

Positive ion chemistry in flames: mass-spectrometric and kinetic modeling study

Denis Knyazkov¹, Andrey Cherepanov^{1,2}, Ilya Gerasimov¹, Tatyana Bolshova¹,
Vitaly Kiselev¹, Andrey Shmakov¹

¹ Voevodsky Institute of Chemical Kinetics and Combustion, 3 Institutskaya str., Novosibirsk, Russia, 630090

² Novosibirsk State University, 1 Pirogova str., Novosibirsk, Russia, 630090

knyazkov@kinetics.nsc.ru

Charged species occurring in flames have been extensively studied for several decades. In the last 10 years, the ion chemistry in flames has again become of considerable interest. This is related to the increased demand for new approaches to monitoring of combustion processes, particularly, with application of electric field and various forms of gas discharge. Recently, the interest in ionic flame chemistry has especially increased in connection with the opportunities offered by the ion sensitive technologies for controlling the operation of engines.

Although the concentration of naturally occurring charged species in flames is low ($\sim 10^8$ - 10^{11} cm⁻³), they can be detected by molecular beam mass spectrometry (MBMS). Since the ion-molecular reactions are rather fast, they are easily equilibrated. Therefore, the concentrations of some neutral species can potentially be derived from the signals of flame-sampled cations if the equilibrium constants of the major pathways of the ions formation and consumption are known. This opens new opportunities for determination of concentrations of those neutral species that are hard to detect by conventional flame-sampling MBMS, such as, for example, polycyclic aromatic hydrocarbons, which play a key role in soot formation as precursors and pose the health hazards in combustion emissions. Thus, understanding the kinetics of cation formation in flames provides the basis for the development of new diagnostic methods.

The kinetic models for ion chemistry in flames presented in the literature are imperfect due to the lack of reliable experimental data for their validation. In this work, the recent data from the laboratory of combustion kinetics ICKC SB RAS of MBMS measurements of spatial distributions cations in premixed burner-stabilized flames of different fuels (methane, ethylene, dimethyl ether, ethanol) are reported. The effect of sampling probe on the measured distributions of cations is discussed. The ion chemistry mechanisms proposed earlier in the literature were validated against the novel experimental data on the spatial distributions of the major cations presenting in all flames, like hydronium (H₃O⁺), HCO⁺, protonated ketene, protonated methanol, C₃H₃⁺. An improved kinetic mechanism for the charged species was developed and its performances as compared to that published recently by Chen et al. [Combust. Flame 202 (2019) 208] are demonstrated. To this end, the highly accurate W2-F12 quantum chemical calculations were used to obtain the reliable formation enthalpies of all cations considered in the mechanism. The mechanism is extended with the reactions involving C₃H₅⁺ cation, which was detected in ethylene flames, and the reaction pathways involving C₃H₃⁺ are revised. The key directions for the further refinement of the mechanism are considered based on the insights derived from the experimental observations.

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