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Calculation of the Arrhenius Parameters for the Pyrolysis of Some Alkyl Vinyl Ethers Using Mopac

T.O. Bamkole

Department of Chemistry, University of Ibadan, Nigreja

Abstract: In this study, using the PM3 Hamiltonian of the computer code called MOPAC, a procedure for the computation of the Arrhenius parameters of the pyrolysis of some alkyl vinyl ethers was reported. The vinyl ethers studied were ethyl, 2-methoxyethyl, 2-chloroethyl, n-propyl, isopropyl, isobutyl and t-butyl. The procedure consists of the following steps: (i) An optimized geometry of the reactant was computed (ii) A reaction coordinate was identified and calculated (iii) By the continuous decrease of this distance from its value in the reactant to its value in the products, presumably through the transition state (ts), an approximate product geometry was obtained and optimized (iv) Thereafter, using a SADDLE calculation, the transition state was obtained and subjected to tests, using Intrinsic Reaction Coordinate (IRC) analysis, which characterize it to be a true transition state (v) By combining the heats of formation of the reactant, the transition state and any rotational barriers that are relevant, both the energy of activation, E_a and the entropy of activation, ΔS^* are computed for each reaction. The rate constants obtained from the computed Arrhenius parameters compare well within an order of magnitude of the experimental values in the literature, showing that the calculation procedure adequately simulates experimental results.

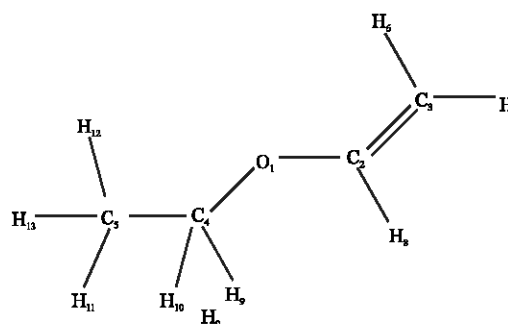
Key words: Kinetics, vinyl ethers, semi-empirical calculation, MOPAC, transition state

INTRODUCTION

In Parts I^[1] and II^[2] of this series, using MNDO of MOPAC and a different procedure, we reported the kinetics of the pyrolysis of ethyl and some chloroethyl vinyl ethers. In that study, because chlorine is a single-atom substituent, no consideration, even if warranted, was given to the effect of internal rotation. Here, using PM3, we explore how to take account of the effect of possible free or restricted internal rotation of multi-atom substituent-groups such as methyl and methoxy. The method is an adaptation of that recently reported by Adejoro and Bamkole^[3] for alkyl acetates. The kinetics of the pyrolysis of the derivatives reported here had been previously studied experimentally^[4-6].

MATERIALS AND METHODS

Geometry definition: The structure below represents ethyl vinyl ether. For the other substrates studied in this research, H9, H10, H11 or H12 or appropriate combinations are replaced by groups such as methyl, methoxy, chloro et cetera. The hydrogen atoms around each carbon atom in the rough trial geometries were fixed consecutively in the order of the dihedrals being about 180, -60 and +60 degrees, respectively. For ethyl vinyl



Ethyl vinyl ether

ether, H13 is the β hydrogen atom eliminated. The usual rules of geometry definition prescribed in MOPAC brochure are applied. Where more than one carbon atom bearing β H atoms occurs in the reactant as in isopropyl and t-butyl vinyl ethers, the one to be eliminated is successively the one with the positive acute dihedral angle on each carbon atom.

Reaction path studies: Reaction path study was performed for each substrate using as reaction coordinate, the H₁₃-C₃ bond length. By decreasing this bond length systematically in many small steps to the bond length in the product (about 1.1nm), an approximate product structure was obtained and optimized.

Other aspects of the procedure: Other aspects of the procedure such as saddle calculation, et cetera up to calculation of the rotational barriers were carried out as previously described for acetates by Adejoro and Bamkole^[3].

RESULTS

Ethyl vinyl ether will be used to illustrate the calculations: Four activities are very important and relevant in our procedure, namely systematically decreasing the H₁₃-C₃ bond length and independently varying the dihedrals 4-1-2-3, 5-4-1-2 and 11-5-4-1 to cover a 360-degree cycle. Figure 1 shows how the values of computed energies (heats of formation) vary with each of the four operations for ethyl vinyl ether. Each of the three dihedrals started at a value close to 180 degrees and may decrease or increase. To obtain Fig. 1, we make the H₁₃-C₃ bond length, used as reaction coordinate (value, about 4.8 nm), coincide with the 180 degrees ordinate axis.

One important observation is that the decreasing of the H₁₃-C₃ bond length caused concomitant variation of energy with the dihedral 5-4-1-2 that is a mirror image of the variation of energy with r.c. about the 180 degree ordinate axis, so that although different barriers were overcome, both operations result in about the same minimum energy of -123.65 kJ mol⁻¹ as found in Fig. 1 (the plot labeled r.c. mod). This is to say that care should be taken not to count the barrier caused by r.c and 5-4-1-2 independently, that is, twice. It looks obvious that the bigger of the two should be adopted.

Thus, the barriers arising from 4-1-2-3 and 11-5-4-1 are additive while those from the reaction coordinate (r.c.) and 5-4-1-2 are competing with each other. The basis of choice between these competing ones has been stated above. The above held regularly for ethyl vinyl ether and other derivatives in which hydrogen atoms on C5, (i.e., β-H's) were substituted.

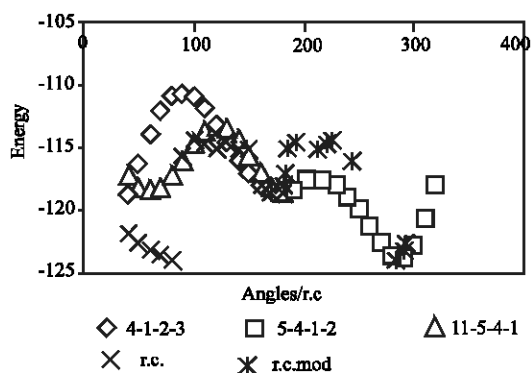


Fig.1: Showing variation of energy with different dihedral angles and H₁₃-C₃ bond length

Table 1: Comparison of normal direction with indication of effect of r.c. on dihedrals using i-prop10 as example

(a) Change of dihedral angles in proceeding from g.s through reac to t.s			
Dihedral	g.s.	reac	t.s.
4-1-2-3	-177.972	-8.906	57.750
5-4-1-2	-162.870	60.915	-17.145
11-5-4-1	177.932	46.390	103.869

Normal for 4-1-2-3 is increase: from -177.970 through -8.910 to 57.750

(b) Indication by changes caused by r.c.

H ₁₃ -C ₃ (nm ⁻¹)	4-1-2-3°	5-4-1-2°	11-5-4-1°	Heat of formation (kJ mol ⁻¹)
4.71	-177.97	-162.87	177.94	-34.470
4.6	-178.00	-161.22	170.37	-34.351
4.5	167.01	-158.07	173.62	-34.294
4.4	166.82	-155.76	166.94	-34.068
4.3	157.82	-147.50	174.20	-33.929
4.2	154.03	-142.16	172.48	-33.722
4.1	152.95	-139.22	161.70	-33.348
4.0	146.22	-128.03	177.18	-33.41

Indication for 4-1-2-3 is decrease: from -177.97 to 146.22 for early portion shown

Table 2: Rotational barriers (kJ mol⁻¹), to serve as corrections to Ea, computed for the various substrates using PM3 Hamiltonian

Vinyl ether	r.c.	4-1-2-3	5-4-1-2	11-5-4-1	rel. total
Ethyl	4.907	8.044	-	5.187	18.138
n-Propyl 11	3.777	9.257	-	5.300	18.334
n-Propyl 12	4.334	8.688	-	2.786	15.808
i-Butyl	4.120	8.278	-	2.631	15.029
2mevet 11	5.430	8.763	-	2.614	16.807
2mevet 12	4.526	7.910	-	-	12.436
2clev 11	7.601	7.295	-	4.258	19.154
2clev 12	5.459	7.663	-	2.685	15.807
i-Prop09	-	-	10.253	5.463	15.716
i-Prop10	-	-	9.717	5.446	15.163
t-Butyl	-	14.264	11.215	11.420	36.899

n-Propyl 11/12 is n-propyl with methyl in 11 or 12 position, i-Prop09/10 is isopropyl with methyl in 9 or 10 position, 2mevet 11/12 is 2-methoxyethyl with methoxy in 11 or 12 position, 2clev 11/12 is 2-chloroethyl with chlorine atom in 11 or 12 position, rel total is total relevant barrier. Barriers that are not relevant are indicated with dash (-)

If a Table 1 is compiled of how the decreasing of the H₁₃-C₃ bond length (i.e., the reaction coordinate) caused each of the dihedrals 4-1-2-3, 5-4-1-2 and 11-5-4-1 to vary (as we show partially for the special case of isopropyl vinyl ether n Table 1b), the dihedral angles (not the energies associated with them) are found to increase (clockwise rotation) or decrease (anticlockwise rotation). The direction indicated for these dihedrals by moving from the value in the stable reactant molecule (GS) through the reactant structure obtained from i.r.c. calculation, (reac), to the Transition State (TS) (Table 1a) for each of the relevant dihedrals may be the same as that caused by the decreasing of the reaction coordinate or may be different. Having chosen between the barriers caused by r.c. and 5-4-1-2, for the remaining two dihedrals, the effect of r.c. on value of the dihedral angle was used. Where it differed from the normal expectation traversing

Table 3: The computed activation parameters

Ether	ΔH_{app}	corr	ΔH_{corr}	E_a	ΔS_{app}	corr	ΔS_{corr}	logA	Expt. (E_a , LogA)	$10^4 k$ (calc, expt)
Ethyl	196.06	18.15	177.91	183.09	-24.24	-17.07	-41.31	11.39	(183.2, 11.43)	(1.10, 1.18)
n-Pr11	187.23	18.32	168.91	174.10	-22.21	-24.76	-46.97	11.09	(177.9, 11.12)	(3.13, 1.61)
n-Pr12	184.39	15.81	168.58	173.77	-21.80	-26.06	-47.86	11.05		(3.03, -)
i-But	177.15	15.02	162.13	167.32	-21.67	-32.96	-54.63	10.69	(174.5, 10.58)	(4.61, 0.894)
2m11	190.21	16.82	173.39	178.58	-27.98	-26.44	-54.42	10.70	(184.9, 11.14)	(0.536, 0.436)
2m12	190.66	12.42	178.24	183.43	-28.65	-14.14	-42.79	11.31		(0.857, -)
cl11	186.77	19.16	167.61	172.80	-26.97	-26.44	-53.41	10.76	(187.2, 11.49)	(1.88, 0.626)
cl12	185.77	15.81	169.96	175.15	-26.28	-27.69	-53.97	10.73		(1.11, -)
i-Pr09	188.36	15.73	172.63	177.82	-17.95	-6.90	-24.85	12.25	(178.0, 12.12)	(22.0, 15.8)
i-Pr10	188.36	15.14	173.22	178.41	-17.62	-6.90	-24.52	12.27		(20.6, -)
t-But	183.17	36.89	146.28	151.47	-5.55	-44.17	-49.72	10.95	(151.3, 10.86)	(179, 150)

reac, that parameter does not contribute any correction to either the apparent enthalpy or the apparent entropy of activation.

The apparent enthalpy and entropy values were obtained by subtracting the values of these parameters for the reactant from those of the transition state at the temperature of choice (623K), using FORCE calculation. In Table 2, we show for each substrate, the estimated rotational barrier components from each relevant dihedral angle. The sum of these, shown in the last column, served as corrections to the apparent enthalpies of activation. The corrected enthalpy values were converted into activation energies through the use of unimolecular reaction rate theory from which $E_a = \Delta H + RT$. The corrections to the apparent entropy changes were calculated using the principle, involving the use of symmetrical co-axial top molecules, discussed by Lewis and Randall^[7] and used by O'Neal and Benson^[8]. Other details can be found in our recent report on alkyl acetates^[3]. Table 3 shows the computed activation parameters for the compounds studied. For ease of comparison, the experimental values are also included in Table 3.

DISCUSSION

It is important to recognize that it is only the variation of the $H_{13}-C_3$ bond length (r.c.) and the rotations about the 1-2, 4-1 and 5-4 bonds that can contribute corrections to the apparent values of the Arrhenius parameters. The normal direction of rotation is that going through reac from the reactant Ground State (GS) to the Transition State(TS).

For ethyl vinyl ether and those derivatives obtained by substituting for hydrogen atoms on C5 (the βH 's), the relevant barriers come from the r.c. and rotations about the 1-2 and 5-4 bonds. For those derivatives obtained by substituting for hydrogen atoms on C4 (the αH 's), the relevant barriers come from the 4-1 (by which the r.c. contribution is voided) and the 1-2 and 5-4 bond rotations. In the case of isopropyl vinyl ether,

contribution from 1-2 bond rotation is also excluded (Table 2) because rotational direction imposed by variation of r.c. is contrary to that indicated by the normal direction of rotation traversing reac (Table 1).

CONCLUSIONS

- It is obvious that the rate constants deducible from the computed Arrhenius parameters are well in agreement with the experimental results.
- The purpose of this investigation is to explore the possibility of using the now available, quantum mechanical molecular orbital codes in a routine manner among chemists as well as specialists in other areas related to chemistry and so popularize quantum mechanics and its capabilities to provide quantitative data among others that are not theoretical chemists. The reasonable agreement obtained between the computed parameters, using PM3 in MOPAC and the experimental values suggests that our aim has been achieved with the substrates under consideration here.

REFERENCES

1. Bamkole, T.O., 1990. Kinetic studies using semi-empirical Self-consistent Field (SCF) Molecular Orbital (MO) method: Part I. A Modified Neglect of Diatomic Overlap (MNDO) study of the pyrolysis of ethyl vinyl ether. *J. Sci. I.R. Iran*, 1: 377-382.
2. Bamkole, T.O., 1990. Kinetic studies using semi-empirical Self-consistent Field (SCF) Molecular Orbital (MO) method: Part II. A Modified Neglect of Diatomic Overlap (MNDO) study of the pyrolysis of chloroethyl vinyl ethers. *J. Sci. I. R. Iran*, 1: 383-388.
3. Adejoro, I.A. and T.O. Bamkole, 2005. Semi-empirical quantum mechanical, Molecular Orbital (MO) method using MOPAC: Calculation of the Arrhenius parameters for the pyrolysis of some alkyl acetates. *J. Applied Sci.*, 5: 1559-1563.

4. Blades, A.T. and W.G. Murphy, 1952. The Pyrolysis of ethyl vinyl ether. *J. Am. Chem. Soc.*, 74: 1039.
5. Bamkole, T.O. and E.U. Emovon, 1968. The thermal decomposition of alkyl vinyl ethers. Part II. The inhibited decompositions of t-butyl, isopropyl and 2-chloroethyl vinyl ethers. *J. Chem. Soc.*, pp: 332- 333.
6. Bamkole, T.O., 1974. The Thermal decomposition of alkyl vinyl ethers. Part III. Maximally inhibited decompositions of n-propyl, isobutyl and 2-methoxyethyl vinyl ethers. *J. C. S. Perkin, II*: 801-802.
7. Lewis, G.N. and M. Randall. 1961. *Thermodynamics* (Pitzer, K.S. and L. Brewer Eds.), 2nd Edn., McGraw-Hill Book Company, ISI Edition, pp: 438-443.
8. O'Neal, H.E. and S.W. Benson, 1967. Method for estimating the Arrhenius A factors for four-and six-center unimolecular reactions. *J. Phys. Chem.*, 71: 2903-2921.