

# Kinetic Energy Release and Energy Partitioning During the Ionic Fragmentation in Metastable Ions

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The kinetic energy released in the unimolecular decomposition of some metastable transitions has been investigated. It was found to have a significant temperature dependence in cases of H<sup>+</sup> loss from molecular ions. This is attributed to the tunnelling of H<sup>+</sup> atom through the centrifugal barrier.

The activation energies of the reverse reactions " $\epsilon_r^\ddagger$ " and the kinetic energy released " $T_B$ " have been determined for the loss of H<sup>+</sup> from acetonitrile and elimination of HCN from benzonitrile. The partitioning energy quotients  $q = T_B/\epsilon_r^\ddagger$  are found = 0.91 and 0.58 for acetonitrile and benzonitrile respectively.

## Introduction

The investigations of metastable ions in mass spectrometer have been shown to reveal many mechanistic details of unimolecular reactions of organic ions [1]. The kinetic energy released in metastable fragmentations is an important thermochemical quantity. It has been widely used as a sensitive means of characterizing reaction mechanisms [2, 3]. Small changes in this kinetic energy can be measured accurately as a function of the temperature of the sample molecules [4–7].

The partitioning of the excess potential energy of the transition states (or the activation energy of the reverse reactions  $\epsilon_r^\ddagger$ ) between the kinetic energy  $T$ , released during the reaction, and the internal energy  $\epsilon^*$  of the products depends strongly and systematically on the thermochemistry of the reaction [8] or the position of the potential energy barrier [9] on the reaction coordinate  $X_0^*$ .

In this paper, further measurements of the released translational energy as a function of ion source temperature in the dissociation of metastable ions of some nitrile compounds are reported. In addition, the energy partitioning accompanying the loss of H<sup>+</sup> loss acetonitrile and elimination of HCN from benzonitrile are discussed.

## Experimental

Metastable ion transitions were measured using the mass – analyzed ion kinetic energy spectrometer

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(MIKES). The MIKE Varian MAT CH<sub>5</sub> reversed Nier-Johnson geometry was operated at 3 kV ion accelerating voltage, 70 eV electron energy, 1 mA total emission current and  $8 \times 10^{-6}$  torr sample pressure. The ion source temperature was varied over the range 150–300 °C. Fragmentations occurring in the second field-free region were detected by sector voltage scan procedure [10].

The metastable peak width at half-height, after correction for the energy spread in the parent ion beam [5], was used to determine the characteristic value of kinetic energy release. Multiple measurements were carried out, and the energy release values were reproducible to better than  $\pm 5$  mev. The maximum value of the kinetic energy,  $T_B$ , was determined from the peak base-width. The reproducibility was  $\pm 8\%$ . Thermochemical data were determined from the literature [11–13].

## Results and Discussion

### *Temperature Dependence of the Translational Energy Release*

The variation in kinetic energy release as a function of ion source temperature in metastable ion dissociation has been investigated for some molecular ions. The data are given in Table 1.

The values of the released kinetic energy in the elimination of HCN from the molecular ions of propionitrile, 2-chloroacrylonitrile and *o*-toluonitrile are not affected by the change in the ion source temperature. Also, the loss of chlorine atom from 2-chloroacrylonitrile shows no change in the kinetic

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Table 1. Dependence of kinetic energy release on the ion source temperature.

Compound	Transition <sup>a</sup>	T (mev)			
		150 °C	200 °C	250 °C	300 °C
Acetonitrile	41 <sup>+</sup> → 40 <sup>+</sup> + 1	97 ± 0.5	100 ± 0.5	103 ± 0.5	106 ± 0.5
Propionitrile	55 <sup>+</sup> → 54 <sup>+</sup> + 1	91 ± 0.5	94 ± 0.5	98 ± 0.5	101 ± 0.5
	55 <sup>+</sup> → 28 <sup>+</sup> + 27	20 ± 2	21 ± 1	22 ± 0.5	23 ± 1
Acrylonitrile	53 <sup>+</sup> → 52 <sup>+</sup> + 1	144 ± 1	162 ± 2	202 ± 2	204 ± 3
2-chloroacrylonitrile	87 <sup>+</sup> → 60 <sup>+</sup> + 27	30 ± 1	32 ± 2	34 ± 2	33 ± 2
	87 <sup>+</sup> → 52 <sup>+</sup> + 35	14 ± 0.5	13.5 ± 1	14 ± 0.5	14.5 ± 1
Benzonitrile	103 <sup>+</sup> → 76 <sup>+</sup> + 27	28 ± 0.5	27.5 ± 1	28 ± 0.5	28.5 ± 1
<i>o</i> -Toluenitrile	117 <sup>+</sup> → 116 <sup>+</sup> + 1	112 ± 1	130 ± 2	172 ± 2	226 ± 3

<sup>a</sup> The shape of metastable peak resulting in these reactions are of Gaussian type.

energy released with the variation of ion source temperature. On the other hand, in the case of hydrogen atom loss from acetonitrile and propionitrile molecular ions, the kinetic energy released showed a slight variation with temperature. This is shown in Figure 1. In addition, the  $T$  released during the loss of a hydrogen atom from either acrylonitrile or *o*-toluenitrile is more sensitive to the change of ion source temperature. This is represent in Figure 2.

According to the quasi-equilibrium theory (QET), the rate of ionic dissociation is a function of the total energy transferred to the molecular ion. This total energy originates from; (a) the thermal energy,

and (b) the excitation energy transferred by the ionization processes. Thus, the variation of the thermal energy by the source temperature has an effect on the angular momentum and the internal energy of the ion. Therefore, two competitive processes may be expected:

(i) A process involving a transition state depending upon the angular momentum.

(ii) A process with different dependence upon rotational energy. As it has been reported [6] the second process exhibits a temperature-dependent energy release. The behaviour of the rotational energy distribution of molecular ion with temperature, might form the basis for an inquiry into centri-

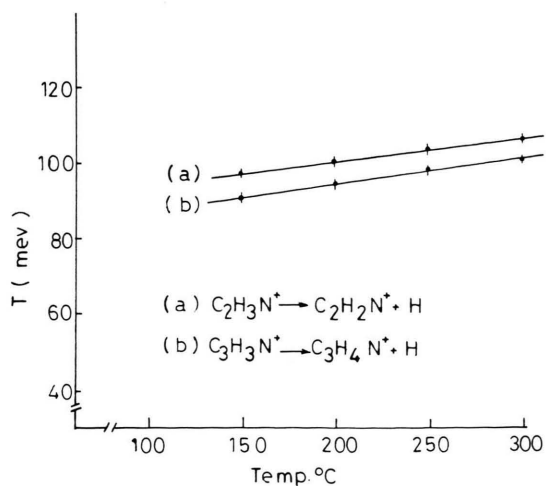


Fig. 1. Variation of  $T$ -values accompanying to loss of hydrogen atom from acetonitrile and propionitrile molecular ions with ion source temperature.

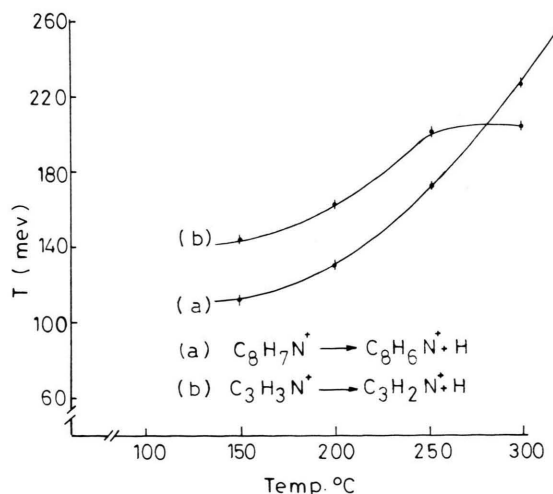


Fig. 2. Variation of  $T$ -values accompanying the loss of hydrogen atom from acrylonitrile and *o*-toluenitrile molecular ions with ion source temperature.

The results obtained for particular ions indicate that the kinetic energy release accompanying uni-

molecular metastable fragmentation of ions formed by electron-impact is approximately dependent on the ion source temperature. It is suggested that the ions are dissociated by a process involving a transition state depending upon rotational energy.

The variation observed in the energy partitioning quotient  $q$  and the reaction enthalpy  $\Delta H_R^\ddagger$  for the two reactions studied is interpreted as an alteration in the position of the transition state. It must be emphasized that the value of  $q$  depends obviously

on the details of the energy hypersurface of the reaction near the transition state.

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