A Theoretical Analysis of the Unimolecular Decomposition
of Ethanol: Internal Energy Effects and Pressure Dependence

Harraed V. Linnert* and José M. Riveros
Instituto de Química, Universidade de São Paulo
Caixa Postal 20780, 01498 São Paulo, SP, Brasil
Received: February 18, 1991; April 30, 1991

A decomposição unimolecular do etanol foi modelada de acordo com a teoria
RRKM com o objetivo de comparar os dados obtidos a partir de excitação multifotoni-
cal vibracional e pirólise convencional. Três caminhos principais foram considerados: (1)
elimição de H₂O, (2) ruptura da ligação C-C, e (3) ruptura da ligação C-O. Os cál-
culos de k(E*) indicam claramente que o canal (1), de menor energia de ativação, é o
dominante para energias de excitação até 85 kcal/mol. O comportamento previsto
para k_{uni} em função da pressão revela que o processo de ruptura da ligação C-C deve
ser o canal principal de reação, a pressões acima de 50 Torr, gerando um mecanismo
radical.

The unimolecular decomposition of ethanol has been modelled by RRKM theory to
reconcile the data from infrared multiphoton excitation and conventional pyrolysis.
Three main channels were considered: (1) H₂O elimination, (2) C-C bond scission, and
(3) C-O bond scission. The calculation of k(E*) clearly predicts that the lowest activa-
tion energy channel (1) will be dominant up to excitation energies of 85 kcal/mol. The
calculated behavior of k_{uni} as a function of pressure reveals that the C-C bond fission
process leading to a free radical mechanism is expected to be the main channel at pres-
ures above 50 Torr.

**Key words:** unimolecular processes, ethanol, RRKM theory.

**Introduction**

The use of methanol and ethanol in the neat or in mix-
tures as fuels has generated considerable interest in the
understanding of their primary dissociation processes and
the subsequent gaseous chemistry. The knowledge of the
elementary reactions is essential in assessing the efficiency
of the combustion processes and the environmental ef-
fects, both of which are presently a matter of controversy.
While many reactions relevant to the combustion of meth-
anol have been described, several questions remain at
large for the case of ethanol.

The pyrolysis of neat C₂H₅OH at 600°C and 185 Torr
has been shown to yield mainly CH₄, CO, CH₃CHO and
H₂ as the final products through a free radical process.
Non-kinetic experiments carried out at similar tempera-
tures suggest a number of likely mechanisms to account
for these products. An alternative view of the primary
processes in ethanol has been provided by the decomposi-
tion induced by vibrational multiphoton excitation with
pulsed HF and CO₂ lasers. The final product distribution
displays a sensitive dependence on gas pressure (in the
range of 100 mTorr to 40 Torr) and on laser energies:
(a) ethylene is clearly the most abundant product at low
pressures; (b) methane, carbon monoxide and hydrogen
decome increasingly important at the higher pressures and
laser energies. Time resolved CARS experiments on nas-
cent C₂H₅ have unequivocally established ethylene as the
product of a unimolecular reaction.

$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{n\text{hv}} \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (1)$$

Recent experiments claim that under collisionless condi-
tions IR laser MPD yields processes (1), (2) and (3) with a
branching ratio of 0.68, 0.26 and 0.05 respectively.

$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{n\text{hv}} \text{CH}_3 + \text{CH}_3\text{OH} \quad (2)$$

$$\xrightarrow{} \text{CH}_3\text{CHO} + \text{H}_2 \quad (3)$$

Process (2) has been confirmed from laser experiments
carried out in the presence of chlorine and iodine as ra-
dical scavengers, whereas reaction (3) has been inferred
from studies with labelled ethanol. Other possible disso-
ciation channels, (4) through (6), have been considered
in the laser driven combustion of ethanol.

$$\text{C}_2\text{H}_5\text{OH} \xrightarrow{} \text{C}_2\text{H}_4\text{OH} + \text{H}^+ \quad (4)$$

$$\xrightarrow{} \text{C}_2\text{H}_4 + \text{OH} \quad (5)$$

$$\xrightarrow{} \text{CH}_4 + \text{CH}_3\text{O} \quad (6)$$

The diversity encountered between the pyrolysis and
the laser driven reactions in ethanol, and the need to re-
concile the existing data has prompted us to survey the
behavior of the unimolecular pathways within the frame-
work of RRKM theory. An earlier publication made use
of RRKM calculations to predict the high pressure rate
expressions for the decomposition of chemically activated
alcohols. A different approach to this problem has been
reported by Yamabe et al. based on ab initio MO calcula-
tions of the transition state topography for processes (1)
and (2).

**Model for RRKM Calculations**

The pyrolysis study of ethanol yielded apparent activa-
tion energies and A factors from (i) the first order dis-
appearance of C₂H₅OH, (ii) the total pressure increase.
The fact that these two methods result in different values clearly reflects the complexity of these reactions. An estimate for these two parameters for reaction (2) was proposed on the basis of single-pulse shock-tube experiments of higher alcohols. However, the absence of reliable thermal data implies that the modelling of the possible unimolecular pathways requires suitable estimates of the activation energies and transition state geometries.

For the bond-fission processes, activation energies were chosen to be equal to the corresponding bond energies, i.e. $E_b = 82$ kcal/mol, $E_b = 90$ kcal/mol and $E_b = 85$ to 92 kcal/mol. The value for $E_b$ was estimated to be in the range of 65 to 70 kcal/mol by taking into account: (i) the empirical relationships that correlates activation energies for HX elimination in alkyl halides with heterolytic bond dissociation energies, and (ii) the activation energy for H$_2$O elimination in n-butanol. An estimate for $E_b$ and $E_b$ is considerably more difficult because no similar systems are available in the literature that can be used as models. Yet, the fact that the theoretical calculations predict $E_b$ to be 40 kcal/mole higher than $E_b$ suggests that processes (3) and (6) may not be significant in the overall kinetics. Thus, no attempt was made to model these two reactions.

The vibrational frequencies for the transition states of the H$_2$O elimination (1), the C-C bond rupture (2) and the C-O bond fission (5) were derived from the parent ethanol molecule. The overall procedure was similar to that used in the case of ethyl chloride. Frequencies were grouped to simplify the calculation of the sum of states according to the well-established procedure in RRKM calculations. Finally, several possibilities were considered for the number of free rotations in the transition state, $r^+$. The parameters used to calculate k(E*) for the three processes under consideration are shown in Table 1. For all cases, the transition state has been assumed to have only one free rotation. The number of vibrational-rotational states and the density of states was calculated according to the method of Whitten and Rabinovitch. The internal vibrational temperature was estimated to be 1500 K corresponding to the laser driven process. This amounts to the absorption of 22 photons and represents the threshold value compatible with the lowest activation energy for ethanol.

Results

A) Energy dependence of k(E*) for the Decomposition of Energized Ethanol.

The rate constants for reactions (1), (2) and (5), of energized ethanol, k(E*), were calculated as a function of energy according to the known procedure outlined by Holbrook and Robinson:

$$k(E^*) = \frac{L^{*\rightarrow}Q^+}{Q} \left\{ \sum P(E_{i}^+)/hN(E^*) \right\}$$

where $L^{*\rightarrow}$ is the reaction path degeneracy:

$$Q, P(E_{i}^+)$$

rotational partition function of the transition state and the reagent molecule:

$$E^+ - E_o = \sum_{i} P(E_{i}^+) = \text{number of vibrational rotational states}$$

of the activated complex with internal energies above the critical energy for reaction $E_o$.

$$N(E^+) = \text{density of vibrational rotational states}$$

of the energized molecule.

The parameters used to calculate k(E*) for the three processes under consideration are shown in Table 1. For all cases, the transition state has been assumed to have only one free rotation. The number of vibrational-rotational states and the density of states was calculated according to the method of Whitten and Rabinovitch. The internal vibrational temperature was estimated to be 1500 K corresponding to the laser driven process. This amounts to the absorption of 22 photons and represents the threshold value compatible with the lowest activation energy for ethanol.

Figure 1 shows the variation of k(E*) as a function of E*.

B) The Variation of kuni with Pressure.

Since the pyrolysis experiments are carried out at pressures where the experimentally measured rate constant corresponds to kuni in the RRKM reaction scheme, the second part of our work involved the computation of kuni for the different channels. This rate constant is also

<table>
<thead>
<tr>
<th>Reactant molecule(a)</th>
<th>H$_2$O elimination</th>
<th>Transition state(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_4$OH</td>
<td>3106, 2946 (3)</td>
<td>3676, 2954 (5)</td>
</tr>
<tr>
<td></td>
<td>2949, 2943</td>
<td>1490, 1246 (2)</td>
</tr>
<tr>
<td></td>
<td>2901, 1490</td>
<td>801, 726 (2)</td>
</tr>
<tr>
<td></td>
<td>1452 (2), 1451</td>
<td>1000 (5), 500 (2)</td>
</tr>
<tr>
<td></td>
<td>1394, 1251</td>
<td>250 (3), 200</td>
</tr>
<tr>
<td></td>
<td>1241, 1089, 1062</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1033, 885, 801</td>
<td></td>
</tr>
<tr>
<td></td>
<td>419, 234, 201</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$E_o$</th>
<th>64.3</th>
<th>77.1</th>
<th>80.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E^{+\rightarrow}$</td>
<td>30.7</td>
<td>17.9</td>
<td>14.8</td>
</tr>
<tr>
<td>$I/10^{-40}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>g cm$^2$</td>
<td>26.2</td>
<td>182.6</td>
<td>25.6</td>
</tr>
<tr>
<td>log A/s$^{-1}$</td>
<td>12.3</td>
<td>15.2</td>
<td>15.0</td>
</tr>
<tr>
<td>r$^+$</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>L$^+$</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta S^{\text{f,iso}}$</td>
<td>$-9.02$</td>
<td>5.57</td>
<td>4.67</td>
</tr>
</tbody>
</table>

Critical energy, $E_o$, and energy for the activated complex, $E^{+\rightarrow}$, in kcal mol$^{-1}$.

Entropy of activation, $\Delta S^{\text{f,iso}}$, in cal K$^{-1}$ mol$^{-1}$, $Z = 1.55 \times 10^7$ Torr$^{-1}$ s$^{-1}$, $\lambda = 1$.

(a) From.

(b) Vibrational frequencies are based on the corresponding parent molecule and final product molecules or characteristics groups, so that desired A-factors is obtained. Transition state was viewed as the result of a diatomic dissociating into atoms with the masses of the fragments.

Several models for the transition states were tested in this case as outlined in Table 2.

**Model for H₂O Elimination.**

The reaction is assumed to proceed through a transition state of the type

\[
\text{C₂H₅OH} \rightarrow \begin{array}{c}
\text{H} - \text{C} - \text{C} - \text{H} \\
\text{H} \cdot \text{O} - \text{H}
\end{array} 
\rightarrow \text{C₂H₄} + \text{H₂O}
\]

for which \( L^+ \) is 2, 1 = 1⁺, and \( Q_v^+/Q_v \) was taken to be unity in accord with a tight activated complex. It was assumed, in a first calculation, that there were no active rotations, and the vibrational contribution to the A-factor was \( \approx 10^{13} \) s⁻¹ at the temperature of 1500 K.

**Models for C-C and C-O Rupture.**

Three models, for the C-C rupture, illustrate the behavior of the variation of \( k_{uni} \) with pressure, the A-factor and the number of internal rotation in the transition states.

Model I was viewed as the result of a diatomic transition state dissociating into atoms with the masses of the fragments. One internal rotation was considered for this transition state while six internal rotations are assumed for model II.

Model III correspond to the geometry of the free radicals obtained by the C-C bond rupture at the CH₄ radical, and \( \text{CH}_3\text{OH} \) based on the \( \text{CH}_3\text{OH} \) molecule inclusion of six internal rotations for the transition state.

The model for C-O rupture corresponds approximately to a symmetric top \( \text{CH}_₃ \) radical and a diatomic OH radical. One internal rotation is assumed for the transition state.

The parameters for \( H₂O \) elimination, C-C and C-O bond rupture are shown in Table 2 while figure 2 shows the calculated values of \( \log k_{uni} \) as a function of pressure for the different models. The calculation of \( k_{uni} \) can be extrapolated to the typical pressures of 37.4 atm and temperatures of 2500 K encountered for ethanol and air in combustions chambers. Under these conditions the calculated rate constants becomes, \( k_{uni} = 2.33 \times 10^4 \) s⁻¹ for

**Table 2. Parameters for H₂O elimination, C-C and C-O bond rupture in kuni calculations**

<table>
<thead>
<tr>
<th>Transition state</th>
<th>H₂O elimination</th>
<th>C-C bond rupture</th>
<th>C-O bond rupture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>model I</td>
<td>model II</td>
<td>model III</td>
</tr>
<tr>
<td>Vibrational frequencies (cm⁻¹)</td>
<td>3106, 2946 (3)</td>
<td>3676, 2954 (5)</td>
<td>3100, 2100 (5)</td>
</tr>
<tr>
<td></td>
<td>1609 (2), 1453 (2)</td>
<td>1490, 1246 (2)</td>
<td>300 (2), 200 (6)</td>
</tr>
<tr>
<td></td>
<td>1341 (2), 1246 (2)</td>
<td>801, 726 (2)</td>
<td>702 (2), 530 (3)</td>
</tr>
<tr>
<td></td>
<td>1056 (3), 972 (2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>843 (2), 201</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( E_v/kcal mol⁻¹ )</td>
<td>63.1</td>
<td>77.1</td>
<td>73.4</td>
</tr>
<tr>
<td>( E_r/kcal mol⁻¹ )</td>
<td>31.9</td>
<td>17.9</td>
<td>21.6</td>
</tr>
<tr>
<td>( 1/10^{13} ) g cm⁻²</td>
<td>182.6</td>
<td>182.6</td>
<td>40.65, 36.56, 9.43</td>
</tr>
<tr>
<td>( \log A/s⁻¹ )</td>
<td>13.4</td>
<td>15.2</td>
<td>15.4</td>
</tr>
<tr>
<td>( r⁺ )</td>
<td>0</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>( L⁺ )</td>
<td>2</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>( ΔS^\text{.cal K}⁻¹\text{mol}⁻¹ )</td>
<td>-3.73</td>
<td>5.57</td>
<td>6.89</td>
</tr>
</tbody>
</table>

A = 1; Z = 1.55 x 10⁷ Torr⁻¹ s⁻¹.

(a) Reactant molecule parameters equal Table 1.

(b) Vibrational frequencies are based on the corresponding parent molecule and final product molecules or characteristics groups, so that desired A-factor is obtained.
Figure 2. Calculated values of log $k_{uni}$ as a function of pressure. $H_2O$ elimination ($\bullet$), C-C bond rupture, model I (+), C-C bond rupture, model II ($\ast$), C-C bond rupture, model III (o), C-O bond rupture (x).

water elimination, $k_{uni} = 2.23 \times 10^8$ s$^{-1}$ for C-C bond rupture, and $k_{uni} = 4.31 \times 10^{9}$ s$^{-1}$ for C-O bond rupture. While it is difficult to assess the reliability of these predictions in a combustion chamber in an air/ethanol mixture and under turbulent conditions, it is interesting to notice the tendency of the C-O bond fission to become the predominant channel.

Discussion

The calculations performed in this work clearly help to understand the outcome of the laser experiments, at low and high pressures, and the observations under pyrolytic conditions.

The results of k(E*) as a function of energy for example show that the C-C bond rupture will begin to be the dominant mechanism at internal energy contents above 85 kcal/mol. This is in agreement with experiments using a shorter CO2 laser pulse at constant laser fluence. While the exact energy at which the crossover occurs will be dependent on the particular models which are used, the trend is not appreciably changed by variations of the transition state parameters. It is also noticeable that the process involving C-O bond rupture is always predicted to be a minor channel in agreement again with experiments which fail to detect final products that could be explained from this mechanism.

While the laser experiments are best analyzed by observing the variation of k(E*), the pyrolysis experiments and the pressure behavior of the laser induced MPD are best compared to the trends shown in Figure 2. Although significant differences can be observed depending on the model used for the transition states, it is clear that the calculations predict that at pressures above 100 Torr the radical initiated reactions will overshadow the elimination process. This is in qualitative agreement with the pyrolysis experiments for which the final products originate from free radical reactions initiated by reactions (3) and (5)\cite{58}. The product distribution of the laser induced process at pressures above 10 Torr also reveals the relative growth of CO and CH$_4$ (products due to free radical reactions) as mentioned in the introduction\cite{58}. The fact that even the laser promoted decomposition at higher pressures favors the bond fission process, is clearly due to the fact that collisions are more effective in relaxing the energized species with longer lifetimes, i.e. those with lower energy content and unable to undergo dissociation prior to collision.

The calculated behavior capable of reproducing the trend of both the thermal and laser experiments also points out that the model outlined here for the primary dissociation processes of ethanol is correct. While considerable improvements could be proposed for the calculations of K(E*)\cite{90} and k$_{uni}$\cite{90} such procedures are not justified at present in the absence of reliable experimental values for the A factors and the activation energies.

While we have neglected to consider the possible contribution of reaction (3) due to the difficulty in estimating the activation energy, it is questionable whether this process can compete effectively with the other elimination channel. Since this reaction also involves a tight transition state, the expected A factor would be in the range of 10$^9$ s$^{-1}$. Given the higher activation energy expected for this path, it is unlikely that this process could be very effective in becoming a dominant channel at higher energies or higher pressures.

Our present work is a good example of how RRK calculations can help not only in understanding the primary dissociation channels of important molecules but also in bridging the gap between low pressure laser driven reactions and high pressure pyrolysis.

Acknowledgments

This work was made possible by the continuous support of Fundação de Amparo à Pesquisa do Estado de S. Paulo (FAPESP), the Conselho Nacional de Desenvolvimento (CNPq), and the Financiadora de Estudos e Projetos (FINEP).

References

17. T. Yamabe, M. Koizumi, K. Yamashita, A. Tachibana, 
22. A.J. Barnes, H.E. Hallam, Trans. Far. Soc. 66, 
   1-82 (1964).
25. P.J. Robinson, K.A. Holbrook, Unimolecular Reac- 
   1883 (1964).
   Phys. 48, 1427-1429 (1968).
29. M.E. Jacox, D.E. Milligan, J. Molec. Spectrosc. 47, 
   148-162 (1973). G. Herzberg, Molecular Spectra 
   and Molecular Structure. II. Infrared and Raman Spectra of 
   Polyatomic Molecules. D van Nostrand, (N.Y., 1945) 
   p. 335. A. Borden, E.F. Barker, J. Chem. Phys. 6, 
   553-563 (1938).
31. R.E. Weston, Jr., Int. J. Chem. Kin. 18, 1259-1276 
   (1986).