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Rearrangements and proton transfer in nitrones by quantum chemistry and molecular dynamics

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Abstract

The structures of intermediates and transition states in rearrangement reactions of nitrone to amide via oxaziridine were calculated at the unrestricted B3LYP level of theory using the 6-31G(d,p) basis set. The same processes were studied by the method of direct molecular dynamics. Both methods reveal two reaction channels from cyclic oxaziridine to amide. One is via the acyclic structure C(O)H2—NH with eclipsed N—H and C—O and then through the intermediate HC(OH)=NH to amide. The other channel, from oxaziridine, is via the structure C(O)H2—NH and then directly to the amide product.

1. Introduction

In the last years, intensive experimental studies in the field of time-resolved optical spectroscopy of molecules in pico- and femtosecond ranges have been carried out [1–3]. To get deeper insight into chemical reaction dynamics, both quantum chemistry (QC) and molecular dynamics (MD) methods can be applied. In recent years such methods as first-principle ab initio MD [4–6] and the direct dynamics method [7–19] have become increasingly popular. In the present work, the processes of rearrangements and proton transfer in nitrone CH_2—N(O)H using QC and MD methods are studied. We use the direct dynamics method, in which the energy and the intermolecular forces of the reacting system are computed directly from a quantum mechanical treatment. Nitrone CH_2—N(O)H can be considered as a model system for more complex derivatives of C, *N*-diphenylnitrones. These systems are known to be photochemically active. Fig. 1 depicts the path of photochemical reaction, in which irradiation of the initial system (a) results in the formation of isomeric oxaziridines (b), which can then be thermally or photochemically rearranged into amides (c) [20]. Therefore these systems can be considered as a good object for optical investigations in pico- and femtosecond ranges.

2. Methods of calculations

We used GAUSSIAN 94 program [21] to perform geometry optimization and reaction path

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