the same level of calculations wherever available. The *gauche* form is more stable for the DFE than the *trans* form but the *trans* form is more stable for DCE and CFE. It is due to the ‘*gauche* effect’, which has been discussed in detail in the literature.²⁶ The complete structural details for the ground and transition states for HX elimination from CFE, FE and DFE are given as supporting information.† Also included in the supporting information are tables of vibrational frequencies of the ground state and TS species for FE, DFE and CFE.

Our main objective in obtaining these results is to calculate the *ab initio* rate constants. Hence, the discussion is limited to some pertinent points only. Four bond distances are crucial in HX elimination reactions. Two existing bonds break (C–H and C–X) and two new bonds form (HX and C=C) during the elimination reaction. In the past, when *ab initio* calculations of the TS structure and frequencies were not feasible, experimental pre-exponential factors were used to deduce the bond orders for these four bonds.^{13,26,28} This then led to a TS model and these bond orders were varied to fit the experimental pre-exponential factors. With *ab initio* calculations, these parameters are not variable any more and one can only comment on how well the theoretical methods do in comparison with experiments.^{8,10,18} Another structural parameter of interest is the dihedral angle involving these 4 atoms which determines if all the four atoms are in the same plane or not.

The TS structures for HF elimination from FE, DFE and CFE are very similar with minor changes in the bond distances, see Tables 1 and 2. It is very similar to the TS for HF elimination from CF₃CH₃ reported by Holmes and coworkers.¹⁰ The percentage changes in C–F, C–H and H–F distances for CFE differ by 2–3 % from those of FE and DFE. For HCl elimination, the structural parameters (C–Cl, C–H and H–Cl distances) for DCE differ from those of CE and CFE by a few percent. It appears that Cl substitution leads to more significant changes in the TS structure than F substitution for both HF and HCl elimination. A careful look at Tables 1 and 2 clearly highlights this difference between F and Cl substitution. These changes do reflect in the vibrational frequencies at the TS, which in turn affect the pre-exponential factors. All the vibrational frequencies are given in the

supporting information† and the rate parameters derived from them are discussed next.

The torsional angle \angle XCCH is included in Tables 1 and 2, as well. It is zero for FE and CE, both of which have the other four atoms as hydrogen. If one of these four hydrogen is substituted by F or Cl, the dihedral angle is not zero. Thus, for CFE, DCE and DFE, the dihedral angle is significantly different from zero. From the data given in the two tables, it is obvious that F substitution leads to a larger change in the dihedral angle than Cl substitution. Thus, at the TS for HF/HCl elimination from CFE/DCE (Cl substitution for H), the dihedral angles are 1–5° at various levels of calculations. On the other hand, the TS for HF/HCl elimination from DFE/CFE (F substitution for H), the dihedral angles vary from 5–13°. In both cases, MP2 level calculations give larger angles than DFT, which in turn gives larger angles than HF level calculations. The TS for ClF elimination from CFE is, not surprisingly, planar with the dihedral angle as 0°. Here again, all the four atoms not involved in the reaction are hydrogen atoms. The other structural parameters at the TS for ClF elimination are discussed next.

III.1.B. TS for ClF elimination from CFE

To explore the possibility of ClF elimination reaction from CFE, HF level calculations were carried out with the same three basis sets. The TS structure for ClF elimination is shown in Fig. 1. The structure and vibrational frequencies are included in the supporting information. The TS structure for ClF elimination should have longer C–F and C–Cl bonds and it is of interest to compare these distances with those of TS for HF and HCl elimination, respectively. The C–F distance at the TS for ClF elimination was 1.806, 1.804 and 1.842 Å with 6-31G*, 6-31G** and 6-311++G** basis sets. At the TS for HF elimination, the corresponding distances were 1.911, 2.027 and 1.845 Å. Thus, with smaller basis sets, the C–F distances look very different but with the larger basis set both TS have nearly the same C–F distance. The C–Cl distances showed little variation with basis size for ClF TS and they were 2.611, 2.610 and 2.615 Å, respectively. However, at the TS for HCl elimination, these distances varied more

Table 1 Summary of C–C, C–X, C–H and H–X distances and % changes and the dihedral angle H–C–C–F calculated for the transition states for HF elimination reactions from FE, DFE, and CFE.^a

Molecule	HF/6-31G**	HF/6-311++G**	MP2/6-31G**	MP2/6-311++G**	B3LYP/6-31G**	B3LYP/6-311++G**
	C–C					
FE	1.396 (–7.6)	1.391 (–7.9)	1.397 (–7.2)	1.404 (–7.0)	1.405 (–7.4)	1.400 (–7.4)
DFE	1.392 (–7.3)	1.387 (–7.7)	1.395 (–6.9)	1.397 (–7.0)	1.403 (–7.0)	1.396 (–7.2)
CFE	1.400 (–7.5)	1.393 (–7.9)	1.400 (–7.3)	1.403 (–7.2)	1.407 (–7.4)	1.401 (–7.6)
	C–F					
FE	1.911 (+39.2)	2.027 (+47.6)	1.845 (+32.2)	1.882 (+34.8)	1.885 (+35.3)	1.970 (+40.1)
DFE	1.916 (+40.3)	2.021 (+48.1)	1.842 (+32.3)	1.876 (+35.0)	1.883 (+35.6)	1.961 (+40.2)
CFE	1.869 (+36.6)	1.985 (+45.1)	1.820 (+30.7)	1.857 (+33.5)	1.856 (+33.5)	1.943 (+38.7)
	C–H					
FE	1.319 (+21.6)	1.264 (+16.5)	1.356 (+24.6)	1.320 (+20.8)	1.360 (+24.3)	1.304 (+19.2)
DFE	1.327 (+22.6)	1.272 (+17.6)	1.365 (+25.5)	1.332 (+22.0)	1.363 (+24.4)	1.313 (+20.2)
CFE	1.348 (+25.0)	1.282 (+18.9)	1.374 (+26.6)	1.336 (+25.4)	1.376 (+26.5)	1.316 (+21.0)
	H–F					
FE	1.257 (+39.5)	1.364 (+52.1)	1.233 (+33.9)	1.289 (+40.7)	1.249 (+35.0)	1.335 (+44.8)
DFE	1.241 (+37.7)	1.342 (+49.6)	1.230 (+33.6)	1.283 (+40.1)	1.248 (+34.9)	1.327 (+43.9)
CFE	1.211 (+34.4)	1.309 (+45.9)	1.212 (+31.6)	1.266 (+38.2)	1.226 (+32.5)	1.309 (+42.0)
	Dihedral angle					
FE	0.0	0.0	0.0	0.0	0.0	0.0
DFE	4.4	5.7	6.7	7.8	6.1	6.6
CFE	2.6	2.3	4.2	4.7	3.1	3.0

^a For C–C, C–X and C–H bonds, the % changes (in parentheses) give the change in these distances compared to the reactant. For both CFE (*trans*) and DFE (*gauche*) the global minimum is used for comparison. For the H–X bond, % change gives the change compared to free HF distance calculated at the same level. The dihedral angle given is for the 4 atoms involved in the reaction, \angle FCCH.

Table 2 Summary of C–C, C–X, C–H and H–X distances and % changes calculated for the transition states for HCl elimination reactions from CE, DCE and CFE.^a

Molecule	HF/6-31G**	HF/6-311++G**	MP2/6-31G**	MP2/6-311++G**	B3LYP/6-31G**	B3LYP/6-311++g**
C–C						
CE	1.377 (–9.2)	1.380 (–8.9)	1.390 (–8.1)	1.397 (–7.8)	1.397 (–8.0)	1.395 (–8.0)
DCE	1.379 (–9.0)	1.381 (–8.7)	1.392 (–7.9)	1.397 (–7.6)	1.399 (–7.8)	1.397 (–7.7)
CFE	1.374 (–9.2)	1.377 (–9.0)	1.387 (–8.2)	1.391 (–8.0)	1.398 (–8.0)	1.394 (–8.1)
C–Cl						
CE	2.735 (+51.9)	2.740 (+52.0)	2.498 (+39.9)	2.459 (+37.8)	2.643 (+45.1)	2.639 (+44.8)
DCE	2.687 (+50.0)	2.695 (+50.1)	2.445 (+37.4)	2.410 (+35.4)	2.599 (+43.3)	2.599 (+43.1)
CFE	2.699 (+51.0)	2.703 (+51.0)	2.471 (+39.1)	2.432 (+36.9)	2.626 (+45.2)	2.624 (+45.0)
C–H						
CE	1.233 (+13.9)	1.227 (+13.3)	1.260 (+16.0)	1.275 (+16.9)	1.265 (+15.8)	1.260 (+15.5)
DCE	1.239 (+14.9)	1.233 (+14.5)	1.274 (+17.4)	1.293 (+18.7)	1.274 (+17.0)	1.268 (+16.7)
CFE	1.229 (+13.7)	1.227 (+13.5)	1.262 (+16.0)	1.285 (+17.8)	1.262 (+15.3)	1.262 (+15.7)
H–Cl						
CE	1.961 (+55.0)	1.977 (+55.7)	1.817 (+44.1)	1.782 (+39.9)	1.818 (+41.4)	1.835 (+42.6)
DCE	1.908 (+50.8)	1.922 (+51.4)	1.776 (+40.0)	1.746 (+37.1)	1.788 (+39.0)	1.804 (+40.2)
CFE	1.983 (+56.8)	1.975 (+55.5)	1.829 (+44.2)	1.773 (+39.2)	1.829 (+42.2)	1.829 (+42.1)
Dihedral angle						
CE	0.0	0.0	0.0	0.0	0.0	0.0
DCE	0.7	0.5	1.5	1.6	2.7	3.1
CFE	5.0	6.8	11.8	13.0	10.0	9.6

^a For C–C, C–X and C–H bonds, the % changes (in parentheses) give the change in these distances compared to the reactant. For both CFE (*trans*) and DCE (*gauche*) the global minimum is used for comparison. For the H–X bond, % change gives the change compared to free HCl distance calculated at the same level. The dihedral angle given is for the 4 atoms involved in the reaction, \angle ClCCH.

and they were 2.735, 2.740 and 2.498 Å. The C–C distances calculated with the three basis sets were in-between those for the TS for HF and HCl elimination at the same level of calculation. To summarize, it appears that the TS structure for ClF elimination could be easily found by comparing the structures of HF and HCl elimination TS.

III.2. Kinetic parameters from theory and experiment for HX elimination reactions

Experimental results for FE,^{29–31} DFE,²⁹ CFE¹⁴ and DCE^{6,32} are limited. For CE, numerous measurements^{33–42} have been reported. For FE, the three different experimental reports (two shock tube^{29,31} and one static cell³⁰) agree reasonably well. The average of the two shock tube experiments ($k = 3.6 \times 10^{13} \exp[-249.6/RT] \text{ s}^{-1}$) is used for comparison with theory. For CE, the experimental results appear to converge with the two most recent measurements^{33,34} giving nearly identical results and it is used for comparison. Single pulse shock tube³⁴ experiment gives $k = 6.31 \times 10^{13} \exp[-241 \pm 5/RT] \text{ s}^{-1}$ and IR laser pyrolysis³³ gives $k = 5.62 \times 10^{13} \exp[-240/RT] \text{ s}^{-1}$. For DFE and CFE only one experimental measurement¹⁴ is available for thermal rate constant. For DCE most of the earlier measurements were affected by heterogeneous reactions, as noted in our recent work.⁶ Recently, we have come across another report by Buravtsev *et al.*³² but their pre-exponential factor of $1.0 \times 10^{16} \text{ s}^{-1}$ appears suspect and our single pulse shock tube result⁶ is used. For DFE,⁴³ CFE¹⁴ and DCE,¹³ chemical activation results are available, which give an independent estimate to E_0 for HX elimination reactions. In general, E_0 and E_a differ by about 8–13 kJ mol^{-1} in the T range of our study, due to the dependence of A on T . Thus, conversion from E_0 to E_a is dependent on the TS model used. Moreover, chemical activation experiments are done at non-equilibrium conditions and the analysis requires RRKM and master equation approaches. In this manuscript, we restrict to comparing the experimental and theoretical $k(T)$ at high-pressure limit.

From thermal activation experimental results, it seems that the activation energy for HCl/HF elimination increases on β -F substitution *i.e.* E_a for CFE and DFE are larger than those

for CE and FE, respectively. On the other hand, β -Cl substitution does not seem to change the activation energy significantly for HF/HCl elimination. The E_a for CFE and DCE for HF/HCl elimination are nearly the same as those for FE and CE, respectively.

Theoretical rate constants for all the HX elimination reactions were calculated using TST expression, eqn. (1). The torsional motion was treated as either harmonic vibration or free rotor for the calculation of partition functions. More accurate partition functions for the torsional motion, treated as a hindered rotor for CE, DCE and CFE, have been reported by Chuang and Truhlar¹⁹ and their effect will be discussed later in this section. The reaction path degeneracy, l , depends on the model¹² and for torsional model it was 1 for CE and FE and 2 for CFE, DCE and DFE. For CE and FE, reaction path degeneracy has been used as 2 by many authors, including us.⁶ However, as clearly explained by Gilbert and Smith,¹² strict applications of eqn. (2) unambiguously show it to be 1. The factor of 2 arises for CFE, DFE and DCE because of the presence of 2 optical isomers at the TS for these molecules *i.e.* $m^\ddagger = 2$ (see Fig. 1). For internal rotor model, it was 3 for CE and FE as $\sigma = 3$ for the molecule and 1 for TS. For CFE, it should be 2/3 if one considers the 3 minima equal.¹² In this case, $\sigma = 1$, $\sigma^\ddagger = 1$, $m^\ddagger = 2$ and $m = 3$. For DCE and DFE, m^\ddagger is 4 and l will be 4/3. Considering the overall uncertainties involved, it was decided to use l as 1 for DCE, CFE and DFE for the free rotor model. In any case, the free rotor model is rather inadequate, as discussed next.

For comparison with the experimental results, thermodynamic formulation of TST [eqn. (3)] was used. With this approach, both A and E_a are temperature dependent though the variation with temperature is small. For example, E_a increases by 0.92 kJ mol^{-1} between 1050 and 1200 K. One could also fit the rate constants calculated from the TST equation to Arrhenius form. In eqn. (1), E_0 is independent of T and A increases with T but the fit forces both these parameters to be constants. As a result, this purely empirical fit results in larger A and E_a compared to that of eqn. (1), in good agreement with the average values from eqn. (3). Tables 3 and 4 summarize the results for HF elimination and HCl elimination reactions.

Table 3 *Ab initio* and experimental rate parameters for HF elimination reactions from FE, DFE, and CFE.^a

Theory	FE			DFE			CFE		
	log <i>A</i>	<i>E</i> _a	<i>k</i> ^b	log <i>A</i>	<i>E</i> _a	<i>k</i> ^b	log <i>A</i>	<i>E</i> _a	<i>k</i> ^b
HF	14.12	310.0	0.25	14.49	337.5	0.03	14.46	328.9	0.069
HF-IR	13.98	313.0	0.13	13.68	341.1	0.003	13.32	332.7	0.003
MP2	13.91	260.7	33.8	14.28	281.6	8.1	14.26	272.2	21.6
MP2-IR	13.77	263.8	17.5	13.48	285.0	0.9	13.10	275.9	1.0
DFT	13.99	240.7	362.8	14.34	254.0	189.3	14.31	247.2	372.4
DFT-IR	13.87	243.8	196.1	13.58	257.8	21.9	13.20	251.1	28.5
CCSD(T)							14.33	275.7	17.3
CCSD(T)-IR							13.22	279.5	0.9
Expt. ^c	13.56	248.9 ± 4.2	55.0	13.39	263.6 ± 2.5	7.5	12.95	251 ± 5	10.7

^a The *E*₀ values follow: For FE: 298.8, 250.5, 230.1; DFE(*trans*): 324.8, 268.6, 242.6; DFE(*gauche*): 325.8, 272.1, 242.5; CFE(*gauche*): 316.2, 260.8, 235.2; CFE(*trans*) 319.6, 262.8, 240.1 at HF, MP2 and DFT levels, respectively. *A* is in s⁻¹ and *E*s are in kJ mol⁻¹. IR denotes internal rotor model for the torsional mode and the previous entry used harmonic oscillator (HO) model for the same mode. Despite the better agreement with experiment for IR model, HO model should be preferred as closer to reality; see text. ^b Rate constant calculated at 1100 K in s⁻¹. ^c Experimental values are from Table 5. See text for the choice of the parameters.

The pre-exponential factor (*A*) calculated with the torsional model is uniformly larger than experimental values. Treating the torsion as a free-rotor significantly lowers the *A*, improving the agreement with experimental results. However, Chuang and Truhlar's detailed calculations give partition functions for hindered rotor (HR) that are closer to the harmonic oscillator (HO) model than the free rotor (FR) model in our *T* range. For example, for CFE at 1100 K, the partition functions are 5.9, 41.5 and 8.8 for the HO, FR and HR models, respectively. For CE and DCE, the agreement between HO and HR model is better than that for CFE. Results from HO and FR models are included in Tables 3 and 4 and despite the better agreement between experiment and theory for FR model, the HO model results are to be preferred as closer to the 'real' theoretical estimates.

III.2.A. HF elimination reactions

The *A* factors for DFE and CFE are predicted to be larger than that of FE at all levels of theory (see Table 3). It is largely due to the reaction path degeneracy, which is 2 times larger and one can note the difference of 0.3 (log 2) in the theoretical *A* factors. However, experimental *A* for DFE is smaller than that of FE. It should be pointed out that the DFE results are from lower *T* (731–820 K) range than FE and CFE. From our TST calculations, the *A* increases by 1.3–1.4 times from 800 K to 1100 K. Even after accounting for this difference, the experimental *A* for DFE is smaller than that for FE. It is

likely that the uncertainty in experimental *A* is larger in both experiments.

The activation energy (*E*_a) for HF elimination is predicted to increase in the order FE < CFE < DFE at all levels of theory. The difference between FE and DFE is larger at HF level (25–29 kJ mol⁻¹) than those at MP2 (12–21 kJ mol⁻¹) and DFT (<12 kJ mol⁻¹) levels. The HF level calculations overestimate *E*_a by ≥ 63 kJ mol⁻¹ while MP2 calculations overestimate *E*_a by about 21 kJ mol⁻¹, for all 3 molecules. The DFT calculations do better at predicting both absolute and relative values of *E*_a. Given the uncertainty in experimental *E*_a (4–8 kJ mol⁻¹), it can be concluded that DFT results are in quantitative agreement with available experimental results. Holmes and coworkers have also observed similar excellent agreement for HF elimination from CF₃CH₃.¹⁰ However, comparison of experimental and theoretical rate constants give a totally different perspective; see Section III.2.D.

III.2.B. HCl elimination reactions

As noted for DFE, the *A* factors for DCE and CFE are also larger than that of CE due to the reaction path degeneracy. This has been experimentally observed in the case of CE and DCE, but the only experimental value of *A* for CFE appears to be low. More experimental results are needed for this reaction.

In terms of activation energy, there is a striking difference between the predictions for HF and HCl elimination reactions.

Table 4 *Ab initio* and experimental rate parameters for HCl elimination reactions from CE, CFE, and DCE.^a

Theory	CE			CFE			DCE		
	log <i>A</i>	<i>E</i> _a	<i>k</i>	log <i>A</i>	<i>E</i> _a	<i>k</i>	log <i>A</i>	<i>E</i> _a	<i>k</i>
HF	14.35	261.8	82.6	14.70	294.8	5.0	14.65	290.6	7.05
HF-IR	13.95	260.2	39.2	13.55	298.6	0.23	13.67	295.3	0.43
MP2	14.30	277.4	13.4	14.75	305.3	1.8	14.68	292.7	6.0
MP2-IR	13.90	275.8	6.4	13.59	308.9	0.1	13.67	297.1	0.37
DFT	14.33	224.6	4104.9	14.64	242.1	1390.6	14.63	240.9	1545.8
DFT-IR	13.96	223.0	2345.5	13.53	245.9	71.7	13.68	244.1	123.3
CCSD		262.3 ^b		14.66	293.2	5.5			
CCSD-IR				13.55	297.1	0.27			
Expt. ^c	13.8 ± 0.2	240.6 ± 4.5	236.8	13.47	263.6 ± 4.2	9.0	13.98 ± 0.8	241.8 ± 8.4	314.4

^a The *E*₀ values follow: For CE: 250.6, 266.5, 213.8; CFE (*gauche*) 283.1, 292.3, 229.6; CFE (*trans*): 286.5, 294.3, 234.2; DCE (*gauche*): 275.3, 277.8, 225.5; DCE (*trans*) 282.8, 283.7, 232.2 at HF, MP2 and DFT levels, respectively. *A* and *k* are in s⁻¹ and *E*s are in kJ mol⁻¹. IR denotes internal rotor model for the torsional mode and the previous entry used harmonic oscillator model for the same mode. Despite the better agreement with experiment for IR model, HO model should be preferred as closer to reality; see text. ^b Ref. 18. ^c Experimental values are from Table 5. See text for the choice of parameters.

The HF level calculations overestimate E_a for HCl elimination reactions as well, but by a smaller margin than that for HF elimination (17–42 kJ mol⁻¹ for the 3 molecules considered here). However, MP2 calculations predict E_a for HCl elimination to be *larger* than that at HF level for all three molecules, thereby resulting in larger deviation from the experimental values. DFT calculations, again, give better agreement with experiment but they clearly underestimate the barrier for both CE and CFE by 21 kJ mol⁻¹. For DCE, the DFT estimate is very much closer to the experimental value, but it could very well be fortuitous.

Experimental E_a values from thermal excitation increase in the order CE \approx DCE < CFE. Results from chemical activation experiments predict this trend as CE < DCE < CFE. Both HF and MP2 level calculations are in qualitative agreement with this trend giving E_a in the order CE < DCE < CFE. On the other hand, DFT calculations give CE < DCE \approx CFE. Considering all the experimental and theoretical results, it appears that for HCl elimination reactions, none of the three theoretical methods used here give reliable results (E_a within 4–8 kJ mol⁻¹ from experimental results). Comparing results in Tables 3 and 4, it is clear that the disagreement between MP2 and experimental E_a increases with the number of Cl atoms for both HF and HCl elimination reactions. Our earlier work on HX elimination from chlorofluoroamines also showed that MP2 level calculations overestimated barrier for HF/HCl elimination reactions in comparison with advanced level calculations.⁴⁴ In order to gain more insight into this problem, CCSD(T) calculations were carried out for HF and HCl elimination reactions from CFE and they are discussed later in this section. Moreover, experimental rate constants are compared to theoretical ones directly for CCSD(T) results in that section (III.2.D).

III.2.C. CIF elimination from CFE

At HF/6-311++G** level, the rate constant calculated for CIF elimination was $3.87 \times 10^{14} \exp[-607/RT] \text{ s}^{-1}$. The pre-exponential factor is comparable to HCl elimination reaction but the activation energy is too high at 607 kJ mol⁻¹, compared to HF and HCl elimination reactions. This is certainly larger than the C–C and C–Cl bond energies as well, and CIF elimination will not be important for CFE. Considering this result along with that of Zhu and Bozzelli¹⁷ for Cl₂

elimination from DCE, one could conclude that X₂/XY elimination reactions from CH₂X–CH₂Y are very unlikely.

III.2.D. HF and HCl elimination reaction from CFE

One of the main objectives of this work was to theoretically predict the kinetic parameters for HF and HCl elimination from CFE. In terms of the A factors, there is good qualitative agreement between theory and experiment. The HF elimination reactions have significantly smaller A than HCl elimination reactions and it is predicted at all levels. The E_a for HF elimination was 13 kJ mol⁻¹ lower than that for HCl elimination. The HF level of theory is completely inadequate as it predicts the order wrong. The DFT calculations predict the barrier for HF elimination accurately but for HCl elimination it underestimates the barrier, leading to the wrong order again. MP2 calculations predict the correct order but a larger difference of 33 kJ mol⁻¹.

McGrath and Rowland¹⁸ have calculated the barriers for HCl elimination from CE at HF, DFT, CCSD(T) and QCISD(T) levels with cc-PVnZ basis sets, extrapolating to complete basis set limit. Our results agree with their report at the same level of calculations. At higher levels, both CCSD(T) and QCISD(T) with cc-PV ∞ Z basis, the activation energy is found to be $262.3 \pm 1.7 \text{ kJ mol}^{-1}$. The error limit was obtained by comparing the results for high-level calculations, which appear to converge. Somewhat coincidentally, this is in excellent agreement with the HF level calculations reported in Table 4. Though the accuracy in E_a determined by comparing high-level calculations looks very good, the E_a differs from all the experimental activation energies listed in Table 5 by more than 21 kJ mol⁻¹. However, with this activation energy, McGrath and Rowland¹⁸ could predict rate constants in excellent agreement with the experimental results of Heydtmann and coworkers³⁵ between 714–767 K. They considered tunneling and they could also explain the D isotope effect quantitatively. The same set of rate constants was empirically fit by Heydtmann and coworkers³⁵ to obtain the activation energy as $235.1 \pm 2.5 \text{ kJ mol}^{-1}$ given in Table 5. Due to the strong correlation between A and E_a , the same rate constants could be fitted reasonably to different values of A and E_a . Encouraged by these observations, single point CCSD(T) calculations, with MP2/6-311++G** geometry, were done to determine the rate constants for HF and HCl elimination reactions from CFE. Kinetic parameters A and E_a were determined using B3LYP

Table 5 Experimental rate parameters for HF/HCl elimination reactions from FE, DFE, CFE, DCE and CE

Molecule	P/atm	T/K	A/s^{-1}	$E_a/\text{kJ mol}^{-1}$	Ref.
FE	3.3–11.8	996–1137	4.67×10^{13}	248.9 ± 4.2	29
	0–0.29	684–739	2.0×10^{13}	243.5	30
	1.05	1280–1660	2.63×10^{13}	250.2 ± 4.2	31
DFE	1.25–3.43	731–820	2.45×10^{13}	263.6 ± 2.5	30
CFE (HF)	1.07–1.2	1360–1790	8.51×10^{12}	254.4 ± 5.0	14
	0.01–0.15	714–769	8.91×10^{12}	251.0 ± 5.0	14
CFE (HCl)	1.07–1.2	1360–1790	2.95×10^{13}	266.9 ± 5.4	14
	0.01–0.15	714–769	3.89×10^{13}	260.2 ± 5.4	14
DCE	10–15	1050–1175	9.55×10^{13}	241.8 ± 8.4	6
	1.01	920–1050	1.26×10^{16}	272	32
CE	0.01	1100–1400	6.31×10^{13}	240.2	33
	7.1–7.8	960–1100	5.62×10^{13}	241 ± 5	34
	0–0.4	714–767	2.14×10^{13}	235.1 ± 2.5	35
	2.8–3.9	990–1200	3.98×10^{13}	233.5 ± 7.1	36
	0–0.01	712–755	2.88×10^{13}	236.8	37
	0.16–0.18	675–794	1.07×10^{14}	227.6	38
	0.07–0.2	692–772	2.88×10^{13}	236.8	39
	0.5–1.6	820–1000	1.45×10^{13}	236.0	40
	—	693–733	8.89×10^{13}	246.9	41
	0.30–0.32	684–744	3.2×10^{13}	236.8	42

frequencies and these are included in Table 3 and 4. Not surprisingly, the E_a determined at CCSD(T) level for HCl elimination was again closer to that from HF level calculations, as noted above for CE. For HF elimination though, CCSD(T) result was closer to the MP2 result.

For HF and HCl elimination reactions, Arrhenius plots were made from experimental and CCSD(T) rate constants and they are given in Fig. 2. It is quite revealing. For HCl elimination reaction, the agreement between experiment and theory is very good in the temperature range 1000–1300 K. For HF elimination reaction, it is within a factor of 2. Considering the approximations involved, agreement within a factor of 2 is very good. At lower temperatures, tunneling contributions should be included and it should improve the agreement between the two results. At higher temperature, the experimental data may not be reliable as bond dissociation reactions are likely to affect the kinetics.

The data shown in Table 3 and 4 and Fig. 2 present the same results in different formats. Several groups have used experimental Arrhenius parameters A and E_a to infer the structural and energetic aspects of the transition state, respectively.^{10–13,27,28} It is a fact that only k is measured experimentally. The experimental pre-exponential factors for a large number of HF/HCl elimination reactions are reasonably close and 10^{13} would be a good guess for A for this type of reactions (see Table 5, for example). This led to the assumption of a ‘tighter’ TS for HX elimination reactions as opposed to the ‘looser’ TS predicted by *ab initio* calculations.^{6–8,15,18} Our results, with that of the extensive calculations reported by McGrath and Rowland¹⁸ suggest that experimental Arrhenius parameters need not reveal the intricacies of the TS structure. However, these parameters will remain valuable for modeling in practical situations such as combustion, incineration, detonation, etc.

Returning to the main objective of this study, the F substitution does lead to a large increase in barrier, ca. 30 kJ mol⁻¹, for HCl elimination at the CCSD(T) level between CE and CFE. It is in close agreement with the MP2 level prediction of 28 kJ mol⁻¹. The increase measured experimentally is 23 kJ

mol⁻¹. These observations suggest that the MP2 results reported¹⁵ for HCl elimination from CH₃COCl and FCH₂COCl should be reasonable. For Cl substitution, MP2 level calculations predict an increase of 15 kJ mol⁻¹ in E_a for HCl elimination between CE and DCE, compared to no increase observed in thermal measurements.

It is clear that experimental rate parameters over a larger temperature range (say 600–1200 K) would be valuable in differentiating between *loose* and *tight* TS for HX elimination reactions. Kinetic parameters at higher temperatures (> 1200 K) would be useful but radical processes would start playing a significant role at these conditions and getting experimental results would be a big challenge.

IV. Conclusions

Ab initio and DFT calculations are reported for HF and HCl elimination reactions from CFE and compared with that for FE, DFE, DCE and CE. At all levels of calculations, the theoretical pre-exponential factors are larger than the experimental results. DFT calculations lead to nearly quantitative agreement with experimental E_a for HF elimination reactions but they underestimate E_a for HCl elimination reactions. MP2 calculations overestimate the activation energy for both HF and HCl elimination reactions, the disagreement being larger for HCl elimination reactions. Higher-level calculations at CCSD(T) level gives results closer to the MP2 level. The rate constants calculated at CCSD(T) level are in reasonable agreement with experiment for both HCl and HF elimination reactions. At all levels, theory predicts that the barrier for HF/HCl elimination from haloethane increases with F/Cl substitution. The limited thermal activation experiments seem to suggest that the β -F substitution increases the barrier for HF/HCl elimination reactions and β -Cl substitution does not.

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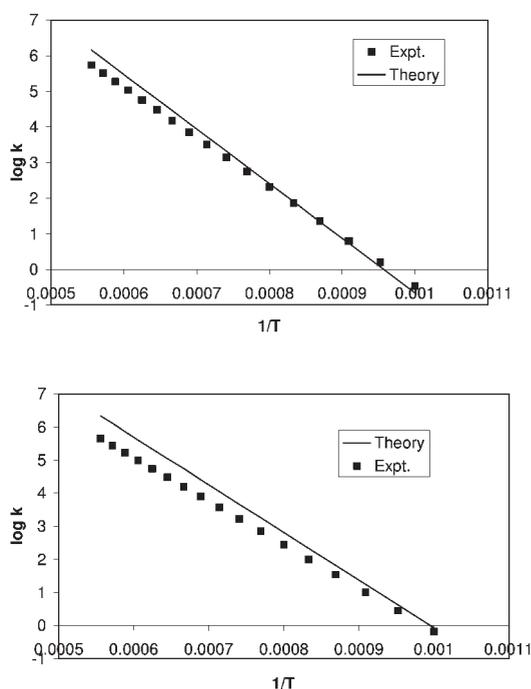


Fig. 2 Arrhenius plot for the HX elimination reaction from CFE. Top = HCl and bottom = HF. The points are experimental results from Table 5. The line is drawn from CCSD(T) results given in Table 3 and 4. The rate constants are in s⁻¹, the temperature is in K.

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