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THE CH_3O_2+ClO ATMOSPHERIC REACTION: THEORETICAL DESCRIPTION AND ROLE IN STRATOSPHERIC OZONE BUDGET

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EXTENDED ABSTRACT

The reaction between methylperoxy radicals and chlorine monoxide,
CH_3O_2+ClO --> products
is an important atmospheric reaction leading mainly to the formation of active atomic chlorine. Consequently it plays a critical role in the catalytic ozone depletion cycle in the lower Stratosphere. For this reason several experimental studies have been devoted to the exploration of the mechanism of this reaction, which have verified the dominant role of the Cl production pathway. Recent experimental findings however, indicate that another pathway producing methyl hypochlorite, CH_3OCl, is also possible thus, reducing considerably the extent of the dominant Cl production pathway and its severe effect on the stratospheric ozone budget.

In the present work we employ high quality quantum mechanical computational methods to investigate the energetics of the possible reaction pathways and the relative importance of each reaction channel :

CH_3O_2+ClO-> CH_3O+ClOO --> CH_3O+Cl+ $(^3\Sigma)O_2$
CH_3O_2+ ClO-> CH_3OCl +$(^3\Sigma)O_2$

The energy calculations indicate that both channels are thermodynamically feasible but the second channel is energetically more favourable than the first. However, it takes place directly on the triplet surface and therefore it presents a lower probability compared to the first route which occurs on the singlet ground state surface of the reaction.
The net conclusion of the present study is that the Cl producing channel is the dominant pathway with whatever consequences may this mean for the stratospheric ozone concentration. Nevertheless, we show that the CH_3OCl producing channel presents also a small but non- negligible probability and weakens the severe effect of the first reaction channel in the stratospheric O_3 world balance.

Key words : methylperoxy radicals, chlorine monoxide, energy calculations