

DIRECT OBSERVATION OF ETHYL RADICAL IN THE PYROLYSIS OF ETHANE

NADAV GENOSSAR-DAN, SHARONA ATLAS, DANA BRESKER, SHANI HAR LAVAN, URI ZAMIR, ILLYA ROZENBERG, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*; THANH LAM NGUYEN, *Department of Chemistry, University of Florida, Gainesville, FL, USA*; PATRICK HEMBERGER, *General Energy, Paul Scherrer Institute, Villigen, Switzerland*; JOSHUA H. BARABAN, *Chemistry, Ben-Gurion University of the Negev, Beer-Sheva, Israel*.

The observation and quantification of reactive intermediates is crucial for the validation and development of kinetic models. However, very often the same reactivity that makes the role of such species important in reaction networks hinders our ability to detect them, due to their low concentrations and short lifetimes. As a result, many kinetic models rely on the formation of various intermediates which were never quantified, and sometimes not even established.

One particularly important case is the pyrolysis of ethane (C_2H_6). As this reaction plays a central role in industrial processes such as production of ethylene (C_2H_4) and combustion of ethane, the understanding of its underlying mechanism is crucial for process optimization, in order to reduce economic and environmental costs. Although ethyl (C_2H_5) is a key intermediate towards the formation of ethylene, it has never been directly observed in this reaction.

We report a double imaging photoelectron photoion coincidence (i^2 -PEPICO) spectroscopy study of the flash pyrolysis of ethane and its isotopologue CH_3CD_3 using VUV radiation generated by the Swiss Light Source (SLS) and a resistively heated SiC microreactor reaching temperatures of up to 1700 K. This apparatus is especially appropriate for the observation of reactive radicals in thermal reactions – the short residence times before quenching of the intermediates, and the low ionization energies of radicals favor their observation. These properties allowed the observation of ethyl and its isotopologues, which were identified through their threshold photoelectron spectrum (TPES), by comparison to reported spectra and simulated ones. Together with observation of isotopic selectivity and comparison to fully coupled computational fluid dynamics and kinetics simulations, these results provide valuable mechanistic insights into the initiation steps of this reaction.