



Figure 2. Kinetic plots of simple deamination (1 step) with variation of reaction order n .

energies.^{8,11} To avoid initiation and termination effects on the kinetics,⁸ the range $0.17 < \alpha < 0.74$ of the deamination step was investigated (see blocked area in Figure 1). The result of the numerical analysis is on Table 1, and plotted in Figure 2. The best fitting straight line is obtained by the second order ($n=2$) equation with the correlation coefficient value of 0.999. With this equation, the activation energy of the deamination step is calculated as 95.3 kJ/mol. It is reasonable to consider that the intermediate of the deamination step involves the elongated state of N-H bond, which requires the

activation energy of 95.3 kJ/mol. According to the previously reported works,^{12,13} the ammonium groups are oriented within the hexagonal siloxane hole on the interlayer surface of layered silicate, accompanied with weak N-H...O hydrogen bond. The N-O distance is reported to be at minimum 2.85 Å.¹³ Therefore it can be concluded that the thermal energy of 95.3 kJ/mol is needed to disorient ammonium groups ionically bonded to the siloxane hole on the silicate and to break N-H...O hydrogen bond.

This research was supported by Korean Science and Engineering Foundation (KOSEF).

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Internal Rotational Barriers of Ethyl Halides from SCF Calculations

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Received March 24, 1987

Dipole moments and barrier heights of internal rotations for ethyl halides (C_2H_5X where $X=F, Cl, Br, I$) exhibit no apparent trends as halogen atom varies from fluorine to iodine. Values of dipole moments and internal rotational barriers are available from experiments¹⁻⁵, but electronic structure calculations may provide detailed informations which are helpful in understanding these properties. In this report, we analyse the result of SCF calculations for ethyl halides with main emphasis on barrier heights of internal rotations. Many calculations on C_2H_5F and C_2H_5Cl , especially those at stable geometries, are available in the literature⁶⁻⁸, but none for

C_2H_5Br and C_2H_5I . We perform SCF calculations for all ethyl halides with the similar basis sets in order to enhance the compatibility among calculated properties.

It is known that values of internal rotational barriers calculated with SCF method agree well with experiment even at SCF level when basis sets used in calculations are of reasonable size. Therefore, we employ 6-31G* basis sets in ab initio SCF calculations for ethyl halides. In order to reduce the size of calculations and also to include relativistic effects, effective core potentials (ECP) of Hay and Wadt⁹ are used for Cl, Br and I. The use of ECP is expected to introduce only

Table 1. Potential barrier heights for internal rotation, V_3 , and dipole moments, D , for ethyl halides. Calculations by SCF methods using 6-31G* basis sets and effective core potentials (ECP) for Cl, Br and I.

Molecule	C ₂ H ₅ F	C ₂ H ₅ Cl	C ₂ H ₅ Br	C ₂ H ₅ I
V ₃ Calc.	3.62	3.94	3.89	3.87
(Kcal/mole) Exp	3.32 ^a	3.7 ^b	3.7 ^c	3.66 ^c
D Calc.	1.97	2.44	2.41	2.31
(Debye) Exp ^d	1.94	2.05	2.03	1.91

^afrom Ref. 2 ^bfrom Ref. 3 ^cfrom Ref. 4 ^dfrom Ref. 5.

small errors in the final results since our test calculations on C₂H₅Cl with and without ECP indicate that ECP introduces negligible amounts of error. Geometries are optimized with a plane of symmetry for both staggered and eclipsed forms of ethyl halides.

Calculated values of potential barrier heights for internal rotations increase from 3.62 kcal/mole for C₂H₅F to 3.94 kcal/mole for C₂H₅Cl, but stay about the same for C₂H₅Br (3.89 kcal/mole) and C₂H₅I (3.87 kcal/mole) as shown in Table 1. The same trends are found for these values in experiments, also shown in Table 1, although calculated values are about 10% higher than experimental values for all ethyl halides. Preliminary study with C₂H₅F implies that these discrepancies may not disappear easily neither by expanding the basis sets nor by including moderate amount of electron correlations¹⁰.

Dipole moments in Table 1 display similar behavior to potential barrier heights, but the agreements between calculated and experimental values for dipole moments are somewhat worse than those for potential barrier heights except for C₂H₅F. Dipole moment increases as the substituent changes from F to Cl and decreases for Br and I.

Due to the exceptional closeness between calculated and experimental values for the dipole moment of C₂H₅F compared with other ethyl halides, dipole moment of C₂H₅I is larger than that of C₂H₅F in the calculations and the opposite is observed in the experiment. At present the reason for this discrepancy is not clear.

A qualitative explanation for the observed and calculated trends for dipole moments and barrier heights can be found in the geometry of ethyl halides shown in Table 2. First, it is noted that calculated structural parameters are in good agreement with those from experiment. The average differences are about 1% for all parameters for all ethyl halides. The most notable geometry changes due to different substituents are distances between C atom and halide atoms (CX in Table 2), which increases as atomic number of halogen atom increases. Barrier heights for internal rotations remain about the same for C₂H₅Cl, C₂H₅Br and C₂H₅I because the contribution from the larger atomic or ionic size of halogens are balanced by the increasing bond lengths. Similar argument is available for dipole moments. Larger electronegativities compensate for the shorter bond distances. Although we do not rule out the possibility that there can be factors other than those considered here, the contributions from all other factors combined are probably small enough to be neglected in qualitative explanations of trends displayed by barrier heights and dipole moments.

The structural parameters for the eclipsed forms of ethyl

Table 2. Structural parameters of staggered(S) and eclipsed(E) forms of ethyl halides. Experimental values are shown in parentheses and calculated values are from SCF optimizations with a plane of symmetry using 6-31G* basis sets and ECP's for Cl, Br and I

Distances(A)		C ₂ H ₅ F	C ₂ H ₅ Cl	C ₂ H ₅ Br	C ₂ H ₅ I
CX	S	1.373 (1.398)	1.791 (1.788)	1.976 (1.950)	2.175 (2.14)
	E	1.374	1.793	1.978	2.177
CC	S	1.513 (1.505)	1.517 (1.520)	1.517 (1.518)	1.519 (1.54)
	E	1.529	1.534	1.533	1.534
CH	S	1.083 (1.095)	1.079 (1.089)	1.078 (1.087)	1.078 (1.087)
	E	1.082	1.078	1.077	1.078
CH ₃	S	1.086 (1.091)	1.086 (1.093)	1.087 (1.093)	1.087 (1.093)
	E	1.083	1.081	1.081	1.081
CH _{3s}	S	1.084 (1.090)	1.083 (1.089)	1.083 (1.093)	1.083 (1.093)
	E	1.084	1.084	1.084	1.084
XCC	S	109.5 (109.7)	111.4 (111.0)	111.6 (111.0)	111.3 (112.2)
	E	110.2	111.0	113.1	113.9
HCC	S	111.6 (112.9)	111.8 (111.6)	112.4 (112.3)	112.5 (112.5)
	E	111.9	113.6	112.6	112.7
H _s CC	S	110.3 (109.7)	109.4 (108.5)	109.1 (110.0)	108.9 (109.5)
	E	108.9	111.1	112.1	112.8
H _{ss} CC	S	110.5 (109.7)	111.0 (110.3)	111.2 (110.0)	111.4 (109.5)
	E	111.9	110.4	109.9	110.3
HCX	S	107.7 (106.1)	106.3 (-)	105.3 (105.4)	104.7 (104.7)
	E	107.1	103.5	104.6	104.0
H _s CH _{3s}	S	108.6 (108.7)	108.5 (108.5)	108.4 (108.9)	108.3 (108.3)
	E	108.0	108.2	107.9	107.7

* Experimental Values are from references 3,4 and 6. ** H_s refers to H atom of the CH₃ group of the plane of symmetry, and H_{ss} to remaining two H atoms in the groups.

halides are also shown in table 2. As expected, internal rotations are fairly close to rigid rotations i.e. structures of CH₃ and CH₂X subgroups are almost same both for staggered and for the eclipsed forms. But the small amount of relaxations for the eclipsed form is detectable in the calculated values i.e.

increase of C-C distance.

Since structural informations for eclipsed form are not readily available from experiment, detailed theoretical investigations for internal rotation seem worthwhile and the work is in progress. We also hope that additional calculations will locate the source of systematic overestimate for barrier heights in the present SCF calculations.

Acknowledgement. This research is, in part, supported by Korea Science and Engineering Foundation. One of the author (YSL) is grateful to Institute for Molecular Science in Japan where a large portion of the calculations have been carried out using a modified version of GAUSSIAN80¹¹

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