



Theoretical study of photochemical processes involving singlet excited states of formaldehyde carbonyl oxide in the atmosphere

P. Aplincourt^a, E. Henon^{b,*}, F. Bohr^{b,*}, M.F. Ruiz-López^{a,*}

^a *Laboratoire de Chimie Théorique, UMR CNRS-UHP N° 7565, Part of the Institut Nancéien de Chimie Moléculaire, Université Henri Poincaré-Nancy I, B.P. 239, 54506 Vandoeuvre-lès-Nancy Cedex, France*

^b *Groupe de Spectrométrie Moléculaire et Atmosphérique (G.S.M.A), UMR CNRS N° 6089, Université de Reims-Champagne-Ardenne, B.P. 1039, 51687 Reims Cedex 2, France*

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Abstract

We report a theoretical study on the photochemical reactivity of formaldehyde carbonyl oxide H_2COO , a compound of atmospheric relevance. Calculations are carried out at the CASSCF and CASPT2 levels with extended basis sets. We are particularly interested in three important unimolecular processes: isomerization into dioxirane, syn/anti isomerization and dissociation into formaldehyde and atomic oxygen. The results suggest that the photochemical reactivity of H_2COO in the troposphere is strongly linked to the properties of the second singlet excited state a^1A' ($\pi \rightarrow \pi^*$) because it is energetically accessible from the ground state and has a large oscillator strength. Construction of potential energy curves reveals that photochemical isomerization into dioxirane is very unlikely to occur whereas syn/anti isomerization should be favorable. Besides, in the a^1A' state, carbonyl oxide spontaneously dissociates into formaldehyde H_2CO and atomic oxygen $\text{O}(^1\text{D})$ in close relationship to the excited 1B_2 state of the isoelectronic ozone molecule occurring in Hartley's band.

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1. Introduction

In the atmosphere, a number of chemical and photochemical reactions involve carbonyl oxides, $\text{R}^1\text{R}^2\text{COO}$. These low-stable compounds are

formed during the ozonolysis of alkenes [1] and take part in air pollution processes in urban areas. Many experimental works have been performed to study the chemical reactivity of the prototypical compound H_2COO [2–15]. Different investigations [2–4] showed that a fraction of this compound (about 60%) undergoes unimolecular reactions that can be gathered in three classes: isomerization, which yields formic acid through formation of dioxirane and dioxymethane [5–8], formation of hydroxyl radical OH [5,9] and elimination of an

* Corresponding authors: Tel.: +33-3-83-68-43-78; fax: +33-3-83-68-43-71.

E-mail addresses: eric.henon@univ-reims.fr (E. Henon), frederic.bohr@univ-reims.fr (F. Bohr), manuel.ruiz@lctn.uhp-nancy.fr (M.F. Ruiz-López).

oxygen atom [6,10,11]. The remaining part (about 40%) is stabilized by collision and interacts with other tropospheric molecules giving rise to bimolecular reactions [1,2,4,12–15]. Such bimolecular reactions can also be classified in three groups: nucleophilic reactions (with alcohols [1], water [12] as well as carboxylic acids [13]), cycloadditions [2,14] and oxygen transfer reactions [15].

Theoretical studies have been performed in parallel to experiments [5,8,16–23]. The wavefunction of carbonyl oxides must be viewed as the superposition of diradical and zwitterionic electronic structures. A detailed analysis using CCSD methods for H_2COO has been reported by Cremer et al. [17]. Other theoretical studies have dealt with the chemical reactivity of carbonyl oxides in gas phase. Cremer et al. [5,17,18] and Anglada et al. [19] have determined the unimolecular decomposition and isomerization mechanisms of H_2COO . Bimolecular reactions with other important atmospheric molecules have also been investigated [21–27]. Recently, Anglada et al. [24] have described several reaction paths for the addition of water to H_2COO . Additionally, Aplincourt and Ruiz-López showed that the isomerization reactions of carbonyl oxide into formic acid assisted by formaldehyde or sulfur dioxide are likely to occur in the troposphere [25]. In another work, the same authors have detailed the mechanisms of the formation of formic acid anhydride $(\text{HCO})_2\text{O}$ from the addition of formic acid or formaldehyde to H_2COO [26]. Finally, oxygen transfer reactions have also been the object of several theoretical studies principally performed by Bach et al. [27].

Based on experimental results, Hatakeyama et al. [2] have suggested that a part of H_2COO is formed in an electronic excited state. However, very few studies have been devoted to the electronically excited states of carbonyl oxides. The first calculations were performed 25 years ago by Goddard et al. [21]. They computed, at the GVB-CI level, the vertical excitation energies for the first excited states of the planar and perpendicular forms of carbonyl oxide. Anglada et al. [19] have performed a study (CASSCF/MRDCI level) in which a dissociation mechanism of simple carbonyl oxides into the corresponding carbonyl compound and $\text{O}(^3\text{P})$ has been described. It involves internal

rotation around the CO bond axis followed by intersystem crossing to the lowest triplet state that proceeds to OO bond breaking through a low energy barrier. However, the authors have predicted a low efficient singlet–triplet intersystem crossing. In another work, Anglada et al. [20] have studied a related photochemical process, the opening reaction of dioxirane into dioxymethane. In this case, the proposed reaction mechanism consists in the vertical excitation to a singlet excited state followed by radiationless decay via intersection points on the potential energy surfaces of appropriate states. The authors have also described the decomposition of dioxymethane into CO_2 and H_2 .

The fact that H_2COO is isoelectronic to ozone suggests that its photochemistry could be very active. To further explore such a hypothesis, we have carried out computations for the potential energy surfaces relative to the low-lying singlet excited states. More precisely, we have considered the mechanisms that could compete with thermal isomerization or dissociation to formaldehyde and atomic oxygen.

2. Computational details

This study requires the use of multiconfigurational methods in order to get a correct representation of the excited state wavefunctions. CASSCF [28] and CASPT2 [29] levels have been used along this work. In the first approach, non-dynamical correlation effects are taken into account whereas both dynamical and non-dynamical effects are included in the second method.

All the geometries have been optimized at the CASSCF(14,10) level using an ANO basis set (10s6p3d/3s2p1d) for carbon and oxygen atoms and (7s3p/2s1p) for hydrogen atoms. In the following, this basis sets will be called BS1. In this active space, there are seven molecular orbitals (MO) of a' symmetry and three of a'' symmetry. Orbitals of a' symmetry correspond to:

- bonding and antibonding MOs for the CO and OO σ bonds,
- the symmetric and antisymmetric combinations of 2s orbitals centered on the two oxygen atoms,

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