ORGANIC MASS SPECTROMETRY, VOL. 28, 1225–1228 (1993)

Unimolecular Reaction Dynamics from Kinetic Energy Release Distributions. 1 — Dissociation of Bromobenzene Ions

J. C. Lorquet and B. Leyh†
Département de Chimie, Bâtiment B6, B-4000 Sart-Tilman (Liège 1), Belgium

Preliminary data on a new method for extracting dynamic data from the kinetic energy release distribution of metastable fragment ions are presented. This method can give information concerning the energy threshold of the reaction and the energy dependence of the rate constant (i.e. its logarithmic derivative). It was applied to bromine loss from bromobenzene cations.

INTRODUCTION

This paper contains preliminary results on the information which can be obtained from an analysis of the distribution of kinetic energy released in a metastable decomposition (KERD). We argue that, if attention is focused on the detailed shape of the distribution function itself and not only on an average kinetic energy release, several important pieces of information can be extracted. The proposed method should be capable of giving three kinds of data: first, the logarithmic derivative of the function $k(E)$ relating unimolecular fragmentation rates with the internal energy E, i.e. the slope d log $k/\mathrm{d}E$; second, the position with respect to the metastable window of the threshold energy E_0 for the onset of fragments; third, we hope, at a later stage of the development of the method, to assess the importance of exit-channel effects which occur as the fragments separate, i.e. potential information on the loose or tight nature of the transition state. We wish to dedicate this attempt to Professor John Holmes. in recognition of his outstanding contributions to the field.

However, we cannot emphasize too strongly that the analysis described below is still incomplete and that we still have to improve on the numerical techniques used in this work. For this first application, the choice of bromine loss from bromobenzene cations was guided by the abundance of reliable experimental data[1–6] on the thermochemistry and on the kinetics of this fragmentation, which is considered to be a paradigm for dissociations proceeding via a loose transition state.

THEORY

Consider a pair of separating fragments during the final stage of the reaction. In the case of a totally loose transition state, no energy conversion takes place as the fragments separate; the experimentally observed kinetic energy release distribution therefore reflects the energy partitioning between the reservoir of $3N - 7$ oscillators which makes up the transition state and the reaction coordinate. A tight transition state, on the other hand, implies that, as the fragments separate, part of their relative translational energy converts into vibrational–rotational energy of the fragments as a result of so-called 'exit-channel interactions.'

We are interested here in unimolecular decompositions occurring in a field-free region of a sector mass spectrometer. In such an experiment, the KERD of a metastable fragmentation is usually obtained using a numerical procedure developed by Holmes and Osborne.[7] The resulting KERD can then be written as an expansion of the form

$$P(\varepsilon) = \exp(-c_5\,\varepsilon/\gamma)\left[\sum_j a_j \varepsilon^{j/2}\right] \quad j = 0, 1, 2, 3, 4 \quad (1)$$

which suffers from the inherent disadvantage that it decreases nearly exponentially as ε increases. On the other hand, the correct (but hypothetical) KERD characterizing the decay of an ion with a sharply defined energy E should reach a value of zero when $\varepsilon = E$, i.e. when all of the available internal energy is converted into translation. The exponential decrease in Eqn (1) simulates the fact that the energy of the transition state is never sharply defined. A further average has to be taken over the collection efficiency $T(k)$ of the metastable species decaying in the relevant field-free region, known to be given by the following expression:

$$T[k(E)] = B\{\exp[-k(E)\tau_1] - \exp[-k(E)\tau_2]\} \quad (2)$$

where τ_1 and τ_2 are the entry and exit times in the field-free region, respectively, and B is a normalization constant.

A more appropriate function for a KERD (at least for not too tight transition states) is

$$P(\varepsilon \mid E) = A\varepsilon^{\alpha}(E - \varepsilon)^{\beta} \quad 0 \leqslant \varepsilon \leqslant E \quad (3)$$

where E is the total energy of the ion, A is a normalization factor chosen so that the zeroth-order moment

---

† Chercheur qualifié du Fonds National de la Recherche Scientifique (Belgium).

0030–493X/93/101225–04 $07.00

Received 25 May 1993
Accepted 14 June 1993

of the KERD should be equal to unity:

$$\int^{E} P(\varepsilon \mid E)\, \mathrm{d}\varepsilon = 1$$

Note that $P(\varepsilon \mid E)$ represents the KERD in the case of an ideally well defined internal energy E.

The exponents α and β are fractional positive numbers which, in the limiting case of a totally loose transition state, can be expected to be related to the density of states of the fragments.[8–11]

As mentioned above, in the kind of experiments considered here, the ions are not energy selected (what is selected is rather a time window) and the theoretical expressions for the observable quantities have to be averaged over the probability of fragmentation in the appropriate field-free region given by Eqn (2).

From Eqns (2) and (3), one obtains, for the nth-order moment of the observed KERD,

$$\mu_n = AB \int^{\infty} \mathrm{d}E\{\exp[-k(E)\tau_1] - \exp[-k(E)\tau_2]\} \times \int^{E} \mathrm{d}\varepsilon\varepsilon^{\alpha+n}(E-\varepsilon)^{\beta} \qquad (4)$$

These moments are experimentally observable. Equation (4) can be analytically evaluated if the rate constant $k(E)$ is assumed to increase with energy as

$$\begin{aligned} k(E) &= \lambda E^{\nu} \quad & E \geqslant E_0 \\ k(E) &= 0 & E \leqslant E_0 \end{aligned} \qquad (5)$$

E_0 is thus the kinetic reaction threshold. In this paper, all energies are measured with respect to the thermodynamic threshold of the reaction, i.e. the energy of the dissociation asymptote.

Equation (2) admits a maximum for a particular value of the rate constant denoted k^{opt}. Let us call E_S the corresponding internal energy. One has (assuming $E_S \geqslant E_0$)

$$k^{\mathrm{opt}} = \ln(\tau_2/\tau_1)/(\tau_2 - \tau_1) = \lambda E_S{}^{\nu} \qquad (6)$$

E_S is close to the average internal energy. This quantity has been determined for several reactions by Burgers and Holmes.[1]

Our goal is to determine the six unknown quantities α, β, E_0, E_S, λ and ν from a knowledge of the first four moments of the KERD (i.e. μ_1, μ_2, μ_3 and μ_4) and other observables such as the energy ε_M at which the experimental KERD goes through a maximum, the height of this maximum, the inflection point of the KERD and the curvature of the KERD at its maximum. This generates a set of non-linear and even non-algebraic equations which cannot be solved by elementary or brute-force methods. It is possible to eliminate some of the unknowns and to reduce the problem to a system involving four unknown quantities: α, β, E_0/E_S and ν. This, of course, reduces the information but increases the numerical stability of the solution. The details are not given here since we do not claim to have completely optimized the algorithm as yet.

What do we learn from the extracted quantities? The values of the exponents α and β are in principle determined by translational, rotational and vibrational state densities,[8–11] at least if no exit-channel effects operate, i.e. if the transition state is totally loose. In particular, the more the exponent α deviates from its *a priori* value, $\frac{1}{2}$, the more effective is the conversion of the translational energy of the separating fragments to internal (rotation–vibration) energy of the fragments.

The ratio E_0/E_S specifies the position of the dissociation threshold with respect to the metastable window. A value of zero indicates that the onset of the reaction lies outside the metastable window, i.e. outside the range of energies where Eqn (2) has non-negligible values. This is the case for the bromobenzene dissociation reported below.

The exponent ν determines the value of the logarithmic derivative of the rate constant. One has, from Eqn (5)

$$\mathrm{d}\log_{10}k(E)/\mathrm{d}E = \nu/2.3E \qquad (7)$$

There is one missing piece of information [i.e. the quantity λ in Eqn (5)] which we have not been able to determine so far from our analysis. It can be considered as the integration constant of the differential Eqn (7). However, considering Eqn (6), we note that several workers[1–4] using PIPECO experimentation have determined the value of the rate constant at least at a particular value of the internal energy. The use of their value allows us to obtain the full function $k(E)$.

EXPERIMENT

The ion kinetic energy spectrum of the $\mathrm{PhBr^+} \rightarrow \mathrm{Ph^+} + \mathrm{Br}$ metastable dissociation was obtained via the accelerating voltage scan (HV scan) technique using a forward geometry AEI-MS9 mass spectrometer. The first field-free region of our MS9 instrument was enlarged owing to the installation of a collision cell. The energy-resolving slit was closed to reach a main beam width of ~3 eV. This energy spread is negligible compared with the natural width at half-height of the metastable peak (50 eV at a kinetic energy of $\mathrm{Ph^+}$ of 3 keV). These kinetic energy spectra were recorded at two values of the fragment ion kinetic energy, viz 3 and 4 keV.

The KERD associated with a metastable fragmentation can be extracted from such a kinetic energy spectrum by differentiation.[7] In this work, this was done using the classical Holmes–Osborne procedure[7] outlined in the Theory section.

The experimental conditions were as follows: trap current, 30 μA; electron energy, 70 eV; ion source pressure (measured at an ion gauge located between the ionization chamber and the source diffusion pump, ~15 cm from the ionization region), 8.0×10^{-7} Torr (1 Torr = 133.3 Pa). Bromobenzene provided by Fluka (purity 99.5%), was used as received.

RESULTS

The KERDs were obtained at both fragment kinetic energies (3 and 4 keV) mentioned above and for the loss

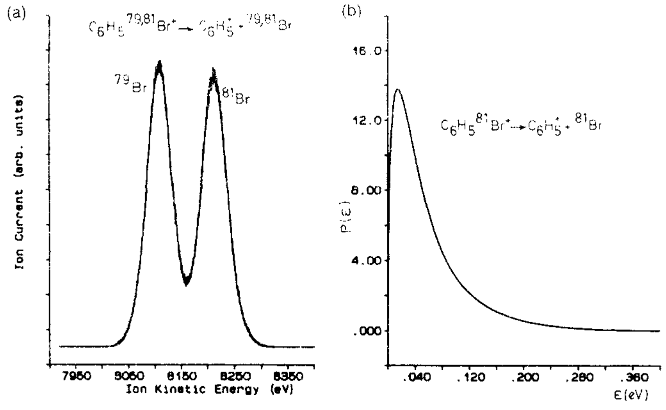

Figure 1. (a) Ion kinetic energy spectrum for the $C_6H_5Br^+ \rightarrow C_6H_5^+(4\ \text{keV}) + {}^{79,81}Br$ metastable decomposition occurring in the first field-free region of the MS9 mass spectrometer. This spectrum was recorded using the accelerating voltage scan technique. (b) KERD obtained from (a) for the $C_6H_5Br^+ \rightarrow C_6H_5^+ + {}^{81}Br$ dissociation using the Holmes–Osborne procedure.[7]

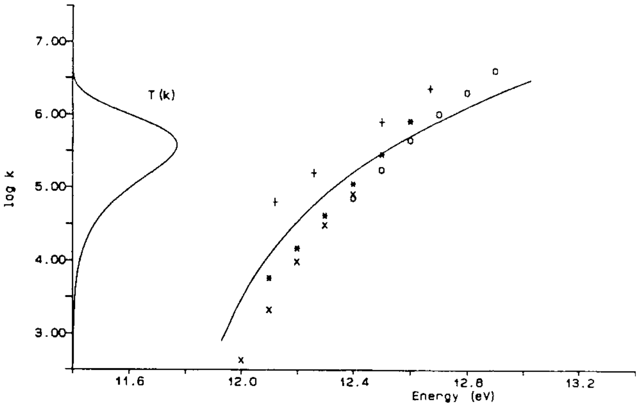

Figure 2. Variation with internal energy of the rate constant for the $C_6H_5Br^+ \rightarrow C_6H_5^+ + Br$ decomposition. Solid line $k(E)$ is given by Eqn (8) using the ν value obtained by our analysis of the KERD; +, Ref. 2; ○, Ref. 3; ∗, Ref. 4; ×, Ref. 6. The transmission function $T(k)$ for the first field-free region [Eqn (2)], displayed on the left-hand side, was calculated for $\tau_1 = 1.74$ μs, and $\tau_2 = 3.77$ μs.

of both ^{79}Br and of ^{81}Br. The agreement between the four KERDs is very good. As an example, Fig. 1(a) shows the ion kinetic energy spectrum corresponding to the $C_6H_5{}^{79,81}Br^+ \rightarrow C_6H_5{}^+(4\ \text{keV}) + {}^{79,81}Br$. The corresponding KERD for loss of ^{81}Br is displayed in Fig. 1(b).

The analysis presented in the Theory section leads to the following results.

The ratio E_0/E_S is equal to zero, which means that the thermodynamic threshold for the reaction lies outside the experimental window. This result is in keeping with the large kinetic shift observed for this reaction.[1-6] As found by many workers using energy-selected electrons,[1] PIPECO measurements,[2,3] photoionization mass spectrometry[4] and time-resolved photodissociation,[5,6] the minimum value of the rate constant is $<6 \times 10^3\ \text{s}^{-1}$.

Concerning the rate constant variation with internal energy [Eqn (5)], we obtain a value $\nu = 4.4$. Under our experimental conditions, $\tau_1 = 1.74$ μs, $\tau_2 = 3.77$ μs and $k^{\text{opt}} = 0.38 \times 10^6\ \text{s}^{-1}$. This particular value of k was obtained by Rosenstock *et al.*[3] for a photon energy of 12.56 eV. Substituting this value into Eqn (5) and adopting the value of 11.73 eV for the energy of the separated fragments,[6] one obtains the following expression for the rate constant:

$$\log k = 5.94 + 4.4 \log_{10}(E - 11.73) \qquad (8)$$

if the energies E are measured from the zero-point energy of the neutral bromobenzene molecule. This function is plotted in Fig 2 and compared with several experimental and calculated data from the literature. The agreement is satisfactory.

The best fit value of α is 0.309. This value has to be compared with the reference value for a totally loose transition state, i.e. 0.5. At the present stage of our investigations it is difficult, however, to interpret this result in terms of exit-channel interactions, since this would require further theoretical developments and a great deal of experience with various cases. Nevertheless, this result is compatible with another observation. In the case of a totally loose transition state, the ratio of the average KER to the value of ε at the maximum of the KERD should be 3, whereas our experimental value for this ratio is equal to 4.2 (3.9 in Ref. 6).

CONCLUSION

The results presented, although preliminary, show that it is possible to extract basic dynamic information from an appropriate analysis of KERD curves.

In the case of the Br loss from bromobenzene, we find that the onset of the reaction lies well outside the metastable window, which is an additional confirmation of the kinetic shift investigated by many workers.[1-6]

Further developments are necessary to be able to extract the complete $k(E)$ law. As illustrated in the bromobenzene case, the present method is limited to a determination of the logarithmic derivative of the function $k(E)$ in the range of values of E where the collection efficiency [Eqn (2)] assumes non-negligible values. The obtention of numerically stable values for E_S and λ would enable us to determine the complete function $k(E)$ and also to carry out a surprisal analysis[8-11] which would shed light on the tight or loose nature of the transition state.

Acknowledgements

We are indebted to Professors J. L. Holmes and Ch. Lifshitz for helpful discussion and for suggesting the case of bromobenzene. B. L. is grateful to the Fonds National de la Recherche Scientifique (Belgium) for a research associate position. This work was supported by research grants from the Fonds de la Recherche Fondamentale Collective (Belgium) and the University of Liège.

REFERENCES

1. P. C. Burgers and J. L. Holmes, *Int. J. Mass Spectrom. Ion Processes* **58**, 15 (1984).
2. T. Baer, B. P. Tsai, D. Smith and P. T. Murray, *J. Chem. Phys.* **64**, 2460 (1976).
3. H. M. Rosenstock, R. Stockbauer and A. C. Parr, *J. Chem. Phys.* **71**, 3708 (1979).
4. S. T. Pratt and W. A. Chupka, *Chem. Phys.* **62**, 153 (1981).
5. R. C. Dunbar and J. P. Honovich, *Int. J. Mass Spectrom. Ion Processes* **58**, 25 (1984).
6. Y. Malinovich, R. Arakawa, G. Haase and C. Lifshitz, *J. Phys. Chem.* **89**, 2253 (1985).
7. J. L. Holmes and A. D. Osborne, *Int. J. Mass Spectrom. Ion* Phys. **23**, 189 (1977).
8. E. Zamir and R. D. Levine, *Chem. Phys.* **52**, 253 (1980).
9. J. Momigny, R. Locht and G. Caprace, *Chem. Phys.* **102**, 275 (1986).
10. E. Illenberger and J. Momigny, *Gaseous Molecular Ions*, pp. 199–202. Springer, New York (1992).
11. R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*. Oxford University Press, London (1987).