LBL-36981
UC-401
Preprint

Lawrence Berkeley Laboratory

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CHEMICAL SCIENCES DIVISION

Submitted to Journal of Physical Chemistry

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March 1995

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098

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This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Methane Loss in the Infrared Multiphoton Dissociation of Acetic Acid

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Abstract

Infrared multiphoton dissociation (IRMPD) was employed to observe the primary dissociation of acetic acid using the technique of photofragment translational spectroscopy. A dissociation pathway with the products carbon dioxide and methane was identified which heretofore had not been observed in the IRMPD of acetic acid under *collisionless* conditions. The average translational energy release was found to be 26.4 ± 2 kcal/mole. A previously observed channel, resulting in the formation of ketene and water, was verified and the average energy released to translation determined to be 18.6 ± 2 kcal/mole. The branching ratio between the dehydration and decarboxylation channels was found to be 65:35 respectively.

Introduction

The earliest studies investigating the thermal decomposition of acetic acid monitored the competition between two molecular elimination pathways, shown below, resulting in either the formation of methane and carbon dioxide (I) or ketene and water (II).[1,2]

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{(I)}$$

$$CH_3COOH \rightarrow CH_2CO + CH_4 \qquad \text{(II)}$$

Recent shock tube studies have identified these two channels as well.[3,4] The range of activation energies determined by these experiments are 62 - 72.5 kcal/mole and 65 - 72.5 kcal/mole respectively, as shown in Fig. 1.[5] The formation of methane as a primary product in this decomposition is not completely accepted. Both pathways have long been thought to proceed through strained four-center transition states.[2] The four-center transition state for the decarboxylation, shown in Fig. 2a, has a pentavalent carbon atom and requires the transfer of a hydrogen atom to an already saturated carbon. This is highly unusual and has not been observed under collisionless conditions. The transition state for the dehydration reaction, Fig. 2b, is more readily accepted with a hydrogen being transferred from a carbon to an oxygen atom and no carbon atom expanded valence is postulated. Because of concern over the involvement of a pentavalent carbon in the unimolecular decarboxylation of acetic acid one of the shock tube studies has been reinterpreted using a methyl radical chain reaction to satisfactorily explain the formation of methane.[6]

With the discovery of infrared multiphoton dissociation processes acetic acid has been reinvestigated using high power pulsed CO_2 lasers. Extensive experiments on many compounds have shown that the primary products in a thermal decomposition are identical to those in an IRMPD experiment.[7] In an investigation of the IRMPD of acetic acid in a photolysis cell with laser induced fluorescence as the detection technique, the dehydration of acetic acid (II) along with a simple bond rupture reaction to produce the hydroxyl radical and the acetyl radical was observed as shown in reaction (III).[8]

$$CH_3COOH \rightarrow CH_3CO + OH \qquad \text{(III)}$$

The energy level diagram in Fig. 1 illustrates the energy needed to produce these dissociation products. The simple bond rupture requires at least 107 kcal/mole if no exit barrier is involved.[9] The fluences used in this experiment were on the order of 40 J/cm^2. A second experiment, using comparable fluences, investigated the decomposition of acetic anhydride to acetic acid which further decomposed to the products ketene, water and methyl radical subsequently detected by VUV photoionization.[10] The formation of CH_3 was attributed to the decomposition of acetyl radical formed in the simple bond rupture reaction (III).

In this research group the IRMPD of ethyl acetate was investigated previously using the photofragment translational spectroscopy technique.[11,12] Using a fluence of 40 J/cm^2, one primary channel resulted in 97% formation of acetic acid and ethylene. Two-thirds of the acetic acid then underwent secondary decomposition to give the products ketene and water with a large translational energy release averaging 23.7 kcal/mole. This large translational energy release is expected due to the tight transition state which acetic acid goes through as shown in Fig 2b. No other products were identified as coming from the secondary decomposition of acetic acid although a second primary channel resulting in the products ethyl radical and acetoxy radical was observed.

There have been a number of theoretical studies on the transition states involved in acetic acid decomposition. A major study in which the transition states shown in Figs. 2a and 2b were investigated was later found to be flawed as the true minima for the transition states were not found.[13] A alternative dissociation mechanism for the elimination of water from acetic acid was proposed in the subsequent paper in which a rearrangement to 1,1 dihydroxyethylene takes place (IV) followed by a concerted elimination occurs through the transition state shown in Fig. 2c.

$$CH_3COOH \rightarrow CH_2C(OH)_2 \qquad \text{(IV)}$$

$$CH_2C(OH)_2 \rightarrow CH_2CO + H_2O \qquad \text{(V)}$$

This was followed up with calculations by a different group on the transition state geometries shown in 2b and 2c as well as activation energy values for the two channels.[14] For reaction (I) the activation energy was found to be 77.7 kcal/mole while an activation energy of 86.0 kcal/mole for reaction (IV) was determined. The second step in the dehydration, (V), is exothermic and the barrier to this reaction lies below the initial activation energy. Very recent calculations show the comparison of activation energies between reactions (I), (II) and (IV) with values of 71.8, 76.4 and 73.1 kcal/mole respectively.[15]

Theory, bulk experimental studies and IRMPD studies all agree that dehydration occurs in the thermal unimolecular decomposition of acetic acid, although the exact mechanism is in debate. It is less clear, however, if the decarboxylation is taking place as this channel was not identified in any of the IRMPD studies and a chain reaction has been postulated to explain the presence of methane in one of the shock tube studies. The experimentally determined activation energy values for the dehydration and decarboxylation pathways are significantly less than the 107 kcal/mole needed for acetic acid to undergo simple bond rupture to produce the acetyl radical and OH as seen in Fig. 1. In principle it should be possible to observe both the dehydration and decarboxylation channels if their activation energies are similar. In practice, however, the two products of the decarboxylation channel, carbon dioxide and methane, are often difficult to detect. Because one of the IRMPD studies used laser induced fluorescence as its detection method it was not sensitive to these two molecular products.[8] In the study by Welge and coworkers the VUV used to photoionize the products did not contain enough energy to ionize either CO_2 or CH_4.[10]

It was not clear that the lack of evidence for the decarboxylation channel in the IRMPD studies in our group is due to its nonexistence. Difficulties in detecting CH_4 and CO_2 which have higher than average background in the detection chamber, as well as the occurrence of a second primary channel, could have obscured these products. In order to resolve whether this channel is taking place as predicted by theory and bulk experiments the present study was undertaken.

Experimental Section

These experiments were performed on a rotating source molecular beam machine which has been described in detail.[16] Briefly, helium was bubbled through glacial acetic acid at room temperature and passed through a pulsed valve[17] with a .020" nozzle, operating at 20 Hz. The equilibrium mixture of acetic acid and its dimer at room temperature and atmospheric pressure is 97% favoring the dimer, so it is crucial to reduce the amount of dimers by heating the nozzle.[18] The optimum nozzle temperature at which signal due to dimer dissociation could be suppressed and the photodissociation signal observed was 340 - 350°C. In order to heat the Trickl type piezoelectric pulsed valve, the tip was water cooled and a copper extension with an orifice of .040" was electrically heated with thermocoaxial wire. A stagnation pressure of 635 torr was used to create a supersonic expansion of approximately 5% acetic acid in He, with a mean velocity of 2050 m/s and a full width at half-maximum (FWHM) spread of 10%. The velocity distribution of molecules in the beam was measured using standard time-of-flight techniques with a spinning slotted wheel.[19]

The molecular beam was collimated with one skimmer resulting in an angular divergence on the order of 4 degrees. Although typically two skimmers are used to collimate a molecular beam, in this case, due to the low signal level the distance between the pulsed valve and the laser was decreased. This created a more intense beam at the interaction region but necessitated removing one skimmer which resulted in a broader angular spread. A Lumonics TEA-820 pulsed CO_2 laser was tuned to the R(20) line of the 9.6-μm branch (1079 cm^{-1}) and crossed the molecular beam at the interaction region. The laser beam was focused to a 2 x 2.5 mm^2 spot resulting in a laser fluence of approximately 12 J/cm^2. The fragments created by IRMPD traveled 36.7 cm to the detector, which consisted of the standard electron impact ionizer, quadrupole mass filter and Daly type ion detector.[20] A multichannel scaler triggered by the laser

collected the detector counts as a function of the time taken for the fragments to travel from the interaction region to the detector.

Results and Analysis

Measurements were taken at detector to source angles of 20, 30, 40, and 50 degrees and dissociation signal was observed at m/e ratios 44, 42-40, 29-28, and 18-12. The resulting data was analyzed using standard forward convolution techniques.[21] A center-of-mass translational energy distribution is assumed and averaged over apparatus functions to yield a time-of-flight distribution in the lab frame. This simulated time-of-flight distribution in the lab frame is compared to the experimental time-of-flight distribution, and the translational energy distribution is modified until the two match. Evidence for both the decarboxylation and the dehydration channel was apparent; these channels will be discussed separately and then compared.

A. Decarboxylation Channel. This channel, leading to CO_2 and CH_4, has not been observed previously under collisionless conditions. The time-of-flight data at m/e = 44 and m/e = 15 at 20° and 40° are shown in Fig. 3. At m/e = 16 it is not possible to separate the methane signal from that of the water due to the dehydration channel, which may also crack in the ionizer to m/e = 16; additionally, m/e = 16 has high background counts. By tuning the quadrupole mass filter to m/e = 15, methane can be observed without any such interference. The center-of-mass translational energy distribution shown in Fig. 4a is derived from the momentum matched fragments and has an average translational energy release of 26.4 ± 2 kcal/mole, peaking at 25 kcal/mole which is indicative of a concerted molecular elimination.

The second peak in the m/e = 15 spectra is attributed to residual dimers in the molecular beam. Neither CO_2 nor CH_2CO can contribute to this peak as fragmentation of either product in the ionizer will not lead to m/e = 15. If this peak was due to a primary process, the most likely candidate would be CH_3CO formed in a simple bond rupture process, which could

undergo secondary dissociation or fragmentation in the ionizer. This same slow peak is observed at m/e = 28, although the signal is quite poor due to high background counts. This peak indicates that the signal at m/e=15 is not due to secondary dissociation of CH_3CO otherwise these peaks would be momentum matched. The lack of OH formation is evidence that CH_3CO is not being formed in a primary decomposition process from acetic acid. Therefore the slow peak in Fig. 3 for m/e = 15 at 20° must be due to photodissociation of acetic acid dimer or higher order clusters. As the source nozzle temperature is increased, the cluster signal becomes less intense relative to the monomer dissociation signal; this is illustrated in Table 1. With the present setup it was not possible to further increase the nozzle temperature and as the dimer signal does not overlap with the relevant dissociation signal, further heating is not necessary for this experiment.

B. Dehydration Channel. As stated before this channel has been observed as a secondary decomposition product of ethyl acetate under collisionless conditions using the photofragment translational spectroscopy technique, and an average translational energy release of 23.7 kcal/mole peaked at 25 kcal/mole was obtained.[11] Since the previous work was under secondary dissociation conditions, the results are inherently more uncertain due to extensive averaging over both the beam velocity distribution and the primary translational energy distribution.[21] In this experiment, the dehydration channel is a primary channel, so such extensive averaging is not included in the final result. The time-of-flight data obtained from m/e = 42 and m/e = 18 at 20° and 40° in this experiment are shown in Fig. 5. These two fragments are momentum matched and the resulting center-of-mass translational energy distribution, shown in Fig. 4b, has an average translational energy release of 18.7 ± 2 kcal/mole, peaked at 17 kcal/mole. Because the primary dissociation of acetic acid is being investigated in this case, the lower average translational energy release is not surprising. In the dissociation of ethyl acetate acetic acid is initially formed via a concerted reaction with a large exit barrier of 37.8 kcal/mole. A large fraction of this energy (43%) was found to go into internal excitation. Subsequent dissociation of acetic acid will then occur from a wide range of internal energy levels, leading to

an average translational energy release greater than that found in the primary dissociation of acetic acid which is initially internally cold.

Two dissociation mechanisms have been discussed for this reaction. Direct elimination of water from a four-center transition state, Fig. 2b, analogous to the decarboxylation of acetic acid has been predicted by many groups.[2,4,11] The second dissociation in which a rearrangement (IV) is followed by decomposition from a second type of four-center transition state, Fig 2c, cannot be ruled out by this experiment. The same products are formed in both instances through a concerted molecular elimination. Both cases would be expected to exhibit similar dynamics with a large translational energy release as observed in this experiment.

C. Branching ratios.[22] Of fundamental chemical interest is the relative ratio of the products produced. In order to calculate branching ratios it is necessary to consider the contributions from all fragments produced in the dissociation process, CO_2, CH_2CO, CH_4, H_2O, and their daughter ions which result from fragmentation in the electron impact ionizer. The relative yield for each ion is determined by summing over all parent and daughter masses and dividing by the total relative yield of all the ions. Then the ionization cross section for each fragment is taken into account to give the relative yield of each fragment. The difficulties in determining ionization cross sections are discussed in detail elsewhere[23] and the method of Fitch and Sauter[24] has been chosen to obtain the ionization cross sections. The uncertainties in the ionization cross section values obtained by this method may be as high as 25%.[23]

The branching ratio between the dehydration and decarboxylation channels has been determined to be 65:35 with an uncertainty as high as ± 15% due mainly to the uncertainty in the ionization cross section. A change of ± 25% in the ionization cross section results in ± 10% uncertainty in the branching ratio. At m/e = 28 and m/e = 16 the difficulty in assigning the proportion resulting from CH_2CO versus CO_2 or H_2O versus CH_4 respectively results in an additional ± 5% uncertainty. The emphasis here should be on the significant amount of methane and carbon dioxide products that are observed, 35% ±15%, under collisionless conditions.

Discussion

A. Methane Production. There had been some question as to whether CH_4 is produced in a primary reaction or whether the CH_3 radical is produced and then participates in a chain reaction to create methane. This is primarily due to concerns that high activation energies must be involved when the carbon valence shell is expanded.[25] Because the only previous experiments which observed the decarboxylation channel of acetic acid were performed under conditions in which collisions might be a factor it has not been possible until now to safely interpret this as a result of unimolecular decomposition. Hydrogen migrations are certainly not a new phenomenon in chemical reactions.[26] Intramolecular hydrogen shifts have been readily observed under collisionless conditions.[27] In these cases the hydrogen shift occurs from a carbon atom to either a nitrogen or oxygen atom as it does in the case of the dehydration of acetic acid. The particular case of decarboxylation in acetic acid is interesting because it is the first time, to our knowledge, that a hydrogen migration has been observed from an oxygen atom to a saturated carbon atom under collisionless conditions.

B. Translational Energy Release. With an average of 26.4 ± 2 kcal/mole the decarboxylation channel has a larger average translational energy release compared to the 18.6 ± 2 kcal/mole average release seen in the elimination of water. This may be partially due to the differences in the heats of formation of the products. As shown in Fig. 1 the formation of water and ketene is endothermic by 34.1 kcal/mole while the production of carbon dioxide and methane is exothermic by 8.6 kcal/mole. If these two channels have similar activation barriers then the decarboxylation channel should have on average more energy available for both translation and internal excitation.

It is also informative to look at the maximum translational energy released in the two primary decomposition channels. The decarboxylation channel has a maximum 50 kcal/mole released to translation while the dehydration channel shows a maximum of 40 kcal/mole. Because the heats of formation differ greatly with the dehydration products being higher in energy by 42.7 kcal/mole, one might expect the maximum translational energy release to the

products of the decarboxylation channel to extend well beyond that of the dehydration channel; however, only a 10 kcal/mole difference is observed. This may be indicative of a difference in the nature of the transition states resulting in different dynamical processes taking place in the two channels. In the decarboxylation of acetic acid the structure of the transition state must be further away from the product equilibrium bond distances resulting in more energy partitioned into internal excitation. This interpretation of the maximum translational energy release was first suggested by reaction path calculations that show the energy partitioning is quite different between the two channels, with significant coupling between vibrational modes occurring after passing through the transition state in the case of the decarboxylation channel.[28]

C. *Comparison with Previous Experiments.* Previous IRMPD experiments did not observe the decarboxylation channel. This may be in part due to limitations in the detection schemes used as discussed earlier. Another factor to consider is the high fluences used in the earlier experiments, ~40 J/cm^2, which may have played a role in obscuring this channel. In this experiment a relatively low fluence of 12 J/cm^2 was utilized. It is well known that the fluence can affect the branching ratio when either the preexponential factors or activation energies of the two channels are different.[7] For example, in the IRMPD of CF_2Cl_2, the molecular elimination of Cl_2 was seen to decrease within the relatively small fluence range from 0.3-8 J/cm^2 as compared to chlorine atom loss.[29] At higher fluences the decarboxylation channel may be produced with such a low yield that it is not feasible to detect the products, methane and carbon dioxide.

The branching ratio determined in this experiment indicates that dehydration is the more favorable reaction. This was also observed in a shock tube study which found at decreasing molecular densities the decarboxylation products decreased from a 1:1 ratio to 0.6:1.[4] Theoretical branching ratios have been calculated showing at higher temperatures the dehydration reaction is favored due to a larger A factor.[15] Using transition state theory at 900 K the ratio of $[CO_2]/[H_2O]$ is 1.6 while at 1500 K a value of 0.7 was determined. In these molecular beam microscopic experiments the concept of temperature is generally not used. However, it has been shown that the differences in the vibrational population distribution

between a thermally heated molecule and an infrared multiphoton excited molecule are slight.[30] The branching ratio determined from this experiment is much less than 1, ~0.5, indicating an initial internal energy distribution closer to 1500 K than to 900 K.

Conclusions

Observation of two molecular elimination channels in the IRMPD of acetic acid, dehydration and decarboxylation, confirmed the competition occurring between these two pathways in agreement with bulk experimental studies. The decarboxylation channel was observed under collisionless conditions for the first time with a large translational energy release which supports the existence of a strained transition state in which a hydrogen is transferred to a saturated carbon. The maximum translational energy release observed in both cases indicates that the energy partitioning in the two channels takes place in different manners and that a higher percentage of available energy goes into internal excitation in the case of decarboxylation.

Acknowledgment. The authors would like to thank Prof. M. Page for supplying preprints of his work and Dr. Arthur Suits for helpful discussions. CAL would like to thank the University of California at Berkeley Chemistry Department for a Department of Education fellowship and Prof. Lin at the Institute of Atomic and Molecular Sciences in Taiwan for providing a pleasant atmosphere during the final drafts of this manuscript. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Registry No. CH_3COOH, 64-19-7.

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Table 1: Dimer Dissociation Signal

Temperature °C	Dimer:Monomer Signal
170	4.2
264	3.5
340	2.9

Table 1. As the source nozzle temperature is increased the relative amount of dissociation signal due to dimers decreases. The integrated area under the two peaks observed at m/e = 15 at 20 degrees was compared for three temperatures.

Figure Captions

FIG. 1. Energy level diagram for acetic acid shown in kcal/mole. The boxes indicate the range of activation energies determined by previous experiments.[1-4]

FIG. 2. Three transition states relevant to the decomposition of acetic acid are illustrated; Fig. (1a) is the transition state which produces the products methane and CO_2, Fig. (1b) is the commonly accepted transition state resulting in ketene and water, Fig. (1c) is an alternate transition state also leading to dehydration, in this case a rearrangement must take place first.

FIG. 3. Time-of-flight spectra m/e = 15 and m/e = 44 at source to detector angles of 20 and 40 degrees indicating that decarboxylation is a primary dissociation channel. The open circles represent data points and the lines represent the calculated time- of-flight from the forward convolution of the center-of-mass translational energy distribution shown in Fig. 4a.

FIG. 4. Translational energy distributions derived from the data in Figs. 3 and 6.

FIG. 5. Time-of-flight spectra for the dehydration channel at source to detector angles of 20 and 40 degrees. The center-of-mass ranslational energy distribution is shown in Fig. 4b.

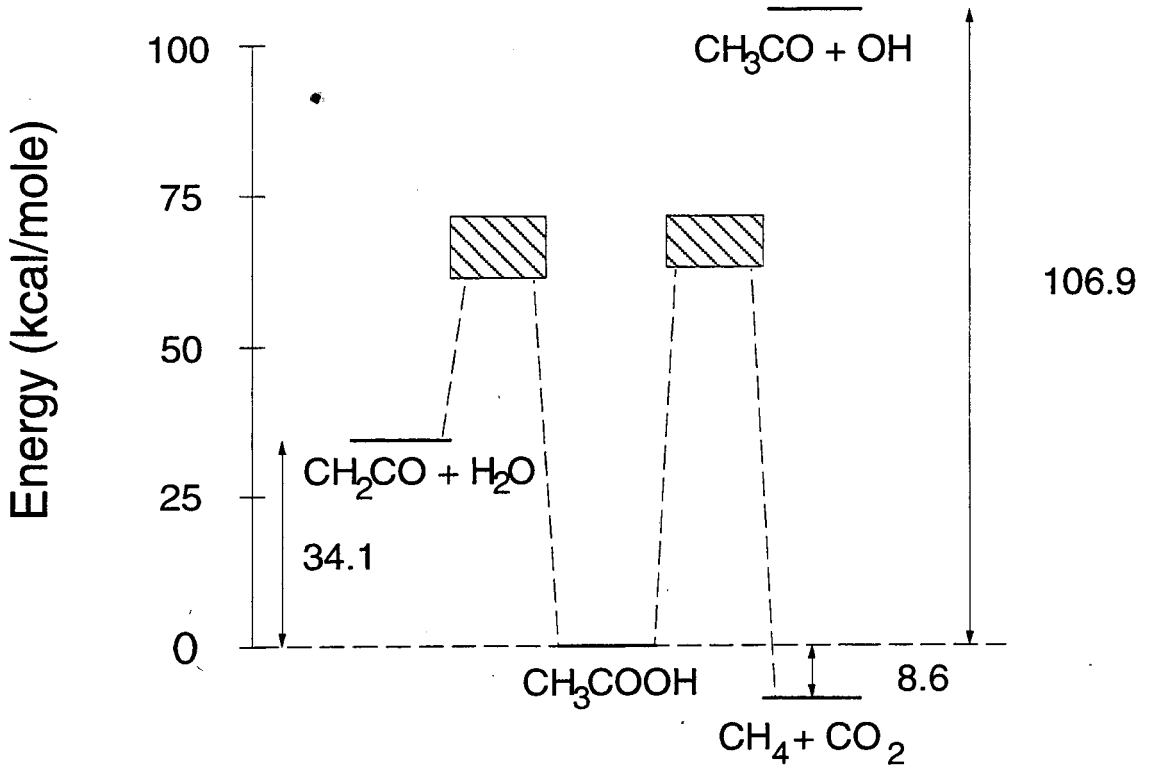
Energy (kcal/mole)
100
75
50
25
0
$CH_3CO + OH$
106.9
$CH_2CO + H_2O$
34.1
CH_3COOH
8.6
$CH_4 + CO_2$

Figure 1

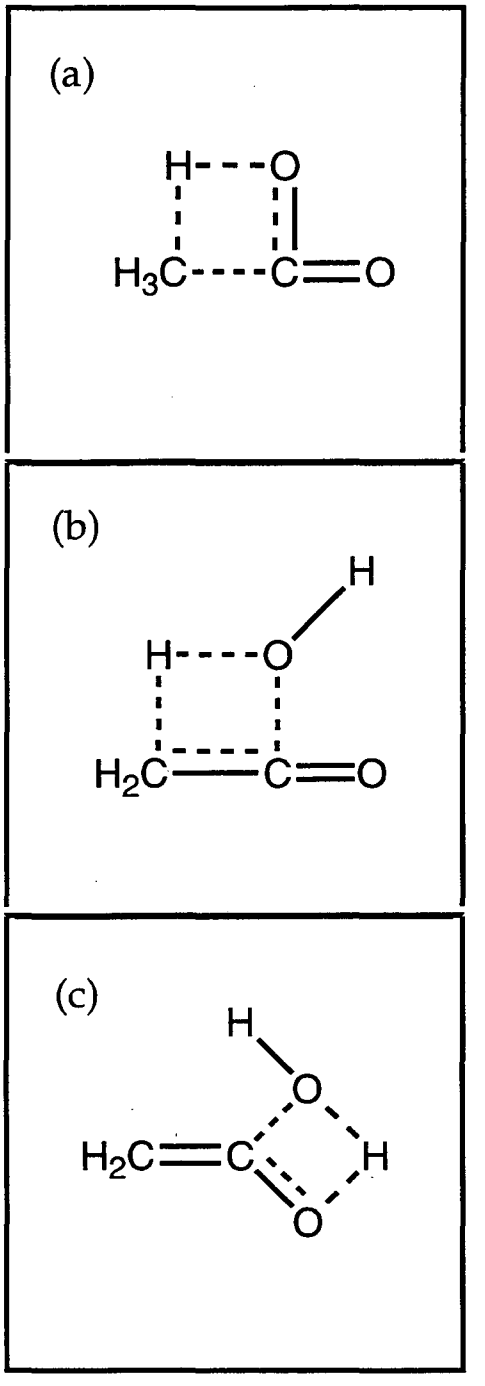

Figure 2

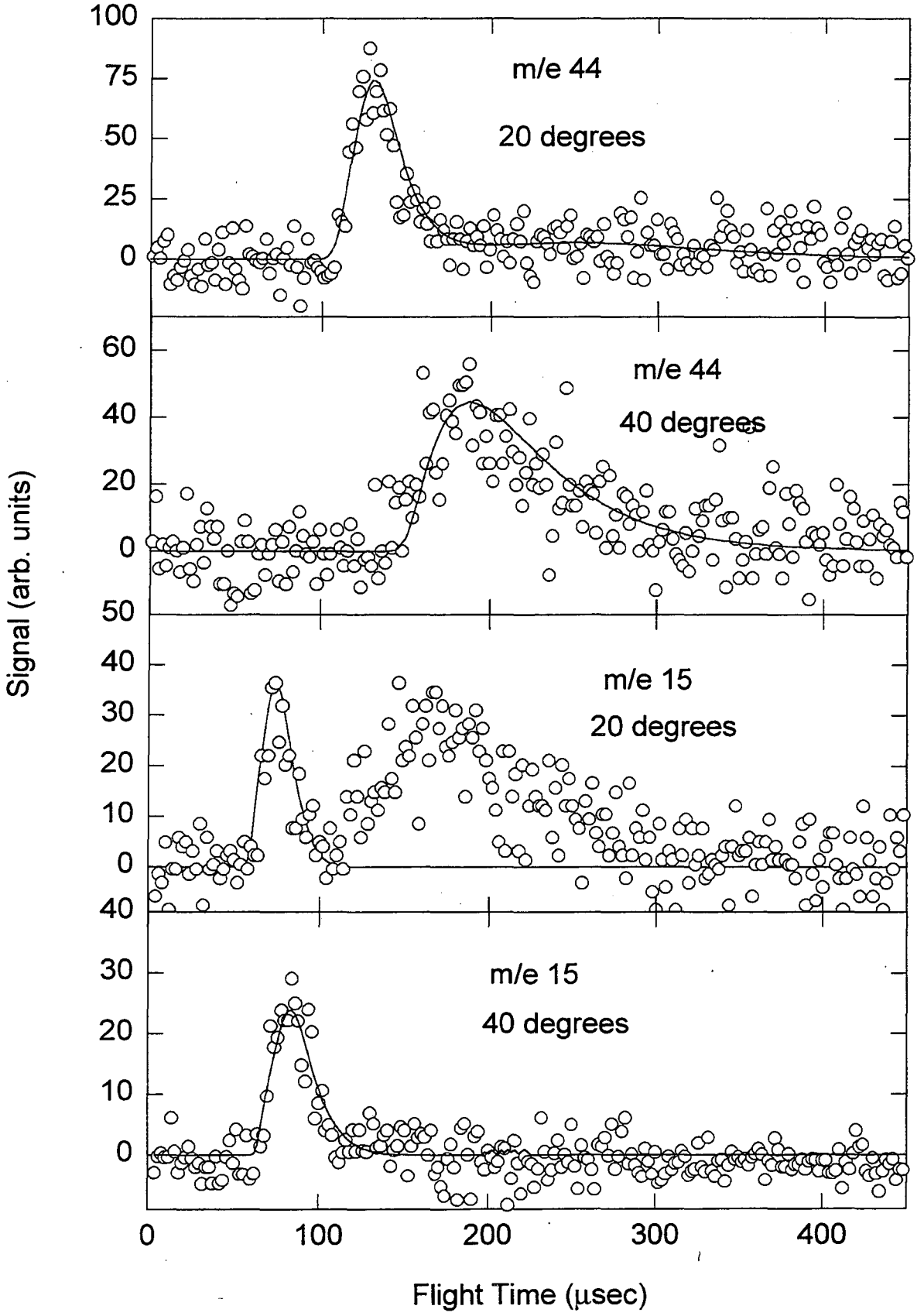
m/e 44
20 degrees
m/e 44
40 degrees
m/e 15
20 degrees
m/e 15
40 degrees
Signal (arb. units)
Flight Time (μsec)
100
75
50
25
0
60
40
20
0
50
40
30
20
10
0
40
30
20
10
0
0
100
200
300
400

Figure 3

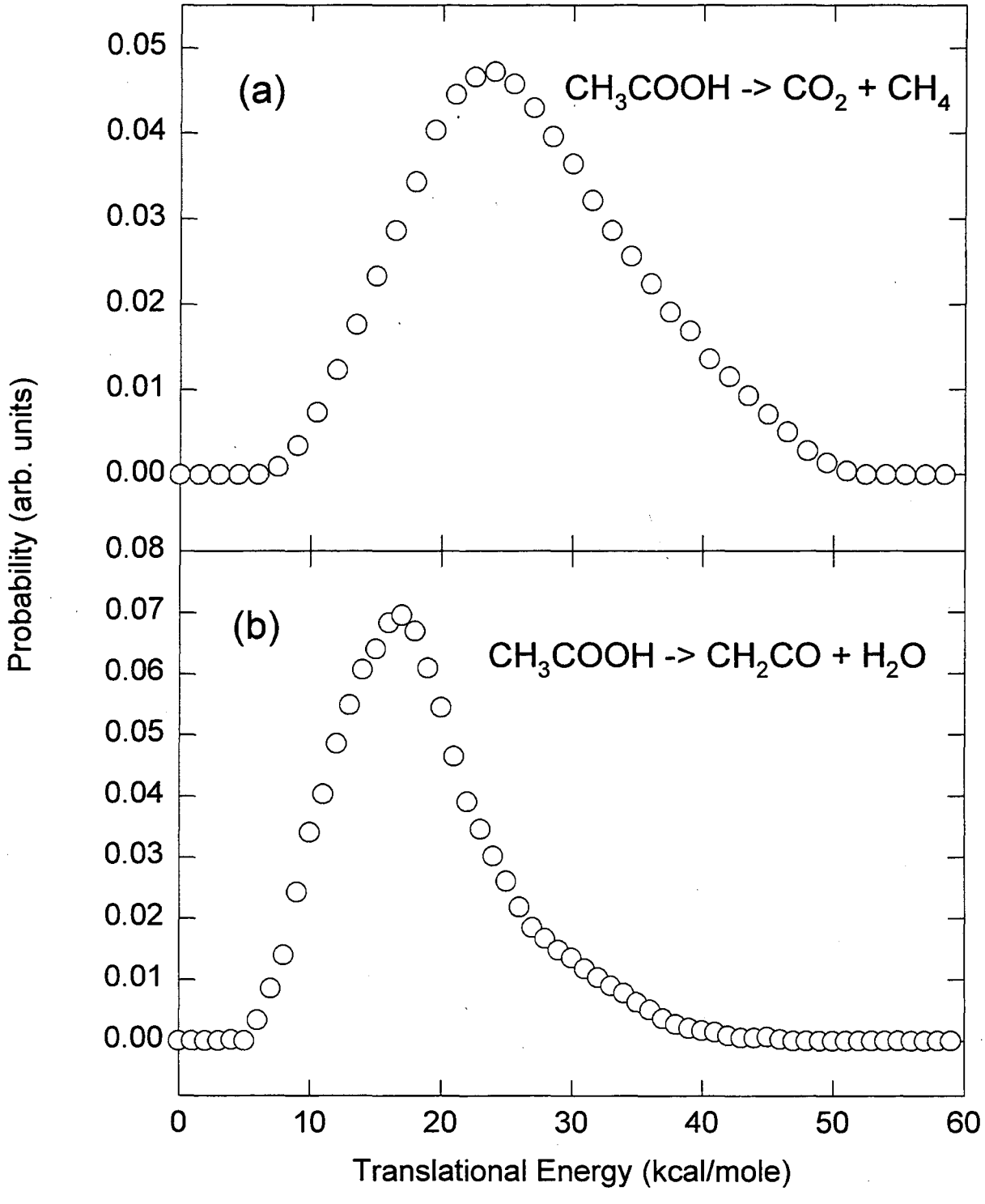
(a)
$CH_3COOH \rightarrow CO_2 + CH_4$
(b)
$CH_3COOH \rightarrow CH_2CO + H_2O$
Probability (arb. units)
Translational Energy (kcal/mole)
0.05
0.04
0.03
0.02
0.01
0.00
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
0
10
20
30
40
50
60

Figure 4

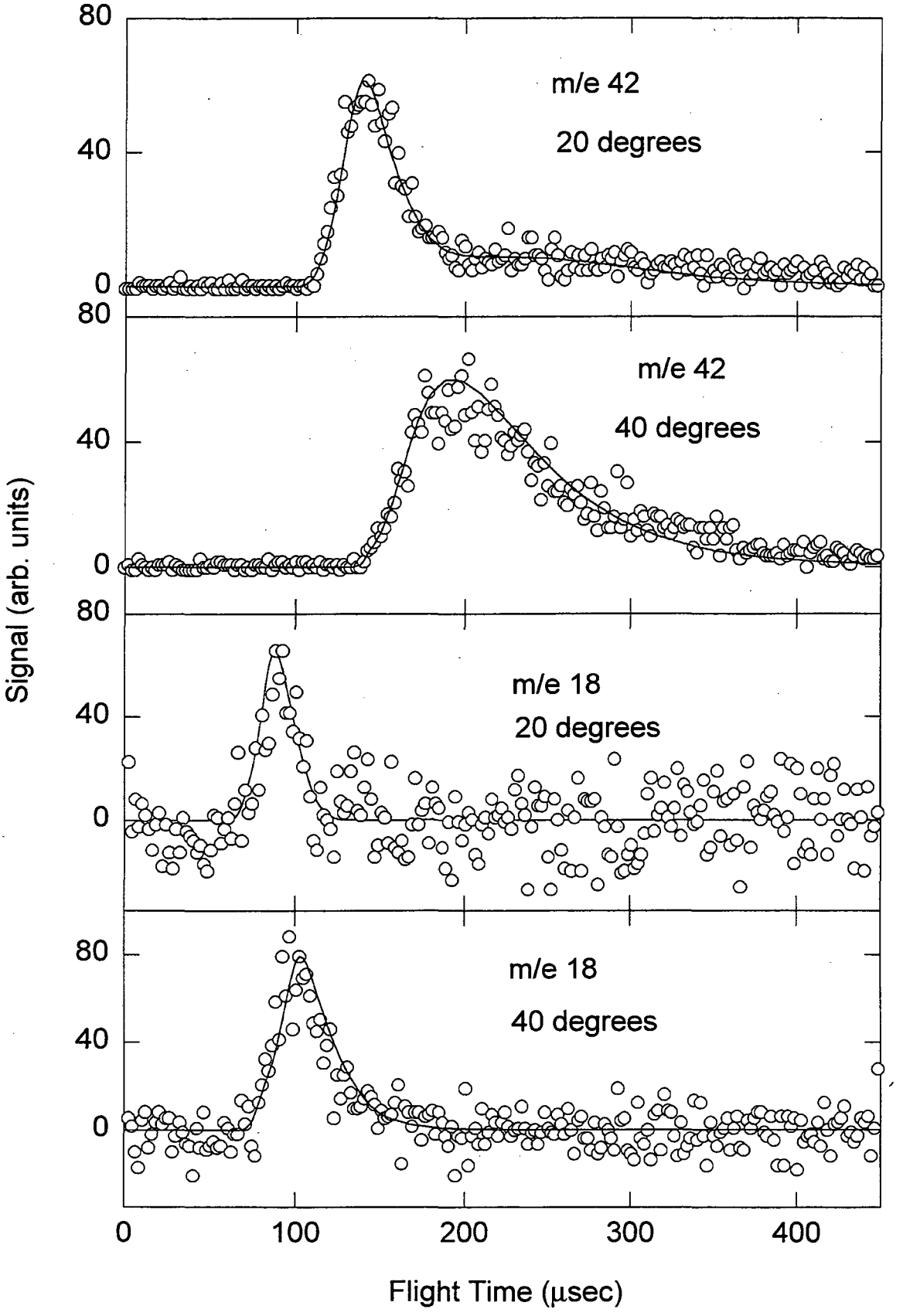
80
40
0
m/e 42
20 degrees
80
40
0
m/e 42
40 degrees
80
40
0
m/e 18
20 degrees
80
40
0
m/e 18
40 degrees
Signal (arb. units)
0
100
200
300
400
Flight Time (μsec)

Figure 5

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