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Chemical Physics 343 (2008) 329–339
Chemical Physics
www.elsevier.com/locate/chemphys

Ultrafast dissociation pathways of diphenylmethyl chloride to generate reactive carbo cations

Benjamin P. Fingerhut, Dorothee Geppert, Regina de Vivie-Riedle *

LMU Department Chemie, Butenandt-Strasse 11, 81377 München, Germany

Received 20 April 2007; accepted 26 July 2007
Available online 3 August 2007

Abstract

The primary processes in the formation of electrophilic precursor ions are studied on a microscopic scale by quantum chemical and quantum dynamical methods. For the competing reaction channels of heterolysis and homolysis in the photochemically induced dissociation of diphenylmethyl chloride, ab initio data for the ground and excited electronic states are evaluated in the gas phase. Here, the simultaneous formation of ionic and radicalic products can solely be attributed to the existence of conical intersections which are localized and characterized for the first time. The interaction of different electronic states also leads to the initial charge transfer from the phenyl π-system to the σ-bond of the leaving group which is essential for the fast dissociation and is explained by orbital analysis. Quantum dynamical calculations in one and two dimensions suggest that in gas phase the ion pair constitutes the main product despite its higher potential energy. Possible changes in polar solvents, where the ionic fragments are stabilized below the radical channel, are discussed.

PACS: 31.15.Ar; 31.50.Df; 31.50.Gh; 82.20.Bc; 82.20.Kh; 82.50.−m

Keywords: Quantum dynamics; Conical intersections; Photodissociation; Ab initio calculations of excited PES; Carbo cations; Charge transfer processes

1. Introduction

The S_N1 reaction is a fundamental mechanism in organic chemistry and has been extensively investigated experimentally and theoretically ([1] and references therein). A major goal of these works is the classification of nucleophiles and electrophiles with respect to their reactivity and the explanation of the latter one with molecular parameters. In many kinetic studies performed to establish a reactivity scale which spans more than 32 orders of magnitude [2–4], diphenylmethyl cations $[(C_6H_5)_2CH^+]$ serve as reference electrophiles because the corresponding intermediates can be identified spectroscopically [5,6]. Despite many efforts, the reaction dynamics on the microscopic scale are still under discussion and further theoretical and time-resolved experimental investigations are necessary to determine which molecular parameters control the reactivity.

We concentrate our investigations on the photochemically induced dissociation of diphenylmethyl chloride (DPMCl). After excitation by a femtosecond laser pulse, the carbo cations are generated in a competing process of heterolytic and homolytic dissociation. In addition to the academic interest, the synthetic potential of photochemical arylmethyl cleavage reactions has been investigated as protectors of functional groups [7]. Of course, to serve as a precursor molecule, the heterolytic dissociation leading to the ion pair must proceed quantitatively. A better understanding of the very first reaction steps could help to

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* Corresponding author.
E-mail addresses: benjamin.fingerhut@cup.uni-muenchen.de (B.P. Fingerhut), dorothee.geppert@cup.uni-muenchen.de (D. Geppert), regina.de_vivie@cup.uni-muenchen.de (R. de Vivie-Riedle).

0301-0104/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2007.07.034

enhance the product yield i.e. the formation of the carbo cation that serves as the electrophile in the subsequent combination reaction with the nucleophile.

Recent time-resolved experiments investigate the dissociation of DPMCl in acetonitrile initiated by a femtosecond laser pulse [8,9]. According to these results, the competing reaction channels arise from one common excited state (S_1). The dissociation of DPMCl leads to the formation of the radical pair within 345 fs and initial formation of a contact ion pair within 833 fs. Such ultrafast reaction times hint at the participation of conical intersections, which have, up to now, not been characterized [1].

In this work we report on our ab initio calculations of the different electronic potential surfaces involved in the photochemical dissociation process in the gas phase. With highly correlated quantum chemical methods, the charge transfer essential for the dissociation process can be explained by orbital analysis. For the first time, conical intersections are localized, linking the competing reaction channels. To gain a deeper insight into the reaction mechanism, quantum dynamical calculations are performed in reduced coordinate space for the initial dissociation process on the femtosecond timescale including excitation with an ultrafast laser pulse.

2. Quantum chemistry

The quantum chemical calculations are performed with the program packages MOLPRO 2006.1 [10] and GAUSSIAN03 [11]. As several interacting excited states are involved in the dissociation process of DPMCl, we use the complete active space self consistent field method CASSCF (8,8) [12–14] with a 6-31G* basis set.

The angle between the phenyl moieties is 79.49°, which confirms the assumption that their π-systems are uncoupled, as it is reported in the literature for triarylmethyl derivatives [15,16]. In principle, two equivalent structures, interconverted by torsion of the phenyl rings are possible. Their degeneracy can be lifted by introducing different substituents on one of the phenyl rings. Recent experiments with such DPMCl-derivatives [17] have shown that these modifications do not affect the primary dissociation. It can be concluded that the excitation occurs on one of the decoupled rings, presumably the one including the highest occupied molecular orbital (HOMO). Therefore we can restrict the CAS space to the π-orbitals of this phenyl ring. To describe the cleavage of the C1–Cl bond (see Fig. 1) the bonding σ- as well as the anti-bonding σ*-orbital are included in the active space. The lone pair orbitals of the Cl atom were neglected as they do not contribute to the dissociation [18]. The whole reactive process including the laser excitation can thus be described with an active space consisting of six π- and two σ-orbitals.

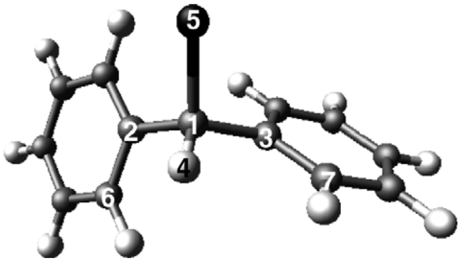

Fig. 1. Optimized ground state geometry of diphenylmethyl chloride DPMCl.

2.1. Geometries

The ground state geometry of DPMCl was optimized on CASSCF level of theory and confirmed by a normal mode analysis (see Fig. 1). The relevant bond lengths, angles and dihedral angles are presented in Table 1. The Cl atom is bound to the central C1 atom (bond length 1.86 Å), which exhibits the typical tetrahedral shape of an sp^3 hybridized carbon atom. The optimized geometries of the photodissociation products, diphenylmethyl cation (DPM$^+$) and diphenylmethyl radical (DPM$^{\bullet}$), are also summarized in Table 1. During the dissociation process the hybridization of the central carbon atom (C1) is changed, resulting in a trigonal geometry (see change of the dihedral angle $\sphericalangle(\mathrm{C2}, \mathrm{C3}, \mathrm{C1}, \mathrm{H4})$). The steric repulsion inhibits planarity of both products. This effect is stronger in case of the DPM radical (angle between phenyl rings 46.85° compared to 31.27° in the cation) where the unpaired electron occupies the anti-bonding HOMO and thereby reduces the π-bond order between the central C atom and the phenyl rings. This is also reflected in the longer C1–C2 and C1–C3 bond length.

To improve the excitation energies, dynamic electron correlation must be considered and CASPT2 [19,20] calculations based on the optimized CASSCF wave functions were performed. The resulting excitation energy for the S_1 state is 253 nm which is in good agreement with experimental data (266 nm) [8]. The excitation energy for the S_2 corresponds to 190 nm.

The S_1 state exhibits a minimum near the Franck–Condon (FC) region with a geometry slightly different from the ground state minimum. Mainly the C1–Cl bond is elongated (1.93 Å) and the C1–phenyl bond length is reduced (1.47 Å) due to its partial π-character arising from the occupation of the LUMO. The longer C1–Cl bond indicates a gradient in the direction of dissociation.

2.2. Potential energy surfaces along the dissociation coordinate

Based on the ground state minimum energy path (MEP) for increasing C1–Cl distances we calculate the potential energies for the four lowest electronic states (Fig. 2). In the FC-region the first excited state S_1 corresponds to a π–π*-excitation.

The second excited state S_2 represents a π–π*-excitation as well, and in addition possesses anti-bonding character