Rate constants calculations of the CH_2 + CH_2CO reactions in triplet and singlet states by ab initio methods

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A variety of oxygen-containing compounds, such as alcohols, aldehydes, ketones, and others, are often formed in combustion flames. One of the simplest and yet important species produced in burning of hydrocarbon fuels is ketene. Mechanism and rate constants of reactions of ketene with methylene radical in triplet and singlet states were characterized through ab initio calculations of the PES combined with RRKM-ME calculations. The reactions have been shown to proceed through four main channels for triplet methylene and three channels for singlet methylene. The most important channels of reaction of ketene with triplet methylene lead to formation $HCCO$ + CH_3 and C_2H_4 + CO products. The alternative reaction pathways, in particular, the formation of allene + O and the production of acetylene and formaldehyde are shown to be insignificant even at the highest temperatures considered. The predominant products of the reaction of ketene with singlet methylene are C_2H_4 + CO. The formation of these products proceeds through a collisionally stabilized intermediate CH_3CHCO. The calculated rate constants at different pressures were fitted by the modified Arrhenius expressions, which are proposed for kinetic modeling of ketene reactions in combustion. The results show that the rate constants to produce C_2H_4 + CO exhibit significant pressure dependence, whereas those to form $HCCO$ + CH_3 are independent of pressure.

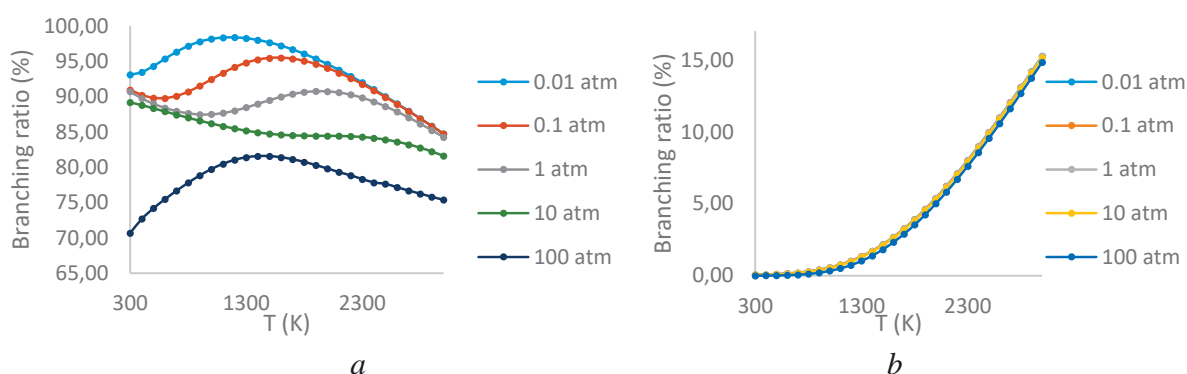Fig 1. Branching ratios of different reaction channels calculated at different pressure: CO+$^1C_2H_4$ (a); H_2CC+^1H_2CO (b).