



Excited-state dynamics of oxazole: A combined electronic structure calculations and dynamic simulations study



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ABSTRACT

In the present work, the combined electronic structure calculations and surface hopping simulations have been performed to investigate the excited-state decay of the parent oxazole in the gas phase. Our calculations show that the S_2 state decay of oxazole is an ultrafast process characterized by the ring-opening and ring-closure of the five-membered oxazole ring, in which the triplet contribution is minor. The ring-opening involves the O–C bond cleavage affording the nitrile ylide and airine intermediates, while the ring-closure gives rise to a bicyclic species through a 2–5 bond formation. The azirine and bicyclic intermediates in the S_0 state are very likely involved in the phototranspositions of oxazoles. This is different from the previous mechanism in which these intermediates in the T_1 state have been proposed for these phototranspositions.

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1. Introduction

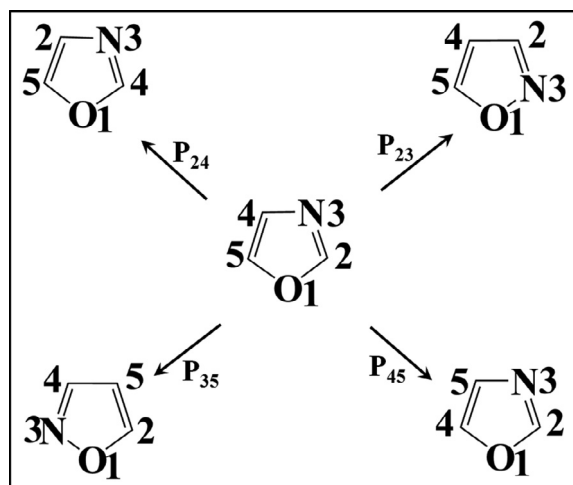
Oxazole and its derivatives are a class of heterocyclic compounds that contain the N=C–O moiety, which can serve as important building blocks for various natural products [1,2], synthetic intermediates [3–5], and pharmaceutical molecules [6]. The oxazole derivatives also have important applications in the field of organic fluorescent materials [7] and industrial chemicals [8]. Some oxazole derivatives have been used in photochemical synthesis of potentially biologically active heteroaromatic compounds with conjugated heteroaromatic systems and synthesis of functionalized heterocyclic compounds [9–15].

Under irradiation with UV–visible light, aryloxazoles were found to yield products derived from rearrangements through the formal 2,3-, 2,4-, 3,5-, and 4,5-transpositions (see Scheme 1) [16–18]. This behavior is in analogy to that of pyrazole [19,20] and isothiazole [21], but the photoinduced reactions of oxazoles are more complex. On the basis of the experimental observations [16–18], the phototransposition mechanism has been explained by the ‘ring contraction–ring expansion’ (RCRE) mechanism as proposed to rationalize the photoisomerization of isoxazoles [21–24] and the ‘internal cyclization–isomerization’ (ICI) mechanism [25].

It is noteworthy that, different from RCRE that involves an azirine intermediate due to the initial O–C bond cleavage, the ICI mechanism firstly involves a bicyclic intermediate through a 2–5 bond formation. The bicyclic intermediate has been assumed to undergo a 1,3-sigmatropic shift of oxygen around the four-membered ring to produce a second bicyclic isomer, followed by re-aromatization to an isoxazole or oxazole isomer. Theoretically, to the best of our knowledge, only one work [26] has been published on the photochemical transposition mechanism of oxazoles. On the basis of ab initio MO-CI calculations with the minimal basis set [26], the 2,3-transposition was suggested to proceed as follows: the 2H-azirine intermediate in the S_1 state is firstly formed, followed by an intersystem crossing (ISC) to the T_1 state and finally yielding isoxazole in the S_0 state. The 4,5-transposition was assumed to occur via the 1H-azirine intermediate in the S_1 state, whereas the 2,4- or 3,5-transposition proceeded through the ICI route with a bicyclic intermediate in the T_1 state as the reaction intermediate. Obviously, the theoretical work of Tanaka et al. [26] is very important for our understanding on the photophysics and photochemical transpositions of oxazole and its derivatives. The previous calculation [26] is based on a relative low theory level, and there are still some unresolved mechanistic questions. Thus it is necessary to re-investigate the photophysics and photochemical reactions of oxazole and its derivatives with more advanced electronic structure calculations.

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Scheme 1. Phototranspositions of Oxazoles.

As a part of our interest in the excited-state dynamics of five-membered heterocycles containing two heteroatoms, we have undertaken a theoretical investigation to the photoinduced reactions of the parent isoxazole by a combination of the advanced *ab initio* calculations and the surface hopping simulations [27]. In the present work, we took the parent oxazole as a model system and investigated its excited-state decay. In light of the present theoretical study, it was found that the S_2 state decay of the parent oxazole is ultrafast by ways of the O–C bond cleavage and C–C bonding of the oxazole ring, producing intermediates through internal conversions (ICs) to S_0 . Accordingly, the azirine and bicyclic intermediates in the S_0 state are very likely involved in the phototranspositions of oxazoles, which is different from the previous proposition that the intermediates in the T_1 state were responsible for the phototranspositions of oxazoles.

2. Computational methods and dynamics details

2.1. Electronic structure calculations

The stationary structures on the potential energy surface (PES) of the S_0 state were optimized with both the DFT with the B3LYP functional [28–30] and the Complete Active Space Self-Consistent Field (CASSCF) [31] methods. The stationary points on the S_1 and S_2 state PESs were fully optimized with the CASSCF energy gradient techniques, and the points of surface crossing between different states were determined by the two-state-averaged (SA2-) CASSCF calculations [32,33]. For equilibrium geometries and transition states, the nature of the critical points was confirmed further by a frequency computation. The calculations described above have been carried out with the Gaussian 09 software package [34]. To describe stationary and crossing structures of the oxazole in/between the low-lying electronic states, one needs the π and π^* orbitals of the C=C and C=N bonds, the occupied and unoccupied σ orbitals of the O–C bond at the O–C–N moiety, and the π orbital of oxygen atom, as well as the nonbonding orbital of the nitrogen atom, that is, ten electrons in eight orbitals, denoted as CAS(10,8) hereafter.

It is well known that the relative energies are usually overestimated by the CASSCF calculation. Thus, it is necessary to take a correction to energies by the inclusion of dynamic correlation. The CASPT2 approach [35,36] as implemented in MOLCAS 7.8 software package [37] is a very efficient algorithm for treating dynamic correlation, and was used to refine the relative energies of the optimized structures. To achieve a balanced description of the states

involved in the vertical excitation at the Franck–Condon (FC) and conical intersection (CI) points, the multi-state (MS-) CASPT2 method [38] was applied. Also, the imaginary shift technique (0.2 a.u.) was employed to avoid intruder-state issues [39] in CASPT2 calculations. For the CASSCF and CASPT2 calculations, the 6-31G* basis set was applied, while the DFT calculations were performed with the 6-311G** basis set. The cc-pVTZ basis set was also used in the vertical excitation energy calculations on the CASSCF optimized S_0 minimum of oxazole.

The CASPT2 single-point energies for all CASSCF optimized geometries involved in deactivation of the S_2 state of oxazole are given in Table S1 of Supplementary Material, which provides an evaluation of the accuracy of the CASSCF calculations. Overall, the relative energies calculated at the CASSCF level are reasonably consistent with those from the CASPT2 calculations. The discrepancy between CASSCF and CASPT2 was found in the vertical excitation energies and the energy gaps at some CI points. A possible explanation for the un-expectedly large energy-difference between CASSCF and CASPT2 at some regions of the PES is that a few electronic configurations that might have noticeable contributions to relative energies of these points at these regions of the PES are not included in the CAS(10,8)/6-31G* wave functions and the CAS(10,8)/6-31G* calculations cannot simultaneously provide an appropriate description of the states of interest. When an extended CAS(12,10) active space was used, as seen in Table S1, it cannot still provide an improvement on the vertical excitation energies, implying that a more larger active space should be used. However, the analytic CI optimization algorithm as implemented in Gaussian 09 software package cannot be performed when a larger active space with more than eight orbitals is used. The necessity for a large active space also imposes a limit on the dynamics simulation.

Finally, it should be mentioned that this inaccuracy on the CASSCF surface should affect the distribution of trajectories among the several reaction pathways and the final product distributions may be seriously disturbed. In addition, the limited CAS(10,8) active space might introduce a bias with respect to what reactions can occur in the simulation. That is, in the present study only the σ and σ^* orbitals of the O₁–C₂ bond are included in the active space, hence the intermediates due to the O₁–C₅ bond cleavage might not be observed in the simulation. Thus, it should be aware that the conclusions drawn here might not be the final answer.

2.2. Dynamics details

In the *ab initio* molecular dynamics [40–42], the nucleus trajectories evolve always on a single adiabatic surface and the nonadiabatic events were taken into account by means of the Tully's fewest-switches surface hopping (FSSH) algorithm [43]. The nucleus trajectories were integrated using the velocity-Verlet algorithm [44] with the time step of 0.5 fs. At each new generated structure, the energies, gradients, and nonadiabatic coupling vectors among different electronic states were computed at the state-averaged CASSCF level. For propagation of the electronic wave function, the fourth-order Runge–Kutta method [45] was used with the integration step of 0.01 fs, where the energies, velocities, and non-adiabatic coupling vectors were interpolated for the intermediate steps. Finally, the nonadiabatic transition probabilities between different electronic states can be computed. In the case of hopping, the nuclear velocities were adjusted in the direction of the nonadiabatic coupling vectors to conserve the total energy of the system.

Here, we will use this method to investigate the electronic and atomic details of the excited-state dynamics of the parent oxazole in the gas phase. The initial geometries and velocities for the simulation were generated by a Wigner distribution for the quantum harmonic oscillator in the specified ground vibrational state at

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