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Short communication

Threshold photoelectron photoion coincidence spectroscopy sheds light on the dissociation of pyrrole and thiophene molecular ions

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ABSTRACT

Threshold photoelectron photoion coincidence spectroscopy was employed to examine the loss of ethyne from ionized pyrrole and thiophene near their dissociation thresholds as a function of internal energy and reaction time. The B3-LYP/6-311+G(3df,3pd) minimum energy reaction pathways for ethyne loss from both ions are presented. The experimental molecular ion breakdown curves were modeled with RRKM theory. For ionized pyrrole, the fitting results in confirmation of the transition state energies in the decomposition pathways. For ionized thiophene, the modeling suggests that ethyne loss is a concerted process rather than a true step-wise reaction. If so, the fitting yields a $\Delta_f H_{298}$ for $CH_2CS^{+\bullet}$ of 1033 ± 2 kJ mol^{-1}.

1. Introduction

In earlier work from the Daresbury Laboratory electron storage ring, the photoelectron spectroscopy and dissociation of ionized pyrrole [1] and thiophene [2] were investigated with tuneable synchrotron radiation from 11.8–27.5 eV (pyrrole) and 12.0–28.0 eV (thiophene). The results were in good agreement with earlier threshold photoelectron photoion coincidence spectroscopy (TPEPICO) work by Baer and co-workers [3,4] and previous tandem mass spectrometry studies [5–7]. In the present communication, TPEPICO was employed to examine the loss of ethyne from the two molecular ions near their dissociation thresholds as a function of ion source residence, and thus reaction, time. The experimental and computational procedures used have been extensively described in a number of previous publications [8–17].

2. Results and discussion

The B3-LYP/6-311+G(3df,3pd) minimum energy reaction pathway for ethyne loss from ionized pyrrole is shown in Fig. 1. This surface was originally presented at the B3-LYP/6-311+G(2d,p)//HF/3-21G* level of theory by Rennie et al. [1] and has simply been re-optimized at the higher level of theory for this study. Competing with ethyne loss is the loss of HCN to form the $C_3H_4^{+\bullet}$ cation. While this surface was also explored by Rennie et al., it is a minor channel and in the present study has been approximated by a single transition state leading to products. To simplify the kinetic treatment, it has been assumed that once the system reaches TSC, it proceeds quickly to products. This results in a two-well surface leading to two products. The kinetic model used for this situation has been described by Baer et al. [18] (case A, since interconversion of the pyrrole ion and isomer X is fast compared to dissociation). The experimental TPEPICO breakdown diagrams (for ion source residence times of 1.116, 3.116 and 5.116 μs) [10,12] and the resulting theoretical fits are shown in Fig. 2. Agreement is very good when employing the B3-LYP/6-311 + G(3df,3pd) relative energies and scaled vibrational frequencies. The only adjustments that were made were to the energy of TSC, and of course the energy of TSE, which was not calculated and represents an effective transition state. The E_0 for TSE of 3.698 eV is only moderately lower than the highest point (4.0 eV) on the B3-LYP/6-311+G(2d,p)//HF/3-21G*

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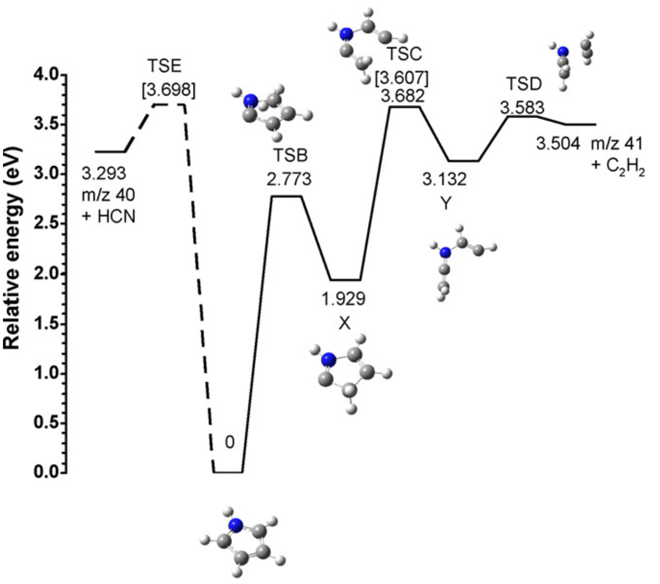

Fig. 1. B3-LYP/6-311+G(3df,3pd) minimum energy reaction pathway for the two competing near threshold dissociation pathways of ionized pyrrole. The channel leading to $C_3H_4^{+\bullet}$ + HCN has been approximated by a single transition state. Values in brackets are from the RRKM fitting of the breakdown diagrams.

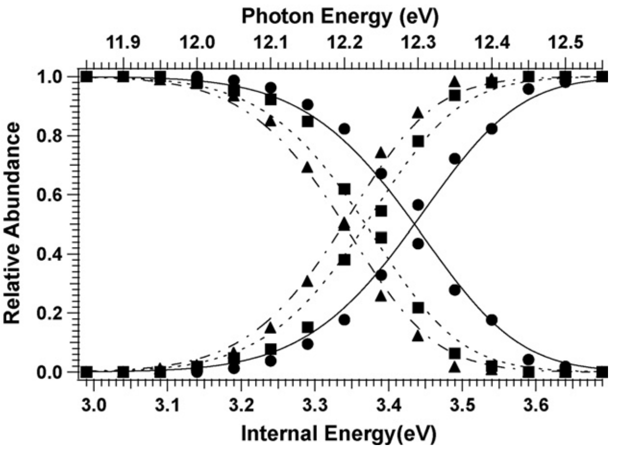

Fig. 3. Experimental TPEPICO breakdown curves for ionized thiophene (points) together with the best RRKM fits (solid lines) at three ion source residence times (●: 1.116, ■: 3.116 and ▲: 5.116 μs).

level of theory surface obtained previously by Rennie et al. [1] Willet and Baer investigated the competitive fragmentation of pyrrole ions also by TPEPICO. They fixed the thermochemistry of the $C_3H_4^{+\bullet}$ channel and derived a Δ_fH_{298} for the $C_2H_3N^{+\bullet}$ ion from the loss of ethyne, of 1004 ± 4 kJ mol^{-1} based on the RRKM fitted threshold of 11.75 eV (relative to neutral pyrrole). Our measured thresholds for the two competing channels clearly relate to barrier heights for isomerization and not products, though the energy of TSC is very close to that of the $C_2H_3N^{+\bullet} + C_2H_2$ products. Note that $CH_2CNH^{+\bullet}$ is the only thermochemically possible product $C_2H_3N^{+\bullet}$ ion in the internal energy regime explored in our experiment. Willet and Baer set the threshold for $C_3H_4^{+\bullet}$ formation at 12 eV, only slightly higher than the 11.91 eV we find, which corresponds to a net barrier for the reaction, and not a threshold for product formation.

In the case of thiophene, the fitted breakdown curves are shown in Fig. 3, and the calculated surface is in Fig. 4. The kinetics were modeled based on a two-well, one product channel approximation, assuming that once the system overcomes TS2 it goes on to form products. The mathematical details of this scenario have been presented by Baer and co-workers in the case of the dissociation of ionized butadiene [19]. There is no effect on the fitting from changing the $\Delta^{\ddagger}S$ associated with TS1 as the sum-of-states cancels out in the model. We can change the energy for TS1 (relative to the molecular ion) within the range 2.267 ± 0.100 and have satisfactory fits to the data. The energy of TS1 dictates the fraction of the products made by the fast and slow components of the rate constant. Raising TS1 cuts back the reverse reaction from X to ionized thiophene, thereby increasing the role of k_{fast} (Fig. 5). The relative energy for the channel leading from isomer X to products needs to be much lower than the B3-LYP/6-311+G(3df,3pd) energy for TS2 (3.034 ± 0.020 eV compared to the calculated value of 3.554 eV) and $\Delta^{\ddagger}S$(300 K) must be considerably higher (∼+45–50 rather than +11 J K^{-1} mol^{-1} calculated for TS2). This implies that TS2 is not even accessed during the reaction. Indeed, this energy is actually very close to the B3-LYP/6-311+G(3df,3pd) energy difference between ionized thiophene and

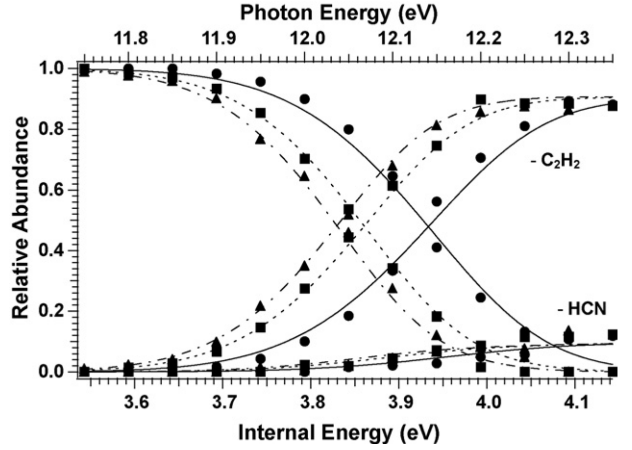

Fig. 2. Experimental TPEPICO breakdown curves for ionized pyrrole (points) together with the best RRKM fits (solid lines) at three ion source residence times (●: 1.116, ■: 3.116 and ▲: 5.116 μs).

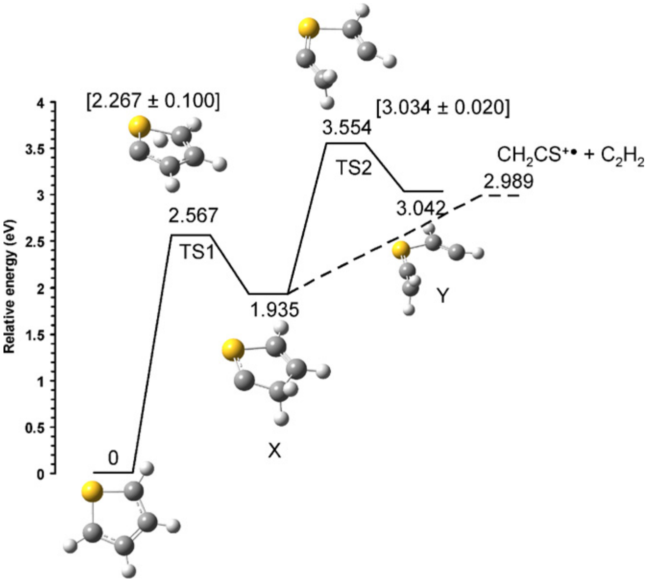

Fig. 4. B3-LYP/6-311+G(3df,3pd) minimum energy reaction pathways for the loss of ethyne from ionized thiophene. Results from the fitting are in brackets.

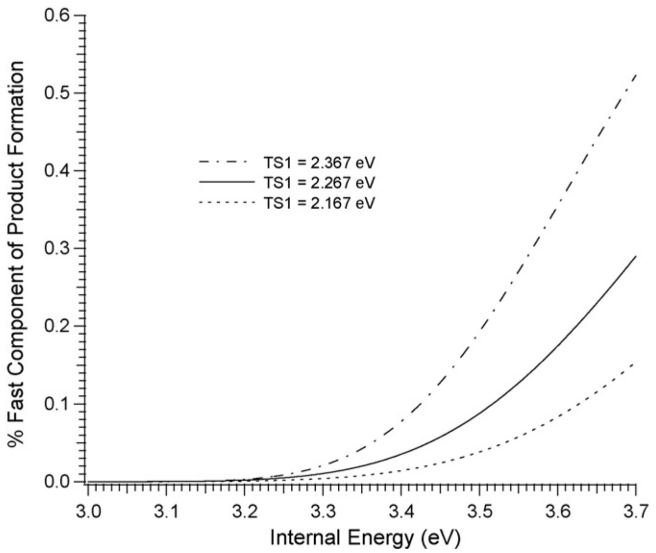

Fig. 5. Calculated participation of the fast-component of the rate constant as a function of the energy of TS1.

the final products, $CH_2CS^{+\bullet} + C_2H_2$ (2.989 eV), indicating that a concerted breaking of both a C—C and C—S bond may occur leading directly to products, rather than the step-wise ring opening to first form isomer Y shown in the figure. Butler and Baer [4] fit their TPEPICO thiophene data and obtained an appearance energy (AE) for C_2H_2 loss of 12.1 ± 0.1 eV. Assuming a single-well potential, this gave a product ion CH_2CS^+ Δ_fH_{298} of 1059 ± 12 kJ mol^{-1}. The present result is 11.89 ± 0.04 eV (3.034 ± 0.020 + 8.86 ± 0.02 eV [20]), provided the reaction skirts TS2 as discussed above. The B3-LYP/6-311+G(3df,3pd) relative energy for the products, $CH_2CS^{+\bullet} + C_2H_2$ is 11.849 (2.989 eV + 8.86 ± 0.02 eV). Together with the experimental Δ_fH_{298} for neutral thiophene (116.4 kJ mol^{-1}) [20] and ethyne (226.73 kJ mol^{-1}) [20] yields a $CH_2CS^{+\bullet}$ Δ_fH_{298} of 1033 ± 2 kJ mol^{-1}. NIST [20] quotes a value of 1010 kJ mol^{-1} without a reference, but this value appears in the earlier Lias et al. [21] compendium, and is actually for CH_3S^+. A more recent value for the Δ_fH_{298} for neutral thiophene (218.4 kJ mol^{-1}) [20] places the $CH_2CS^{+\bullet}$ Δ_fH_{298} at 1134 ± 2 kJ mol^{-1}.

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