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Potential energy profiles for unimolecular reactions of organic ions

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Simple organic ions, generated in a mass spectrometer, are investigated when undergoing unimolecular dissociation some 10^8 vibrations after generation and excitation. Under these conditions, the slow step in the pathway to dissociation products normally occurs with only a few kilojoules per mole of excess energy in the transition state. Moreover, the kinetic energy released in the dissociation step can be measured. By the use of heats of formation of reactants, intermediates and products, and deuterium labelling, potential energy profiles for reaction can be constructed. It is shown that a general cause of the release of a range of kinetic energies in a unimolecular reaction is a rate-determining isomerization, followed by a more energetically facile dissociation with excess energy in the transition state for dissociation. The approach is exemplified by the construction of a potential energy profile for the unimolecular reactions of ionized acetic acid and its enol form.

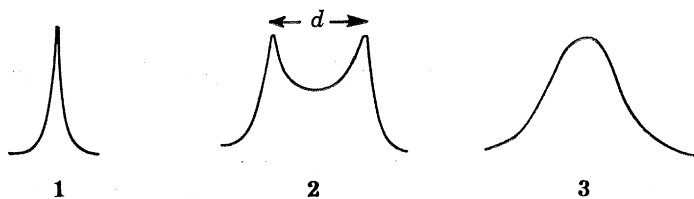
INTRODUCTION

The characteristic reactions by which small isolated organic molecules fragment or rearrange, given the minimum energy required for such processes, are clearly of fundamental interest. For the cases where the molecules carry a charge, i.e. organic ions, an almost ideal experiment can be conveniently carried out in a mass spectrometer.

In the work to be described, an ion of a given structure is generated by electron impact upon an appropriate neutral. The fragmentation of this ion is then examined some 10^8 vibrations (*ca.* 10^{-5} s) after the time that the ion was energetically excited. The elapsing of a time that is very large compared with vibrational and rotational periods ensures that only just sufficient energy is available to lead to fragmentation. Had more energy been available, then fragmentation would have occurred earlier. Primary deuterium isotope effects establish that for reactions occurring some 10^8 vibrations after excitation, the excess energies in the transition state for the rate-determining step are commonly a few kilojoules per mole (Williams 1977).

Additionally, the completion of *ca.* 10^8 vibrations before reaction ensures that almost any required reacting geometry will be sampled if it is energetically accessible. Thus, the ability of one reaction channel to compete with another is little dependent on the relative probabilities of attaining the two (in general) different geometries required for reaction, i.e. 'entropies' of activation are relatively unimportant, energies of activation being the dominant parameters.

The experiment is designed so that the signal detected is caused by the ion produced by fragmentation. If the fragmentation occurs with the release of kinetic energy then, depending on the orientation of the reactant ion relative to the direction of the ion beam at the instant of dissociation, product ions may increase or reduce their momentum in the direction of the ion beam. By a quantitative treatment of the problem, Beynon & Fontaine (1967) showed that the narrow peaks, **1**, associated with negligible kinetic energy release upon dissociation are replaced by two component peaks, **2**, when there is a relatively specific kinetic energy release and when certain instrumental requirements are satisfied. The distance *d* can be directly related to the kinetic energy released upon dissociation.



A third type of signal, **3**, is frequently observed. Clearly, this corresponds to a dissociation in which a range of kinetic energies is released. The average kinetic energy released can then be calculated from the width of this peak at half height (Terwilliger *et al.* 1974). In the following we consider a general origin of such broad peaks.

DISCUSSION

Since it has been argued above that energy is the dominant parameter in determining the observed slow reaction of isolated ions, the experiment is well suited to the determination of potential energy profiles for the unimolecular reactions of organic ions. For simple ions, the heats of formation of reactants and products are usually known. Among many methods, determinations may be made from electron impact measurements (see, for example, Lossing 1972) or ion cyclotron resonance (see, for example, Aue *et al.* 1976). The energy of the transition state for the rate-determining step is available from the appearance potential of the product ion.

The potential energy profiles that we have studied can be divided into several types. First, there are those in which the pathway from reactant to products is essentially continuously endothermic: there is no significant reverse activation energy, and the signal due to product ions must be narrow. A system whose behaviour follows this type is the dissociation of protonated propionaldehyde to protonated formaldehyde and ethylene (figure 1). The appearance potential of the product ion is, within experimental error, equal to the sum of the heats of formation of products and the product ion signal is therefore narrow. The reaction is believed to proceed, in part, by successive (and reversible) 1,2-hydride shifts followed by direct dissociation of the primary cation $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$ (Bowen *et al.* 1978*b*).

Secondly, there are those cases where a reverse activation energy exists, and some of this reverse activation energy may appear as a release of kinetic energy in the dissociation step. Such a profile is found for the dissociation of protonated propylene imine to protonated methylene imine and ethylene (figure 2). The measured transition state energy (930 kJ mol^{-1} , i.e. an activation energy for reaction of 290 kJ mol^{-1}) is in reasonable agreement with the estimated heat of formation of $^+\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ (Williams & Bowen 1977). The kinetic energy release in the dissociation is 38 kJ mol^{-1} , and therefore approximately one-third of the reverse activation energy is released as kinetic energy, the rest remaining in internal modes of the products. It is noteworthy that the potential energy profiles shown in figures 1 and 2 are basically different because of the greater stability conferred when an amine group (rather than a hydroxyl group) is used to stabilize a positive charge.

A third type of potential energy profile is found when an ion, generated as A^+ , undergoes isomerization to an ion B^+ in a process that is energetically favourable over any direct dissociation of A^+ ; dissociation of B^+ is also facile relative to reversion to A^+ (figure 3). Thus, the isomerization of A^+ to B^+ is rate-determining in the dissociation of A^+ which always occur via B^+ . Moreover, starting from A^+ , the dissociation of B^+ occurs with an excess of energy

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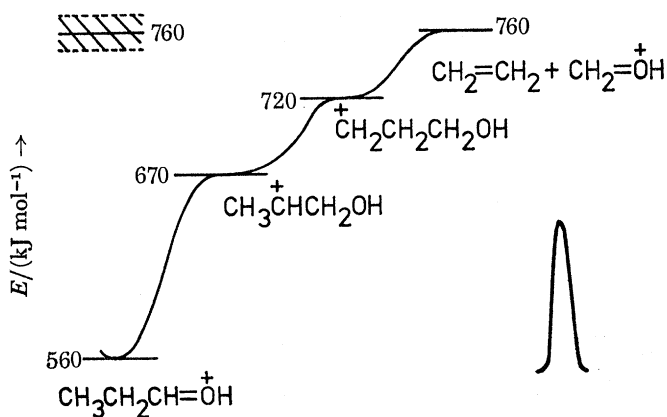


FIGURE 1. Proposed stepwise rearrangement and dissociation of $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{H}$. The kinetic energy release profile given in the figure corresponds to an average kinetic energy release of 3.10 kJ mol^{-1} .

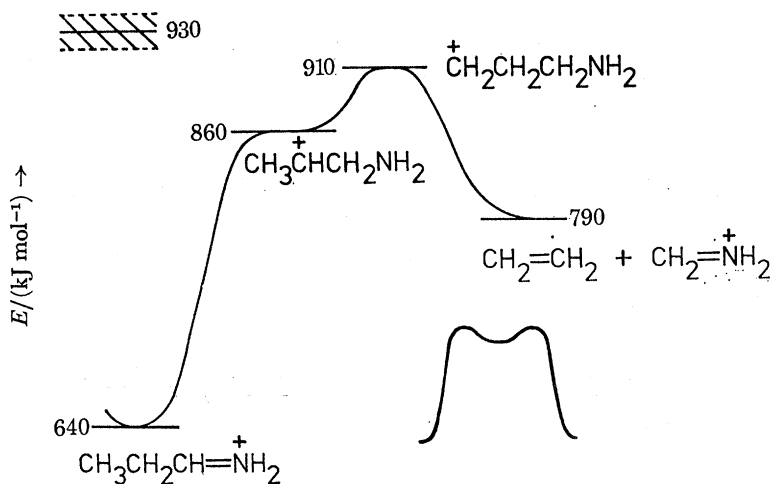


FIGURE 2. Proposed stepwise rearrangement and dissociation of $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{H}_2$. The kinetic energy release profile given in the figure corresponds to a kinetic energy release of 38 kJ mol^{-1} .

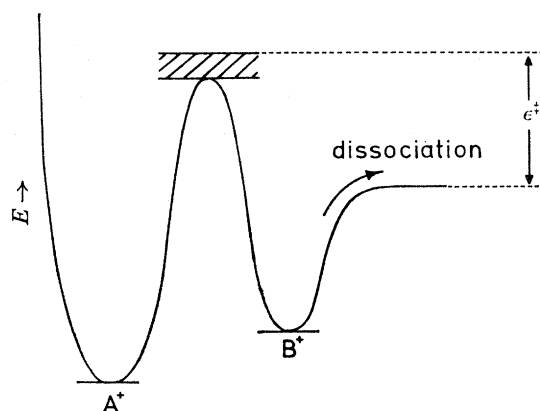


FIGURE 3. Potential energy profile for the rate-determining isomerization of an ion A^+ to B^+ , followed by dissociation of B^+ with excess energy ϵ^+ in the transition state.

ϵ^\ddagger in the transition state for the dissociation step. We have concluded that it is the fluctuation of some of this excess energy, on a statistical basis, into the reaction coordinate for dissociation that is a general cause of the broad peaks depicted in 3.

The occurrence of this type of profile can be shown by measuring the activation energies for dissociation of A^+ , which must correspond to a level higher than that observed for dissociation of directly generated B^+ . Some examples are now cited.

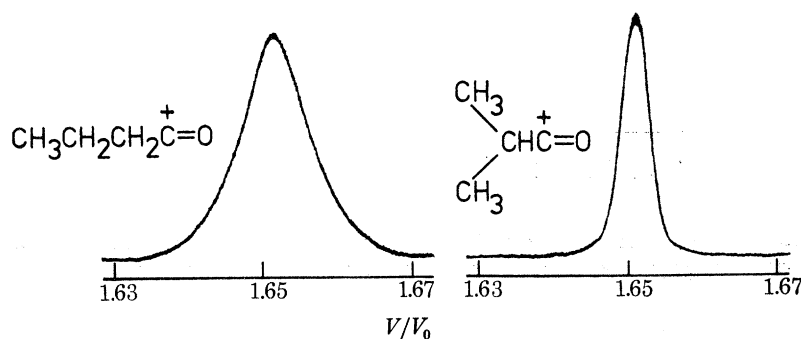
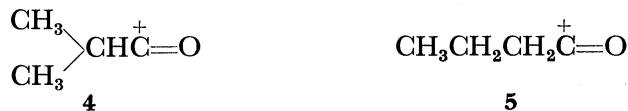
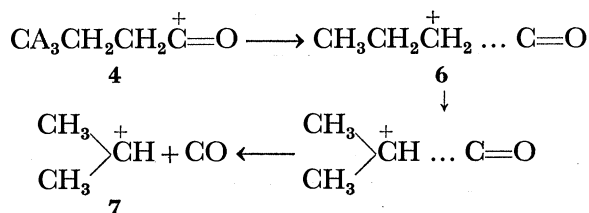


FIGURE 4. Peaks due to $C_3H_7^+$ ions formed by dissociation of the given isomeric acylium ions, some 10^8 vibrations after their generation. The dissociations were observed by scanning the accelerating voltage (to V from V_0) at constant electric sector voltage and magnetic field strength.

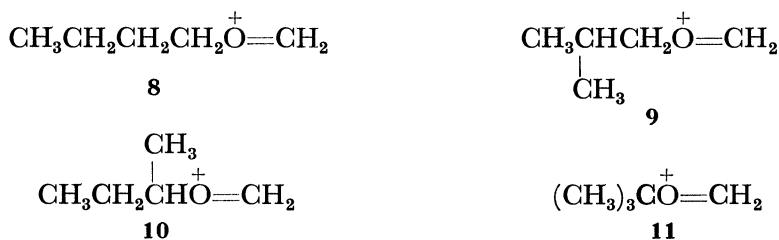
If the acylium ion, 4, is generated, its sole slow unimolecular dissociation is via CO loss, and the profile detected for the product isopropyl ion is narrow (figure 4). In accord with this finding, the sum of heats of formation of the products is equal, within experimental error, to the appearance potential of $(CH_3)_2CH^+$.



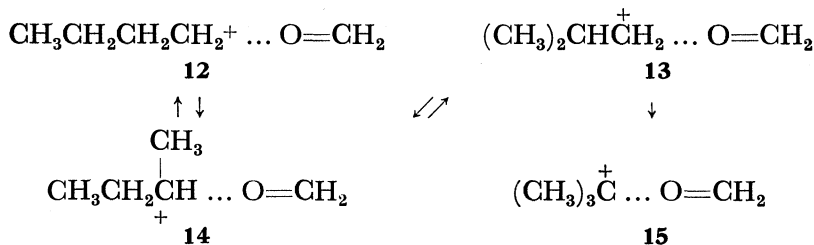
However, the loss of CO from the isomeric acylium ion, 5, gives rise to a peak that is broad (figure 4), and clearly in this dissociation a larger average kinetic energy release occurs (2.9 kJ mol^{-1} compared with 0.4 kJ mol^{-1}). Furthermore, appearance potential measurements establish that the dissociation that occurs via CO loss requires insufficient energy to produce $\text{CH}_3\text{CH}_2\text{CH}_2^+$ and CO. We therefore conclude that the rate-determining step in dissociation of 5 produces a partial separation of the CO (see 6), but that the incipient *n*-propyl ion then isomerizes to the *sec*-propyl cation which is more stable by *ca.* 67 kJ mol^{-1} . The energy required to produce 6 is more than that needed to allow dissociation to the product combination 7. The observed peak broadening therefore represents a direct observation of some of the energy release when a primary carbonium ion isomerizes to a secondary carbonium ion.



If CO is replaced as the leaving group by O=CH₂ which, in the present context, has a significant dipole moment (2.0 D[†]), then an ion-dipole interaction becomes important in determining which step is rate-determining. For example, the ions **8–11** all lose O=CH₂ in dissociations occurring some 10⁸ vibrations after their production and excitation. On the basis of the discussion thus far, it might be anticipated that the dissociation of **8** and **9** would result in the release of a range of kinetic energies, with the peaks for these dissociations being broader than those due to dissociation of **10** and **11**. This would follow since CH₃(CH₂)₂CH₂⁺ and (CH₃)₂CHCH₂⁺ do not exist in potential wells, and can rearrange exothermically to *sec*-butyl and *tert*-butyl cations, respectively.



However, experimentally it is found that O=CH₂ loss from **8**, **9** and **10** produces broad peaks corresponding to an average release of 4.2–5.0 kJ mol⁻¹ of kinetic energy: only **11** dissociates with the production of a narrow peak (average release of 0.8 kJ mol⁻¹ of kinetic energy) (Bowen *et al.* 1978*a*). The reason for this behaviour is evident from a consideration of the now significant ion-dipole interaction. As O=CH₂ leaves a cation considered as a point charge with the formaldehyde dipole moment μ orientated along the cation-dipole axis, the energy of the system is lowered by μ/R^2 , where R is the distance between the point charge and a point dipole. For O=CH₂ as leaving group, this energy is *ca.* 84 kJ mol⁻¹ at a distance R of 0.3 nm. Thus, the complex **14** (formed from **10** during dissociation) is still bound by *ca.* 84 kJ mol⁻¹ although the C—O bond is effectively broken and CH₂CH₂CH⁺CH₃ may display cationic properties. If **14** contains a further 67 kJ mol⁻¹ of vibrational energy, this is insufficient to overcome the ion-dipole interaction, but can be converted to electronic energy in isomerizing the incipient *sec*-butyl ion to an incipient *n*-butyl or *iso*-butyl ion (see **12** and **13**, respectively). Thus, the ion-dipole interaction can allow interconversion of **12**, **13** and **14** without dissociation.



However, once **12**, **13** and **14** have equilibrated, there is now a possible route for dissociation for all of them *via* **13** → **15**. The isomerization of **13** → **15** is of a primary to a tertiary cation and this should release *ca.* 126 kJ mol⁻¹. This energy release is greater than the ion-dipole interaction: hence starting from **8**, **9** or **10** all dissociate *via* **11**, and in all the cases there is excess energy in the transition state for the dissociation **11** → **15** → (CH₃)₃C⁺. In contrast,

† 1 D (debye) = 3.336 × 10⁻³⁰ C m.

when directly generated **11** dissociates, the highest point on the potential energy profile is that corresponding to the separated products and a narrow peak due to dissociation is observed.

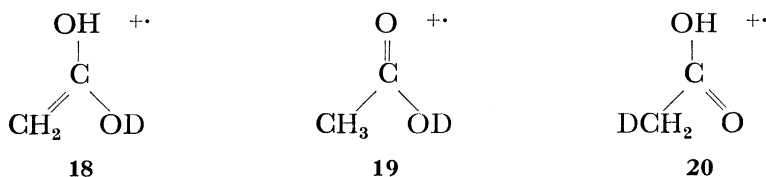
The above model can be subject to further tests in experiments yet to be carried out. It clearly predicts equilibration of primary and secondary cations before dissociation only if the ion-dipole interaction is greater than 67 kJ mol^{-1} .

The principles outlined in this paper have been applied to establish the potential energy profile for unimolecular reaction of ionized acetic acid, **16**, and its enol form, **17** (Schwarz *et al.* 1978; see also Levsen & Schwarz 1976).



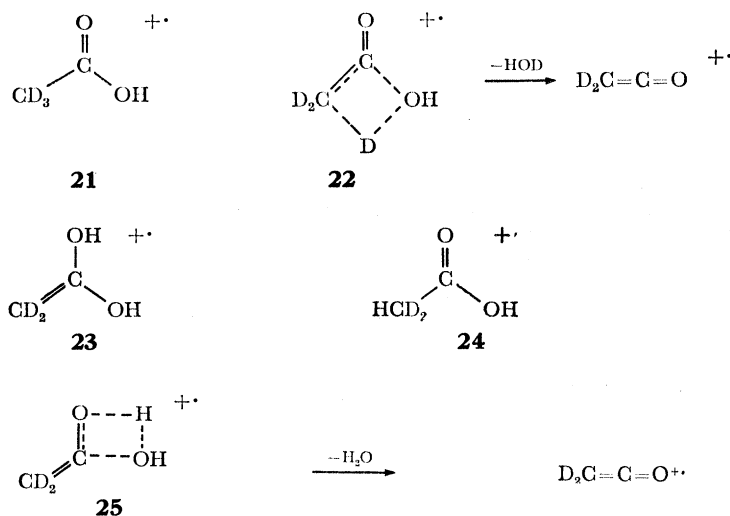
Both **16** and **17** dissociate via the loss of a hydroxyl radical, and deuterium labelling of **16** establishes that the original hydroxyl group of **16** is eliminated without prior rearrangement (and with an activation energy of *ca.* 90 kJ mol^{-1}). However, appearance potential measurements establish that in losing a hydroxyl radical, **17** cannot dissociate directly because the process requires *ca.* 220 kJ mol^{-1} , insufficient internal energy to produce $\text{CH}_2=\text{C}=\overset{+}{\text{O}}\text{H}$ together with a hydroxyl radical. Therefore, **17** must rearrange before hydroxyl radical loss. One possibility is rearrangement to **16** via a 1,3-hydrogen shift requiring *ca.* 220 kJ mol^{-1} . Thus, this rearrangement would be rate-determining and followed by fast dissociation of the **16** thus generated, with excess energy in the transition state for dissociation. This situation is supported by the dissociation of directly generated **16** with an average kinetic energy release of only 1.3 kJ mol^{-1} , whereas OH loss from **17** (presumably via **16**) occurs with an average kinetic energy release of 9.2 kJ mol^{-1} .

The occurrence of a rate-determining isomerization $\mathbf{17} \rightarrow \mathbf{16}$ before OH loss starting from **17** is also supported by a primary deuterium isotope effect. In a rate-determining isomerization of **18** to the corresponding acetic acids, hydrogen should migrate faster than deuterium owing to a primary deuterium isotope effect. Indeed, experimentally for reactions occurring *ca.* 10^8 vibrations after generation of **18**, **19** is produced with 2.6 times the frequency of **20** (as evidenced by this preponderance of loss of OD over OH).



Both **16** and **17** undergo a second unimolecular decomposition by loss of H_2O . The competition of this process with OH radical loss in each case leads to the expectation that the activation energies for the processes will be similar. This is so: H_2O and OH losses from **16** require approximately 80 and 90 kJ mol^{-1} , respectively; H_2O and OH losses from **17** require approximately 200 and 220 kJ mol^{-1} , respectively.

The process of H_2O loss from **16** is a direct 1,2-elimination without prior rearrangement, as established by deuterium labelling. Thus, **21** loses only HOD. In reactions occurring *ca.* 10^{-5} s after excitation of **16**, the ratio of OH to H_2O losses is 92:8, and in **21** is 95:5. The occurrence of the primary deuterium isotope effect establishes that a C—D bond of **21** is stretched in the transition state, **22**, for HOD loss.



However, deuterium labelling establishes that H_2O loss from the enol form, **17**, unlike OH loss, does not occur via rearrangement to ionized acetic acid, **16**. Thus, for example, **23** loses only H_2O ; if it rearranged to **24** before water loss, then losses of both H_2O and HOD would be observed.

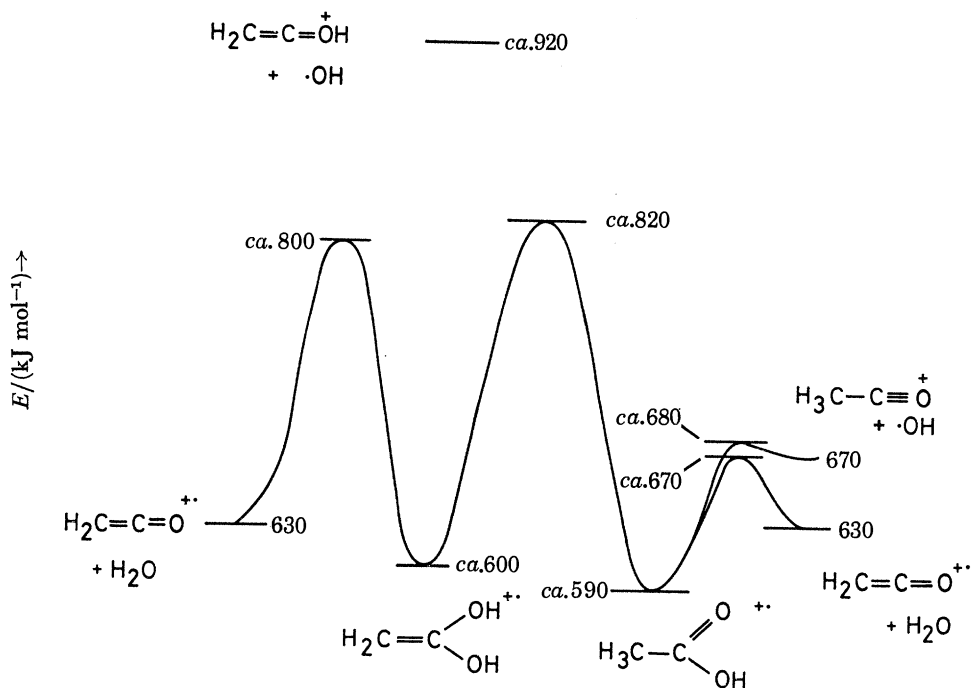


FIGURE 5. Potential energy profile (heats of formation of ions in kilojoules per mole) for the unimolecular reactions of ionized acetic acid and its enol form.

Therefore water loss from the enol form is a direct 1,2-elimination involving both hydroxyl groups (**23** → **25**). The detailed potential energy profile for reaction of ionized acetic acid and its enol form is summarized in figure 5.

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