

Methyldyne radical reactions with hydrocarbons: kinetics at low temperature and product branching ratios

Astrid Bergeat^{1,2}, Philippe Caubet¹, Michel Costes¹
Nicolas Daugey¹ and Jean-Christophe Loison²

¹ First experiment and ²Second experiment in Laboratoire de Physico-Chimie Moléculaire CNRS UMR5803, Université Bordeaux 1, F-33405 Talence Cedex, France
email: a.bergeat@lpcm.u-bordeaux1.fr

Abstract.

CH radical reactions with hydrocarbons could play a role in the atmospheres of Titan, Pluto or Triton as well as in interstellar clouds (ISCs), where the hydrocarbon compounds were detected and the temperatures are very low, *i.e.* ~ 95 K down to ~ 38 K at the surface of these satellites and planet and from 50 K down to 10 K in ISCs. In fact, in modelling the processes occurring in these low-temperature environments, researchers generally still have to extrapolate the high-temperature kinetic data mainly obtained in the temperature range above 300 K. However, for many neutral-neutral reactions studied, the rate constants exhibit essentially non-Arrhenius behaviour at low temperatures.

The temperature dependences of the methyldyne radical reactions with methane, allene, methylacetylene and propene were studied in our new supersonic flow reactor coupled with pulsed laser photolysis (PLP) and laser induced fluorescence (LIF) techniques. Three Laval nozzles were designed to provide uniform supersonic expansions down to 77 K. The rate constants for the CH + CH₄ reaction are in good agreement with the temperature dependence proposed by A. Canosa et al., *i.e.* $3.96 \times 10^{-8} \times (T/K)^{-1.04} \exp(-36.1K/T)$ in the range 23–298 K. The rate constants of the CH + C₃H₄ (allene), CH + C₃H₄ (methylacetylene) and CH + C₃H₆ (propene) reactions exhibit a small temperature dependence between 77 and 170 K, are close to the gas kinetic limit and could thus contribute to the chemistry in the dense molecular clouds or outer planets atmospheres (Titan, Pluto and Triton for example) rich in hydrocarbons.

The reactions of CH radical with several saturated and unsaturated hydrocarbons were studied, at room temperature, in a low-pressure fast-flow reactor. The absolute atomic hydrogen productions were determined at 300 K by V.U.V. resonance fluorescence, the reference used being the H production from the CH + CH₄ and H₂S reactions. *Ab initio* studies of the different stationary points relevant to some of those reactions and RRKM calculations have been performed for extrapolations at low temperatures. For the CH + saturated hydrocarbons reactions (C₂H₆, n-C₃H₈, n-C₄H₁₀, n, iso and neo-C₅H₁₂ and n-C₆H₁₄), the H production is rarely the main channel, which means that these reactions lead to a large variety of unsaturated hydrocarbons and radicals. On the other hand, CH radical is a good candidate in the synthesis of large organic molecules, by producing mainly H atoms and larger carbon skeleton when CH radical reacts with the unsaturated hydrocarbons C₂H₂, C₃H₄, C₂H₄, C₃H₆ and C₄H₈, compared to the carbon atom reactions that we have studied previously.

Keywords. Astrochemistry, molecular processes, methods: laboratory

References

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