Theoretical study of the methyl peroxy self-reaction: the intermediate structure

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Received 27 June 1996; in final form 12 November 1996

Abstract

Local and non-local density functional theory as well as ab initio computations have been carried out to study methyl peroxy and its adduct CH3O2CH3 involved in the self-reaction. Comparing computed frequencies with experimental data, an equilibrium geometry is proposed for the adduct which is found to be a 'single chain' tetroxide in the two radicals perpendicular approach.

1. Introduction

Alkyl peroxy radicals, RO2, play important roles as reaction intermediates in tropospheric chemistry [1–3] as well as in the combustion process [4]. For instance, RO2 radicals are responsible for the formation of ozone in urban areas.

Multiple experimental studies (for a review, see Refs. [5,6]) have been devoted to the investigation of the peroxy radicals reaction kinetics in the gas-phase in order to improve atmospheric process chemical models. However, there remain large uncertainties concerning the kinetics and mechanisms of many important aspects in the chemistry of these species. In particular, there is still controversy over the mechanism of the primary step associated with the peroxy radicals self-reaction.

The reaction scheme in Fig. 1, which involves an intermediate adduct, has been suggested by several authors [6–8] in order to account for the following experimental observations.

Firstly, the kinetics of the total self-reaction vary greatly with the identity of the alkyl group (at the same temperature):

\[ k_{CH3O2} > k_{C2H5O2} > k_{i-Pr3O2} > k_{t-But3O2}. \]

Secondly, the least reactive radical (in the above RO2 family) shows the most positive temperature dependence of the total global rate constant.

Finally, there is a major change in the branching ratio with the temperature change: the observed trend is a rapid increase in the importance of channel 'a' with increasing temperature.

However, the nature of the intermediate is still uncertain. Moreover, the adduct could be implicated in an alternative mechanism as proposed by Howard and Bennett [9] and explained by Minato et al. [8]:

\[ RO4R \rightleftharpoons 2ROO \rightarrow \text{(b) products} \]

Therefore, investigation of the tetroxide adduct structure and stabilization energy is necessary for a more complete self-reaction understanding.