On the absolute photoionization cross section of two reactive ketenes: fulvenone and 2-carbonyl cyclohexadienone

Zeyou Pan1,2, András Bodó1, Jeroen A. van Bokhoven1,2 and Patrick Hemberger1

1 Paul Scherrer Institute, Forschungsstrasse 111, 5232 Villigen, Switzerland
2 ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

Salicylamide pyrolysis

Advantage:
1. Detect elusive and short-lived intermediates, like radicals.
2. Identify isomers.

ms-TPES of 6-carbonyl-2,4-cyclohexadien-1-one

Fig. 3 | ms-TPES (black trace) and PI spectrum (grey trace) of 6-carbonyl-2,4-cyclohexadien-1-one together with Franck-Condon (FC) simulations for the \( \tilde{A} \rightarrow \tilde{X} \) (red trace) and \( \tilde{A} \rightarrow \tilde{X} \) (green trace) transitions. The harmonic frequencies and geometries of neutral and ion are calculated at B3LYP/6-311+G(dp) level of theory.

ms-TPES & theoretical calculations / reference data

Fig. 1 | Temperature-dependent ToF mass spectra of salicylamide pyrolysis @ \( hv = 10.5 \) eV. Products were identified by ms-TPES.

Fig. 2 | Potential energy surface of the salicylamide pyrolysis. The internal energies were calculated using G4 composite methods. Interestingly, 2 not only can lose CO producing fulvenone but also can ring-close to the almost isoenergetic 6 subsequently forming 5 by CO loss.

Fig. 5 | The ionization cross section of fulvenone shown with a 20% range of uncertainty. \( \text{NH}_3 \) was used as calibrator for fulvenone PICS and the \( \text{NH}_3 \) PICS was relied on the determination of XIA et al. The same method was applied to Fig. 6.

Fig. 6 | The lumped photoionization cross section (red curve) of the \( \text{m/z} \) 120 species 2-carbonyl cyclohexadienone 2 and benzpropiolactone 6 along with the fulvenone fragment (blue curve). Effective PICS of the ketoketene 2 is depicted in black. We assume a conservative error bar of 40%.

Acknowledgement

1. Z. Pan et al., Chemical Science, 2021, 12, 3161-3169

Reference