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

T. Bamkole

Department of Chemical Sciences, Ogun State University, P. M. B. 2002, Ago Iwoye, Ogun State, Nigeria

Abstract

Using a computer code called MOPAC, an acronym for a general Molecular Orbital Package (Quantum Chemistry Programme Exchange (QCPE) Programme No. 455), the geometries and heats of formation of the reactant, the products and the transition state were computed by the MNDO semi- empirical self consistent field (SCF) method for the pyrolysis of ethyl vinyl ether. «Force» calculation on the reactant and the transition state also gave the enthalpies and entropies at various selected temperatures. In the temperature range of the experimental pyrolytic study, the above calculations yielded the Arrhenius parameters of the reaction in excellent agreement with reported experimental results. This is significant in that it supplements the number of instances [1, 2, 3(a)- (g)], not exhaustively enumerated here, in which a semi- empirical SCF method has been successfully used to study the reaction mechanisms of many- atom molecules.

Introduction

Three states are of great interest in the study of the mechanism of an elementary reaction, namely the two minima corresponding to the reactants and products respectively and the intervening transition state. Efficient computer codes involving the use of some semiempirical SCF molecular orbital (MO) method have been developed during about the last two to three decades for determining the geometries and related thermodynamic properties of stable organic molecules and so the properties of the reactants and products can be easily calculated. These codes have been elaborated by many groups of theoretical chemists, prominent among which are *Dewar* [5, 6, 7, 8] and his collaborators. Starting with an approximation due to *Pople* [4] called INDO (Intermediate Neglect of Diatomic Overlap), *Dewar* and his group have successively developed improved methods called MINDO/1

[5] (Modified Intermediate Neglect of Diatomic Overlap), MINDO/2 [6], MINDO/3 [7] and now the best of all MNDO [8] (Modified Neglect of Diatomic Overlap). Codes using these methods are obtainable from Quantum Chemistry Programme Exchange (QCPE) of Indiana University's Chemistry Department and are capable of providing fairly accurate quantitative data in the areas, among others, of molecular geometries, thermodynamic properties and spectroscopic data like vibrational frequencies. The location of the transition state was until lately a major problem, but it became easier to tackle following the work of *Dewar* [2] and his team and the appearance of a general molecular orbital package from them called MOPAC (also obtainable from QCPE). MOPAC provides a means by which calculations, by the MINDO/3 method or the MNDO method, of vibrational spectra, thermodynamic properties, isotopic substitution effects and force constants are combined into a package. It is also suitable for studying chemical

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reactions as it also contains a transition state locating routine and two transition state optimising routines.

Though one is aware of the possibility of using semi-empirical methods to reproduce experimental kinetic results, for example, the *Benson* and *O'Neals's* [9] method of semi- empirical estimation of entropies of activation of reactions involving four- and six- membered cyclic transition states where one has to use some empirical rules to estimate the vibrational frequencies, particularly of the transition state, the use of MOPAC is more definitive and less open to scepticism as the geometries and vibrational frequencies of the transition state are calculated, not guessed. The above represents a rationale for trying to study again by means of MOPAC pyrolytic reactions which have been studied in detail experimentally starting with alkyl vinyl ethers.

Pyrolysis of alkyl vinyl ethers:

Reports of the study of the kinetics of the pyrolysis of alkyl vinyl ethers have appeared in the literature [10,

11, 12, 13(a) & (b), 14(a) & (b), 15]. On pyrolysis in the region of 623K upwards, alkyl vinyl ethers with at least a ß-H atom give an alkene and ethanal.

The mechanism proposed involved the attack of a ß-H atom of the alkyl portion on the electron-rich terminal carbo of the vinyl group, and the subsequent cleavage of the alkyl- oxygen bond. Thus there is involved a H-C bond- making and both C-H and C-O bond- breaking. Experimental evidence is that the C-O bond-breaking is significantly rate-determining [14 (b), 15] i. e. the slow- step. The problem is to see whether one can get MOPAC to predict, fairly accurately, the Arrhenius parameters and confirm the mechanistic details.

The Computation:

The MNDO option was used throughout. Using MOPAC, the geometries of the reactant 1 and products 2 and 3 were predicted to be as shown below with heats of formation (shown in Table I) in good agreement with experimental literature values [16].

1

2

3
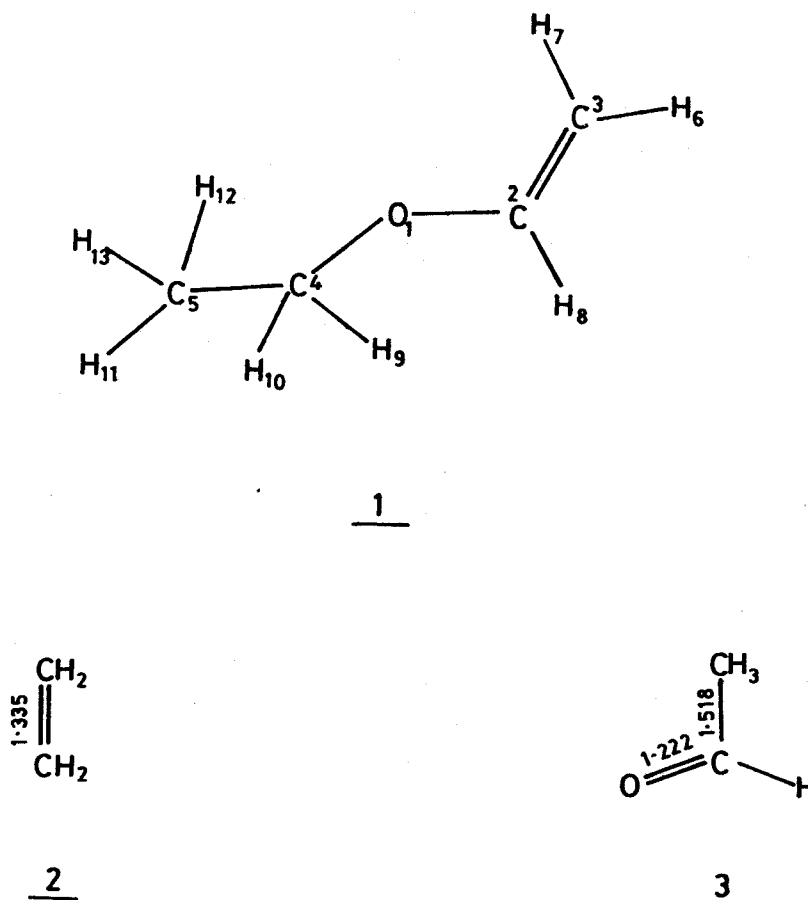
Path Studies were conducted on ethyl vinyl ether using H_{12}-C_3 as reaction co-ordinate by varying it from its value of 0.4892 nm in the stable reactant molecule to 0.110 nm, its approximate value in the stable product molecule. As reported elsewhere [17] for other similar work, instead of the energy passing smoothly through a maximum, it rose to an unexpectedly high value and at some unpredictable point, the geometry abruptly suffered a sudden large relaxation to a product- like structure with a concomitant drop in heat of formation to some value approximately the same as the sum for the expected products. The product- like structure was then optimised to give the result stated above with heat of formation in agreement with the sum of the individually determined values for ethene and ethanal. Path Studies of this type using different connectivities of the reactant were used to provide corresponding product geometries which were used in the SADDLE (the transition state locating routine) calculation.

The Calculation of the SADDLE point

The principle and procedure have been described previously [2]. Several different sets of connectivities were used in the geometry specification and SADDLE calculation carried out until one was found which tended to give convergent heats of formation and geometries for both the reactant and products. The *McIver- Kormonicki* [16, 1] gradient minimization procedure was then used to optimise the resulting approximate transition state geometry and determine its heat of formation.

«Force» Calculation

The basis of the procedure used to calculate vibrational frequencies and associated properties at various temperatures for the species of interest, had been described previously [3(b)]. The implementation procedure is described in the brochure supplied with MOPAC.

Results

The results are assembled in Tables I and II.

Table I: Heats of formation (ΔH^o_f for 1 and 3) corresponding to the optimised geometries:

(1)	ethyl vinyl ether	-137.23kJ mol^{-1}
(2)	transition state	176.11kJ mol^{-1}
(3)	the products (i.e. ethene and ethanal)	-112.46 kJ mol^{-1}

Table II: Calculated thermodynamic properties at relevant temperatures using «force» calculation:

	Temp/K	Enthalpy/ J mol^{-1}	Entropy/ J mol^{-1} K^{-1}
(1) ethyl vinyl ether	298	19614.783	339.981
	773	88562.626	471.069
(2) transition state	773	83743.099	429.073

Discussion

The optimised transition state geometry **4** given by the procedure above is depicted below:
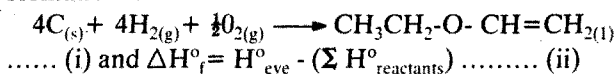

4
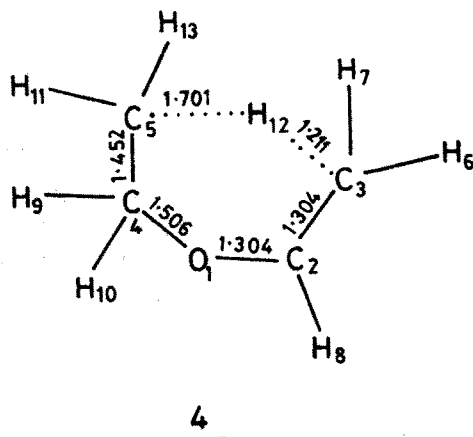
It is encouraging that this transition state satisfies the four criteria prescribed by *Kormonicki* and *McIver* [1].

From this report, it is obvious that the results are of the right trend qualitatively; viz

(1) that the mechanism involves a cyclic transition state in which a ß-H atom, attacking the terminal vinyl carbon atom, is part of a six- membered cyclic transition state.

(2) The above is corroborated by a negative entropy of activation determined experimentally [11] to be -42.67J mol^{-1} K^{-1} at 803K and computed by this calculation to be -42.00J mol^{-1} K^{-1} at 773K.

(3) It is seen that in the transition state, the alkyl-oxygen bond is being stretched, whereas the C_5-H_{12} bond is now a «long» bond and virtually broken while the C_3-H_{12} bond is almost fully formed showing that the bond breaking (alkyl-oxygen) rather than the C_3-H_{12} bond- making is the slow rate- determining step as concluded on experimental grounds

We may also evaluate the results quantitatively. For ethyl vinyl ether, the reaction used to define the heat of formation is

$$4C_{(s)} + 4H_{2(g)} + \tfrac{1}{2}O_{2(g)} \longrightarrow CH_3CH_2\text{-}O\text{-} CH=CH_{2(l)}$$

...... (i) and $\Delta H^\circ_f = H^\circ_{eve} - (\Sigma\, H^\circ_{reactants})$ .... (ii)

where H°_{eve} is the enthalpy of ethyl vinyl ether (abbreviated «eve» and used as subscript) in the liquid state under a pressure of 1.013×10^5 Nm^{-2} and 298K.

According to this standard state, the enthalpy of the reactants is zero.

Thus $\Delta H^\circ_f = H^\circ_{ve}$ .... (iii)

This can be regarded as a scale of enthalpies based on 298K as standard state.

However for the statistical calculation of enthalpies, expressions such as

$$C = a + bT + cT^{-2} .... (iv)$$

are generally used to define analytically the heat capacity, C, where a, b and c are constants and T is the Kelvin temperature. This can be taken as a scale based on the absolute zero of temperature as reference point or better still as the «ideals gas standard state».

On this latter scale, the enthalpy of the formation reaction at temperature T is

$$\Delta H^\circ_f = I + \int \Delta C_p\, dT$$
$$= I + \int \{(a' + b'T + c'T^{-2}) - \Sigma\,(a + bT + cT^{-2})\}\, dt$$
$$= I + \int (a' + b'T + c'T^{-2})dT - \int \Sigma(a + bT + cT^{-2})dT$$
...... (v)

where a', b' and c' refer to the product, i. e. ethyl vinyl ether (eve) and a, b and c refer to the reactants.

Heat capacity data are obtainable from various sources, for example *K. S. Pitzer* and *L. Brewer* [18], gave data valid, of course, from 298K to 2000K, from which the third term on the right hand side (RHS) of equation (V) is calculated at 298K to be 69.65kJ.

Thus for 298K

$$\Delta H^\circ_f = 137.23 = \Delta H^*_{eve} - 69.65$$

where the first two terms on the RHS have been replaced by ΔH^*_{eve} which is a constant characteristic of eve at 298K on the ideal gas scale denoted by the asterick (*).

Thus $\Delta H^*_{eve} = -67.58kJ = H^*_{eve(g.298)}$

This enthalpy value has taken care of the conversion of the liquid ether at a pressure of 1.013×10^5Nm^{-2} and 298K to gaseous ether at 298K under such reduced pressure that it now behaves as an ideal gas, such as is approximated under conditions of experimental pyrolysis.

For temperatures T above 298K,

$$(\Delta H^*_f)_T = H^*_{298} + \Delta H^T_{298}$$

where ΔH^T_{298} is the enthalpy change in heating the ether behaving as a perfect gas from 298K to TK, which value is obtained by «force» calculation between 298K and TK.

The temperature T should be in the range in which the pyrolysis occurs readily and measurably. In the case of ethyl vinyl ether, a temperature of 773K is chosen which is within the experimental range for the study by *Blades* and *Murphy* [11] with which comparison is made

in Table III.

Thus using the data in Table II

$(\Delta H^*{}_f)_{773} = -67.58 + (88.56 - 19.61)$

$= 1.37 kJ \, mol^{-1}$

Therefore, the enthalpy of activation $(\Delta H^{\pm})$ at 773K is given by the difference between the heat of formation of the transition state and the enthalpy of formation of the unactivated molecules at that temperature.

i.e. $(\Delta H^{\pm})_{773} = 176.10 - 1.37 = 174.73 kJ \, mol^{-1}$

Also, from Table II, the entropy of activation $\Delta S^{\pm}$ at 773K is $-42.00 J \, mol^{-1} \, K^{-1}$.

But by the thermodynamic treatment of the transition state theory for a unimolecular process, the activation energy E_A and the entopy of activition $\Delta S^{\pm}$ are given by the relationships:

$E_A = \Delta H^{\pm} + RT$ and

$A = (ekT/h) \exp (\Delta S^{\pm}/R)$

Thus $E_A = 174.73 + 6.43 kJ \, mol^{-1} = 181.16 kJ \, mol^{-1}$

and $A = 2.80 \times 10^{11}$ or $\log A = 11.45$

considered here do have internal rotations. The agreement is probably due to fortuitous compensation arising from similar rotations occurring in the reactant as well as in the transition state. As observed earlier, in the transition state the H_{12}-C_5 bond is virtually broken already while the C_3-H_{12} bond is also virtually formed. Thus the H_{12} has virtually transferred from C_5 to C_3 while the C_4-O_1 bond is in the process of breaking. Thus rotations present in the reactant are not very different from those in the transition state.

Table III: Comparison of results

Parameter compared	Experimental	Calculated	Transmission Coefficient
$E_A/kJ \, mol^{-1}$	183.22	181.16	
A/s^{-1}	2.70×10^{11}	2.80×10^{11}	
k_{723}/s^{-1}	1.565×10^{-2}	2.30×10^{-2}	0.68
k_{773}/s^{-1}	1.124×10^{-1}	1.614×10^{-1}	0.70
k_{823}/s^{-1}	6.351×10^{-1}	8.943×10^{-1}	0.71

Table III shows a comparison of the experimental and calculated results.

This looks a remarkable success for the study via a semi- empirial MNDO SCF method of the reaction of a many- atom molecule. This is surprising for two reasons, First, the calculation has not taken into account the possibility of electron correlation, and the inclusion of configuration interaction in the calculation did not provide a self- consistent field result. Secondly the «force» calculation used here for the thermodynamic calculation is limited to molecules that do not have internal rotations and the species being

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