Theoretical Study of the Peroxy Radicals
RO₂ Self-Reaction: Structures and
Stabilization Energies of the
Intermediate RO₄R for Various R

F. BOHR,¹ E. HENON,¹ I. GARCÍA,² M. CASTRO³
¹Laboratoire de Chimie Physique, GSMA, UPRES-A 6089, Faculté des Sciences de Reims, Moulin de
la Housse, B.P. 1039, 51687 Reims Cedex 2, France
²Programa de Simulación Molecular, Instituto Mexicano del Petróleo, 07730 México, D.F., México
³Departamento de Física y Química Teórica, DEPg, Facultad de Química, Universidad Nacional
Autonoma de Mexico, Ciudad Universitaria, Mexico D.F., C.P. 04510, México

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ABSTRACT: We have determined the lowest-energy structures of the RO₂
[R=CH₃–, CH₃CH₂–, CH₃CH₂CH₂–, CH₃–CH₂CH₂–, CH₃CH₂CH₂CH₂–,
(CH₃)₂CH–, (CH₃)C–, (CH₃)₂C(CH₃)CH–, (CH₃)₂CHCH₂–, CH₃–CH–,
CH₃CH=CH–, and CH₃=CH–CH₂–] peroxy radicals. Further, the self-reaction
of these peroxyls may produce RO₄R tetroxide adducts, for which the influence of the
nature of R on their structure and stability was examined. These studies were done using
theoretical calculations, of the all-electron type, performed at the MP2, DFT, and HF–DFT
levels of theory. All calculations (optimization, frequencies, and total energies) were done
using 6-31G** basis sets for each method. In all cases, we used HF frequencies on the
MP2 geometry to compute Gibbs free energy from MP2 energy. DFT calculations were
done using the BLYP functional, while for HF–DFT, the B3LYP scheme was used.
Our main findings for RO₂ are the following: The three methods provide rather similar
distances and angles. The O–O distance does not change significantly with increasing
the size of R and with the branching, but it is more sensitive when a double bond is
immediately neighboring. The C–O distance is more sensitive to the kind of R.
Concerning the RO₄R adducts, they were located as local minima, that is, they behave
as intermediates. It was found that there is a dissymmetry between the structural
parameters of the peroxy “a” and those of “b.” The O–O distances of peroxy increase by
more than 0.1 Å when going from the isolated peroxy to the intermediate. Similarly, the
C–O distances show a decrease of about 0.02–0.03 Å. In the searched RO₄R intermediates,