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Tetrahedron Letters 44 (2003) 7265–7268

TETRAHEDRON
LETTERS

Theoretical calculations of product percentage yields for the thermal decomposition of 2-chloro-1,1-difluoroethane

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Received 25 June 2003; revised 28 July 2003; accepted 4 August 2003

Abstract—Theoretical calculations of the product percentage yields for the thermal decomposition of CHF_2CH_2Cl are consistent with the experimental percentage product yields supporting the proposal that the unexpected formation of 1,2-difluoroethene can be explained by a 1,2-FCl interchange converting CHF_2CH_2Cl into $CHFClCH_2F$, which then undergoes a 2,1-HCl elimination. Thermal activation rate constants and threshold energy barriers for dominant reactions in this system were calculated. Theoretical product percentage yields varied greatly because different basis sets produced a wide range of threshold energy barriers, but the computational results were generally consistent with a recent experimental report.

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1. Introduction

Experimental product percentage yields from the thermal decomposition of 2-chloro-1,1-difluoroethane at 650°C were published by Dolbier et al. as follows: 53% *E*- and *Z*-CHF=CHF, 32% $CH_2{=}CF_2$, and 13% *E*- and *Z*-CHF=CHCl.[1] A two step mechanism to explain 1,2-difluoroethene as the major product was proposed to be a 1,2-FCl interchange converting CHF_2CH_2Cl to $CHFClCH_2F$ that subsequently undergoes a 2,1-HCl elimination to produce *E*- and *Z*-CHF=CHF. This interchange mechanism was found to be competitive with the 1,2-HX and 2,1-HX (X = Cl, F) elimination reactions. The unusual 1,2-FCl interchange was first proposed to explain the production of $CF_3CF{=}CH_2$ from chemically activated $CF_2ClCF_2CH_3$.[2,3] In this letter, product percentage yields predicted using density functional theory, DFT, to calculate input parameters for thermal rate constant calculations will be compared to experimental results from thermal activation. Also, changes in product percentage yields resulting from raising and lowering the calculated threshold energy barrier, E_0, will be examined.

2. Methods and results

To determine the significant reaction channels of CHF_2CH_2Cl, thermal activation rate constants and product percentage yields were determined at 800 K using DFT with the GAUSSIAN 98[4] package to compute energies, vibrational frequencies, and moments of inertia for the reactant and transition states using the B3PW91/6-31G(d) methodology, see Table 1. Table 1 also has the difference in vibrational plus rotational entropy between the transition state and the reactant, $\Delta S^{\dagger}$, the Arrhenius activation energy, E_a, and the threshold energy barrier, E_0. These E_0 include zero point energy corrections and are based on the degenerate *anti* conformers of CHF_2CH_2Cl which are 1.3 kcal/mol lower in energy than the *gauche* conformer. For CHF_2CH_2Cl, the major products predicted were $CF_2{=}CH_2$ from 1,2-HCl elimination (6.32%), *E*- and *Z*-CHF=CHCl from 2,1-HF eliminations (58.6%), and $CHFClCH_2F$, the product from the 1,2-FCl interchange (34.9%). The 1,1-HF elimination that forms the $CFCH_2Cl$ carbene was predicted to contribute less than 0.002% to the product yield. If the carbene isomerized to CHF=CHCl via H-migration, the product is identical to that from 2,1-HF elimination, thus the products from the two different reaction pathways could not be distinguished experimentally. The transition state structure for the possible 2,2-HCl elimination from CHF_2CH_2Cl could not be found using the DFT methods, presumable because the enthalpy of formation of the CHF_2CH: carbene is too high. This pathway only occurs when the energy of the singlet carbene is stabi-

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Keywords: unimolecular; elimination; interchange mechanism; density functional theory.

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doi:10.1016/S0040-4039(03)01883-5

Table 1. Reaction path degeneracies (all conformers), change in entropy to form the transition states, threshold and Arrhenius activation energies, thermal activation rate constants, and reaction percentage yields for CHF_2CH_2Cl (*anti* conformers only) and $CHFClCH_2F$ at B3PW91/6-31G(d) with T = 800 K

Reaction of CHF_2CH_2Cl	σ[a]	$\Delta S^\dagger$ (cal/K)[b]	E_0 (E_a) (kcal/mol)	k ($\times 10^{-6}$ s^{-1})	Percentage yields
1,2-HCl elimination	2/3	3.1	70.9 (73.4)	1.320	5.33
1,1-HF elimination	2	7.0	78.7 (81.2)	0.001290	0.005
Z-2,1-HF elimination	4/3	1.2	68.1 (70.2)	7.845	31.7
E-2,1-HF elimination	4/3	1.4	68.1 (70.2)	8.307	33.5
1,2-FCl interchange	2/3	0.4	66.3 (68.2)	7.273	29.4
					Total = 100.0

Reaction of $CHFClCH_2F$	σ[a]	$\Delta S^\dagger$ (cal/K)[b]	E_0 (E_a) (kcal/mol)	k ($\times 10^{-6}$ s^{-1})	Percentage yields
1,2-HF elimination	2/3	1.6	69.9 (72.2)	41.33	0.137
Z-2,1-HF elimination	2/3	1.4	68.6 (70.7)	3.0567	0.01
E-2,1-HF elimination	2/3	1.4	69.6 (71.8)	1.521	0.005
Z-2,1-HCl elimination	2/3	3.2	58.3 (60.4)	4879	16.3
E-2,1-HCl elimination	2/3	2.9	59.1 (61.1)	2594	8.61
1,1-HCl elimination	1	6.3	67.5 (69.7)	87.46	0.22
1,2-FCl interchange	1/3	0.2	57.4 (59.2)	1250	4.15
					Total = 29.4

[a] σ is the reaction path degeneracy.

[b] The $\Delta S^\dagger$ is the difference in the rotational and vibrational entropy of the transition state and the reactant and are for reaction path degeneracy of one.

lized by the presence of halogen substituents.[5] For $CHFClCH_2F$, the major products predicted were *E*- and *Z*-CHF=CHF from 2,1-HCl elimination. As Dolbier et al. assumed,[1] the 2,1-HCl elimination rate is at least thirty times faster than the rate of any other elimination from $CHFClCH_2F$. The reaction to convert the $CHFClCHF_2$ back into CHF_2CH_2Cl was also a significant reaction channel. Less important reaction channels were the possible 1,2-HF and 1,1-HCl eliminations. In Table 1, the product percentage yields for reactions of $CHFClCH_2F$ add to 29.4%, which is the percentage of CHF_2CH_2Cl that reacts via the 1,2-FCl interchange mechanism. Overall, the theoretical calculations agree with the dominant pathways observed experimentally, but the specific theoretical percentage yields differ by a factor of 2–6 when compared to experimental results.

It is interesting to note that the theoretical calculations predict a *Z*/*E* ratio of 0.94 for CHF=CHCl with 68.1 kcal/mol as the threshold energy to form either isomer. The B3PW91/6-31G(d) calculation predicted that the *Z*-CHF=CHCl isomer is 0.70 kcal/mol more stable than the *E* isomer. Whereas for CHF=CHF, the rate constant calculations predict a *Z*/*E* ratio of 1.88. Threshold energies for CHF=CHF differ by 0.8 kcal/mol: E_0 for *Z* is 58.3 kcal/mol and E_0 for *E* is 59.1 kcal/mol. The calculations predict that the *Z*-CHF=CHF isomer is 0.14 kcal/mol more stable than the *E* isomer suggesting that the difference in E_0 is only weakly related to the stability of alkene products. Also, the B3PW91/6-31G(d) predicted the $CHFClCH_2F$ formed from the 1,2-FCl interchange to be 8.8 kcal/mol less stable than the CHF_2CH_2Cl reactant.

Calculations were also performed at 948 K, using the B3PW91 and B3LYP methods with various basis sets (shown in Table 2) as well as CBS-QB3[6] to examine the influence of different basis sets and methods; see Table 2. The graphical abstract has E_0, calculated at B3PW91/6-311+G(2d,p) for reactions of CHF_2CH_2Cl. Comparing results from Tables 1 and 2 show that there was little change in product percentage yields for the B3PW91/6-31G(d) method and basis set when the temperature was changed from 800 to 948 K. An important finding is that threshold energies varied widely, up to 10 kcal/mol, depending on basis set employed, and this leads to large variations in the theoretical thermal rate constants and the product percentage yields.

Since reaction path degeneracy, threshold energy barriers, and the tightness of the transition state influence the rate constant for a particular reaction, comparisons between threshold energy barriers, E_0, and $\Delta S^\dagger$, calculated via different DFT methods, B3PW91 and B3LYP, can be useful. For the 1,2-FCl interchange and 1,2-HCl elimination, B3LYP consistently predicted lower E_0 than B3PW91 while both methods predicted similar energies for the 2,1-HF elimination reaction. B3LYP also consistently predicted less rigid transition state structures, i.e. larger $\Delta S^\dagger$, for all reactions than B3PW91. This trend can be seen somewhat in calculations at 6-31G(d), but it is more pronounced in calculations performed at 6-311+G(2d,p). Rate constants vary by as little as a factor of two up to as much as a factor of 30 between methods due to the rate constant's dependence on E_0 and $\Delta S^\dagger$.

In general, the variation between rate constants calculated with the same basis set using different methods, is

Table 2. Comparison of thermal activation product percentage yields calculated using B3PW91 and B3LYP with a range of basis sets and CBS with QB3 to experimental product percentage yields at $T = 948$ K

	1,2-FCl interchange				1,2-HCl elimination				2,1-HF elimination			
Basis set	k ($\times 10^{-2}$ s^{-1})	% Yield	E_0 (E_a)[a] (kcal/mol)	$\Delta S^\dagger$ (cal/K)[b]	k ($\times 10^{-2}$ s^{-1})	% Yield	E_0 (E_a)[a] (kcal/mol)	$\Delta S^\dagger$ (cal/K)[b]	k ($\times 10^{-2}$ s^{-1})	% Yield	E_0 (E_a)[a] (kcal/mol)	$\Delta S^\dagger$ (cal/K)[b] (Z, E)
B3PW91												
6-31G	119	82.8	56.0 (57.9)	0.34	4.37	3.04	64.7 (67.5)	2.80	20.4	14.2	63.5 (65.8)[c]	1.09, 1.33
6-31G(d)	0.71	28.0	66.3 (68.2)	0.20	0.187	7.37	70.9 (73.7)	3.16	1.64	64.6	68.1 (70.4)	1.32, 1.37
6-31+G(d)	2.57	23.2	64.1 (66.0)	0.20	0.146	1.32	71.2 (74.0)	2.95	8.35	75.5	65.1 (67.4)	1.36, 1.46
6-311+G(d)	3.89	38.2	63.3 (65.2)	0.24	0.192	1.88	70.6 (73.4)	2.74	6.11	59.9	66.0 (68.3)	1.76, 1.83
6-311+G(d,p)	4.26	10.3	63.1 (65.0)	0.22	0.688	1.67	68.1 (70.9)	2.66	36.3	88.0	62.4 (64.7)	1.27, 1.33
6-311+G(2d,p)	7.68	16.5	61.8 (63.6)	–0.10	0.747	1.60	67.9 (70.6)	2.56	38.2	81.9	62.0 (64.3)	1.04, 1.15
cc-pVTZ	2.77	11.4	63.6 (65.4)	–0.14	0.771	3.18	67.9 (70.5)	2.67	20.7	85.4	63.1 (65.4)	0.87, 1.01
B3LYP												
6-31G(d)	3.12	12.7	63.8 (65.7)	0.40	4.79	19.5	69.2 (72.0)	3.24	16.6	67.7	68.2 (70.5)	1.47, 1.56
6-311+G(2d,p)	36.0	41.5	59.0 (60.8)	0.04	1.61	1.85	66.5 (69.2)	2.67	49.2	56.7	61.7 (64.0)	1.18, 1.31
CBS-QB3	11.7	37.9	61.2 (63.0)	0.20	2.30	7.40	65.8 (68.5)	2.72	16.9	54.7	63.6 (65.9)	1.19, 1.32
Experimental		53.0				32.0				13.0		
Product of reaction	$CHFClCH_2F \rightarrow$ E- and Z-CHF=CHF					CF_2=CH_2			E- and Z-CHF=CHCl			

[a] E_0 is the threshold energy. E_a is the Arrhenius activation energy. Both are in kcal/mol.

[b] All $\Delta S^\dagger$ are for reaction path degeneracy of one.

[c] E_0s were identical for E and Z isomers for each basis set except 6-31G where Z is shown and E was 0.4 kcal/mol lower at 63.1 kcal/mol.

influenced predominantly by the change in E_0 rather than by the change in $\Delta S^\dagger$. For example, at 6-311+G(2d,p), the 1,2-FCl interchange rate constants vary by a factor of 4.69 from B3PW91 to B3LYP. The E_0 change from 61.77 kcal/mol at B3PW91 to 59.00 kcal/mol at B3LYP creates a difference of a factor of 4.35 between rate constants, while the increase in $\Delta S^\dagger$ from −0.10 to 0.04 increases the rate constant only by 7%, creating a net difference in rate constants of a factor of 4.66.

Overall, the theoretical predictions always underestimate the importance of the 1,2-HCl elimination channel from CHF_2CH_2Cl, always overestimate the contribution of the 2,1-HF elimination reaction, but bracket the contribution from the 1,2-FCl interchange mechanism. Also, according to the calculations of $\Delta S^\dagger$, the bridged transition state structure involved in the 1,2-FCl interchange is the most rigid, followed by the 2,1-HF elimination four-centered transition state, with the four-centered transition state of the 1,2-HCl elimination being the least rigid.

Calculated transition state geometries and their vibrational frequencies, moments of inertia, and $\Delta S^\dagger$, vary little with change of method and basis set, however there is no lower bound to the transition state energy and hence improvements to basis set do not necessarily improve the E_0. Improved agreement between experiment and theory can be achieved by changing the E_0s using either of the following methods. First, assuming the B3PW91/6-31G(d) method and basis set predict accurate rate constants for HF elimination,[7] the E_0s for the 2,1-HF elimination that produces E- and Z-CHF=CHCl was kept constant while the E_0s for the other pathways were lowered. The E_0 (1,2-HCl elimination) was lowered by 5.5 kcal/mol and the E_0 (1,2-FCl interchange) was lowered by 3.5 kcal/mol. Resulting product percentages, calculated at 800 K, were: 32.0% CH_2=CF_2, 53.0% E- and Z-CHF=CHF, and 13.0% E- and Z-CHF=CHCl, which were in close accord with experimental results. An alternative method for achieving agreement between experiment and theory involves raising the threshold energies for the 1,2-FCl interchange and the 2,1-HF elimination while allowing no change in the threshold energy of the 1,2-HCl elimination. The threshold energy for 1,2-FCl interchange was raised by 2.0 kcal/mol and the threshold energy for 2,1-HF elimination was raised by 5.5 kcal/mol to achieve product percentages of 33.9% CH_2=CF_2, 53.1% E- and Z-CHF=CHF, and 13.0% E- and Z-CHF=CHCl. Either of these schemes, or other appropriate adjustments, result in acceptable agreement with experiment and is within the threshold energy variation between basis sets. The equilibrium interconverting CHF_2CH_2Cl and $CHFClCH_2F$ via the 1,2-FCl interchange has been neglected which adds additional uncertainty to the theoretical product percentage yields. However, since there is large variation between methods and basis sets, this uncertainty does not significantly alter product percentages. The absolute rate constants would be markedly different for the two adjustment methods, thus experimental Arrhenius A-factor and activation energies for comparison to the predicted results would be useful.

This unexpected interchange mechanism may have occurred in other studies of hydrohalocarbons, for example, the decomposition mechanism for CF_3CH_2Cl may be a 1,2-FCl interchange followed by 2,1-HCl loss rather than the assumed mechanism of a 2,2-HCl elimination reaction followed by 1,2-F migration in the CF_3CH carbene.[8–11]

3. Conclusions

The formation of *E*- and *Z*-CHF=CHF during the thermal decomposition of CHF_2CH_2Cl can be explained by a unique, two-step mechanism involving a 1,2-FCl interchange, followed by a 2,1-HCl elimination reaction. Absolute rate constants for thermal pyrolysis at several temperatures would be very useful so the Arrhenius parameters for all reaction pathways could be compared to theoretical predictions.

Acknowledgements

We gratefully acknowledge support from the National Science Foundation, CHE-0239953 and Paul T. Beaton for assistance with preliminary calculations. We would also like to acknowledge Professor William J. Dolbier, Jr. for helpful discussions and continued beneficial collaborations.

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