

KINETIC STUDIES USING SEMI-EMPIRICAL SELF-CONSISTENT FIELD (SCF) MOLECULAR ORBITAL (MO) METHOD: PART II [1] A MODIFIED NEGLECT OF DIATOMIC OVERLAP (MNDO) STUDY OF THE PYROLYSES OF CHLOROETHYL VINYL ETHERS

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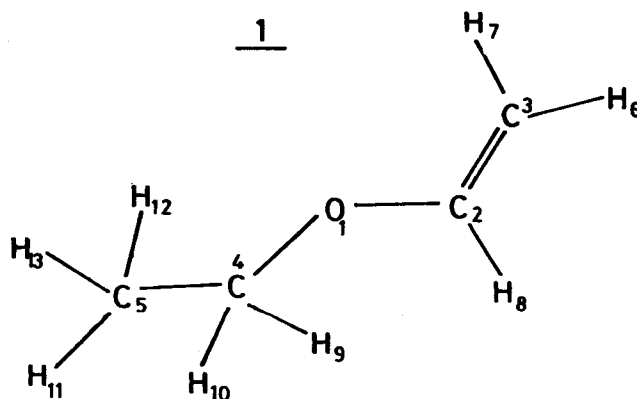
Abstract

The effect of monochloro and dichloro substitution into the ethyl portion on the pyrolysis of ethyl vinyl ether has been studied. This involved four possible mono-substituted derivatives and six disubstituted derivatives. For the monochloro derivatives, β -chloro substitution enhanced the rate constant while α -chloro substitution depressed it noticeably. For the dichloro derivatives, substitution of both chlorine atoms on the same carbon atom, whether α or β hardly made any difference, while for substitution on different carbon atoms, substrate resulting in *trans*-dichloroethene is facilitated relative to that resulting in the *cis* product. These results are interpreted in terms of the effect of the substituent(s) on the electronic charge density distributions over the key atoms in transition state geometries calculated.

Introduction

In Part 1 [1] of this series, the Arrhenius parameters for the pyrolysis of ethyl vinyl ether were computed using MOPAC. In the present work, the effect of

chloro-substitution into the ethyl portion of the substrate is reported. The structure for ethyl vinyl ether (1) is shown below:



Key Words: Pyrolytic Studies Semi-Empirical MO Method

Four monochloro derivatives are possible depending on whether H₉, H₁₀, H₁₁ or H₁₃ is replaced. For the dichloro derivatives, six derivatives are possible, two in which the two chlorine atoms are substituted on the same carbon atom and four in which each chlorine atom is substituted on different carbon atoms. These ten possible derivatives are given number designations as in Table I where the H atoms replaced are indicated in brackets after the IUPAC names. If **4a** produces *cis* dichloroethene, **4b** will produce *trans* dichloroethene. Similarly **5a** will produce the *trans* product while **5b** will produce the *cis* product.

Normal chemical practice would not recognise any difference between **1a** and **1b** or between **2a** and **2b**. Similarly, substrates containing one chlorine atom on each carbon atom will not be differentiable except in so far as they may result in *cis* or *trans* products. Thus, **4a** and **5b** yielding the *cis* product will not be distinguishable nor will **4b** and **5a** yielding the *trans* product be distinguishable. Detailed calculations were done on each compound ignoring these possible equivalences in order to see the extent to which these assumptions are correct as well as to provide comparison with previous experimental results on 2-chloroethyl vinyl ether.

Experimental Section

The computational procedure as previously described in detail in Part 1 of this series was repeated for each derivative. Only in these cases, detailed path studies were avoided. Trial transition state geometries were guessed by taking the transition state geometry for

ethyl vinyl ether reported in Part 1 and substituting chlorine for the appropriate hydrogen atom(s). In some cases, optimised transition state geometries were readily obtained while in others, a few trial guesses were necessary. Overall this procedure is less expensive than the combination of detailed path studies with SADDLE Calculation used previously to locate the approximate saddle point.

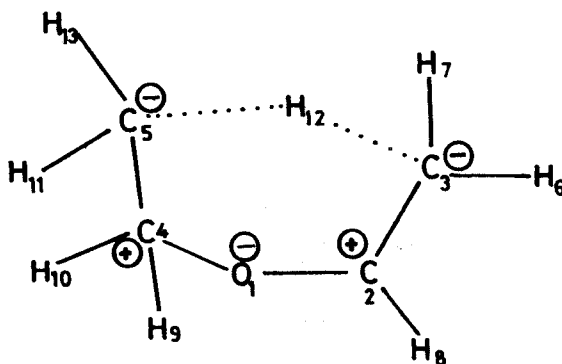
Results

The results are assembled in Tables II, III and IV. Table II shows the calculated enthalpies of formation of the chloroethyl vinyl ethers and their optimised transition states (T. S.). Table III contains the thermodynamic properties of these same species at the relevant temperatures obtained by «force» calculation. Table IV contains the resulting calculated Arrhenius parameters for the pyrolyses of the chloroethyl vinyl ethers and the calculated rate constants at 698K. Where experimental results are available, they are included for comparison.

It was also ascertained in each case that the expected products were obtained from the calculated transition state geometries by merely decreasing the H₁₂-C₃ bond distance a little bit from the optimised transition state values and minimising the energy. Table V shows the heats of formation of products obtained in this manner from the transition state geometries.

Discussion

From Table III, it can be readily seen that the entropy of activation for each substrate at 698K is



negative as expected for a cyclic transition state. The temperature 698K was chosen because it was the uppermost region in which the experimental pyrolysis of 2-chloroethyl vinyl ether had been studied previously [2]. Using the heat capacity data from K. S. Pitzer and L. Brewer [3] along with the data assembled in Tables II and III, the computational procedure previously outlined [1] for obtaining the Arrhenius parameters gave the data in Table IV.

It is found that for each saddle point, O₁, C₃ and C₅ are all negatively charged while C₂ and C₄ are positively charged as shown in structure 6.

It is easy to conjecture that the process of reaction involved the following four steps which have advanced to a considerable extent in the formation of the transition state

- (i) the transfer of H₁₂ from C₅ to C₃
- (ii) the transfer of electronic charge on O₁ into the O₁-C₂ bond to give a carbonyl group
- (iii) the transfer of electronic charge from C₅ into the C₅-C₄ bond to give an alkene, and
- (iv) the complete separation of O₁ and C₄.

Thus discussion of results would centre around the effect of the substituent(s) in the alkyl portion on some or all of these steps.

(a) Effect of chloro substitution

(i) **On C₄:** This would cause C₄ to be more positively charged and be more avid to share the C-O bond pair electron, thus reducing the electron density on O₁. A reduced electron density on O₁ would retard O₁-C₂ double bond development. Thus chloro substitution on C₄ would retard the formation of the transition state relative to the unsubstituted derivative. This effect will increase with disubstitution. Note however that increase in the positive charge on C₄ will indirectly facilitate the C₅-C₄ double bond development and would, by that token, facilitate the reaction somewhat. Therefore, there are two opposing effects but the former most likely predominates.

(ii) **On C₅:** Chloro substitution will make H₁₂ more acidic and ready to transfer to C₃ as a proton leaving C₅ relatively more negatively charged. This would directly facilitate C₅-C₄ double bond development. There is no obvious effect on the O₁-C₂ double bond development. Expected overall effect is rate enhancement relative to the unsubstituted derivative.

(iii) **One on each carbon atom:** There are two opposing effects and the overall effect is not obvious. However, exceptional facilitation of the transition state may be expected in the cases where the chlorine atoms on each carbon atom are as far as possible from

each other to reduce chlorine-chlorine repulsions. This would mean that formation of transition states leading to *trans* products will be facilitated relative to those leading to *cis* products.

The relative rates recorded in Table IV bear out this analysis. Thus both **2a** and **2b** have larger rate constants than the unsubstituted derivative **1** which in turn has a larger value than both **1a** and **1b**. Similarly, both substrates (**4b** and **5b**) yielding the *trans* product are faster than their analogous **4a** and **5a** yielding the *cis* product. However, **3b** expected to be faster is just about as fast as **1** and **3a** has about the same magnitude. It is seen that the activation energy for this compound (**3b**) is quite favourable but the entropy of activation is very unfavourable. This very unfavourable entropy of activation arises from the fact that the two chlorine atoms both bearing negative charges are bonded to C₅ which is also negatively charged. The inter atomic coulombic repulsions thus arising would cause considerable destabilisation of the transition state, and thus lower the rate of reaction than expected.

Finally the only other result needing some comment is the experimental result obtained for 2-chloroethyl vinyl ether [2] compared with the result of calculation reported here for **2a** or **2b**.

The experimental value is between the calculated value for **1a** or **1b** and **2a** or **2b**. It is in fact much closer to the value for the former than the latter for which it is supposed to be. The experimental result was obtained on a commercial product purified by distillation only and subjected to gas-liquid chromatography (glc) to ascertain purity. One wonders whether the commercial 2-chloroethyl vinyl ether could have been converted into a mainly 1-chloro derivative during the pyrolytic process by a process of dehydrochlorination followed by rehydrochlorination with a reversed orientation! The experimental result would suggest that what was pyrolysed was a mixture of about 85% 1-chloro-ethyl vinyl ether with 15% 2-chloro-ethyl vinyl ether.

The Pyrolytic Products:

From Table V, it is seen that the products from the compounds **1a**, **1b**, **2a** and **2b** have approximately the same ΔH° value which is consistent with the fact that the products expected from them are the same, namely ethanal and chloroethene. The average value of ΔH° is -157.23kJ.

Using the MNDO calculated value of -176.86kJ mol⁻¹ for ethanal obtained in this work, the value for chloroethene is 19.63 kJ mol⁻¹. Similarly, the estimated

ΔH_f° values for the other chloroethenes recorded in Table V are obtained. The literature values [5] for these chloroethenes are inserted in brackets after each estimated value. The differences are probably due to the heats of mixing of the products (i. e., the ethanal and the chloroethene or dichloroethenes) which are each polar and so cannot be expected to form completely ideal mixtures. These give respectively the estimates of

the heats of mixing given in Table VI. The boiling points (b. p) reported therein are obtainable from the literature [6]. These estimates do not look unreasonable for the mixing of two polar organic gases (as for products from **1a**, **1b**, **2a** and **2b**) or the solution of a polar organic gas, ethanal in a polar organic liquid (as for the other cases). They are in the range expected for dipolar interactions, for example H-bonding.

Table I: Relating names of compounds to their numerical designations

| Number | Name of Compound |
|-------------------------|---|
| 1 | Ethyl vinyl ether |
| 2 | 2- chloroethyl vinyl ether |
| 1a or 1b | 1- chloroethyl vinyl ether (9) or (10) |
| 2a or 2b | 2- chloroethyl vinyl ether (11) or (13) |
| 3a | 1,1- dichloroethyl vinyl ether (9, 10) |
| 3b | 2,2- dichloroethyl vinyl ether (11, 13) |
| 4a, 4b, 5a or 5b | 1,2-dichloroethyl vinyl ether (9, 11), (9, 13), (10, 11) or (10, 13) |

Table II: Enthalpies of formation of chloroethyl vinyl ethers and their transition states (T. S.)

| | Compound | H_f° for ether/ kJ mol ⁻¹ | ΔH_f for T.S/ kJ mol ⁻¹ |
|-----|-----------|--|---|
| 1. | 1a | -176.81 | 142.27 |
| 2. | 1b | -176.85 | 144.21 |
| 3. | 2a | -168.11 | 130.68 |
| 4. | 2b | -171.51 | 128.01 |
| 5. | 3a | -187.67 | 135.61 |
| 6. | 3b | -181.05 | 100.35 |
| 7. | 4a | -194.70 | 112.31 |
| 8. | 4b | -199.57 | 96.27 |
| 9. | 5a | -203.99 | 104.01 |
| 10. | 5b | -199.57 | 113.39 |

Table III: Thermodynamic Properties of the Reactants (evet) and the Transition States (T. S.) at relevant temperatures

| | Compound | T/K | Enthalpy/ J mol ⁻¹ | Entropy/ J mol ⁻¹ K ⁻¹ | Entropy of activation/ J mol ⁻¹ K ⁻¹ |
|-----|----------|-----|----------------------------------|---|--|
| 1. | 1a | 298 | 21430.67 | 366.32 | |
| | | 698 | 82163.08 | 490.52 | |
| 2. | 1a T.S | 698 | 77974.04 | 452.07 | -38.45 |
| | | 298 | 21419.50 | 365.52 | |
| 3. | 1b | 698 | 82151.10 | 489.72 | |
| | | 298 | 21419.50 | 365.52 | |
| 4. | 1b T.S | 698 | 78014.84 | 451.21 | -38.51 |
| | | 298 | 21444.15 | 377.17 | |
| 5. | 2a | 698 | 81053.13 | 498.84 | |
| | | 298 | 21444.15 | 377.17 | |
| 6. | 2a T.S | 698 | 77010.03 | 451.66 | -47.18 |
| | | 298 | 21739.72 | 373.14 | |
| 7. | 2b | 698 | 81454.30 | 495.07 | |
| | | 298 | 21739.72 | 373.14 | |
| 8. | 2b T.S | 698 | 77014.92 | 451.95 | -43.12 |
| | | 298 | 21808.06 | 387.09 | |
| 9. | 3a | 298 | 21808.06 | 387.09 | |
| | | 698 | 84549.62 | 515.83 | |
| 10. | 3a T.S | 698 | 86905.13 | 492.75 | -23.08 |
| | | 298 | 24048.18 | 399.26 | |
| 11. | 3b | 698 | 88961.17 | 532.37 | |
| | | 298 | 24048.18 | 399.26 | |
| 12. | 3b T.S | 698 | 84949.33 | 444.77 | -87.60 |
| | | 298 | 23633.13 | 399.87 | |
| 13. | 4a | 698 | 88700.60 | 533.24 | |
| | | 298 | 23633.13 | 399.87 | |
| 14. | 4a T.S | 698 | 84894.37 | 491.87 | -41.37 |
| | | 298 | 23717.15 | 398.30 | |
| 15. | 4b | 698 | 88878.04 | 531.90 | |
| | | 298 | 23717.15 | 398.30 | |
| 16. | 4b T.S | 698 | 84902.07 | 491.39 | -40.51 |
| | | 298 | 23698.68 | 399.09 | |
| 17. | 5a | 698 | 88876.01 | 532.72 | |
| | | 298 | 23698.68 | 399.09 | |
| 18. | 5a T.S | 698 | 85054.62 | 491.43 | -41.29 |
| | | 298 | 23762.56 | 406.10 | |
| 19. | 5b | 698 | 88925.66 | 539.70 | |
| | | 298 | 23762.56 | 406.10 | |
| 20. | 5b T.S | 698 | 85277.82 | 497.15 | -42.55 |
| | | 298 | 23762.56 | 406.10 | |

Table IV: Calculated Arrhenius Parameters and rate constants at 698K

| | Compound | Activation Energy E _A /kJ mol ⁻¹ | log A | 10 ³ k ₆₉₈ / s ⁻¹ |
|-----|------------------|---|-------|---|
| 1. | 1a | 192.57 | 11.59 | 1.52 |
| 2. | 1b | 194.58 | 11.59 | 1.07 |
| 3. | 2a | 173.42 | 11.13 | 14.26 |
| 4. | 2b | 174.06 | 11.35 | 21.18 |
| 5. | 3a | 192.77 | 12.39 | 9.25 |
| 6. | 3b | 148.72 | 9.02 | 7.80 |
| 7. | 4a | 174.18 | 11.44 | 25.54 |
| 8. | 4b | 162.92 | 11.48 | 194.80 |
| 9. | 5a | 175.06 | 11.44 | 21.95 |
| 10. | 5b | 180.04 | 11.38 | 8.10 |
| 11. | 1 | 181.16 | 11.45 | 7.85 |
| 12. | 1 (exptal, [4]) | 183.22 | 11.43 | 5.27 |
| | 2* (exptal, [2]) | 187.20 | 11.49 | 3.04 |

* 2 is used to designate 2- chloroethyl vinyl ether ignoring whether it is H₁₁ or H₁₃ that is replaced.

Table V: Heats of formation (ΔH_f°) of products obtained from the transition states of designated compounds

| Compound | ΔH_f° of products/kJ | Expected alkene | Estimated ΔH_f° of the alkene/ kJ mol ⁻¹ |
|----------|-----------------------------------|--------------------------|---|
| 1a | -157.34 | chloroethene | 19.63 (35.14) |
| 1b | -157.34 | chloroethene | |
| 2a | -157.15 | chloroethene | |
| 2b | -157.08 | chloroethene | |
| 3a | -178.47 | 1,1-dichloro ethene | -1.39 (-25.10) |
| 3b | -178.25 | 1,1- dichloro ethene | |
| 4a | -189.93 | cis-dichloro ethene | -13.34 (-28.03) |
| 4b | -192.71 | trans-dichloro ethene | -15.81 (-25.52) |
| 5a | -192.62 | trans-dichloro ethene | |
| 5b | -190.46 | cis-dichloro ethene | |

Table VI: Estimates of heats of mixing of the product chloroalkene indicated with ethanal (b. p. 294K)

| | Product alkene | b.p | Mixture type at 298K | ΔH mixing/ kJ mol ⁻¹ |
|----|-----------------------|-------|-------------------------|--|
| 1. | chloroethene | 259.6 | Gas/Gas | -15.51 |
| 2. | 1,1- dichloroethene | 310.0 | Gas/Liquid | 23.60 |
| 3. | trans- dichloroethene | 320.5 | Gas/Liquid | 9.71 |
| 4. | cis-dichloroethene | 333.3 | Gas/Liquid | 14.69 |

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