Journal of Fluorine Chemistry 188 (2016) 171–176

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Position-dependent fragmentation mechanism for radical anions of fluorinated benzoates

Dmitry E. Mashkantsev[a,b], Irina V. Beregovaya[a,*], Lyudmila N. Shchegoleva[a]

[a] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 9 Lavrent'ev Avenue, Novosibirsk 630090, Russia
[b] Novosibirsk State University, 2 Pirogov Street, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 25 May 2016
Received in revised form 30 June 2016
Accepted 1 July 2016
Available online 2 July 2016

Keywords:
Fluoroarene radical anions
Potential energy surfaces
Pseudorotation
C–F bond cleavage
Regioselectivity

ABSTRACT

DFT calculations were used to study the potential energy surfaces (PESes) of a full series of fluorinated benzoate radical anions (RAs). The sections of PESes along the C–F bond cleavage coordinates in polar media were built, and the transition states for RA fragmentation with fluoride anion elimination were located. The estimated reaction barrier heights let us interpret the experimental regularities of the RA decay including the process regioselectivity.

The fragmentation mechanism was shown to depend on the position of the leaving fluorine atom. When defluorination occurs at an *ortho*- or *meta*- position to the CO_2^- group, the reaction coordinate involves pseudorotation as a way for odd electron density transfer to the breaking C–F bond.

Additional gas phase calculations were performed to confirm the pseudorotational architecture of the PESes of polyfluorinated benzoate RAs. The results obtained clearly demonstrated that the multihole PES structure gives rise to the multichannel mechanism of RA cleavage.

1. Introduction

Radical anions (RAs) of polyfluorinated arenes play an important role as intermediates of reductive defluorination of their neutral precursors [1,2], which yields partially fluorinated compounds that are potentially valuable starting materials for synthesis [3]. The regiodefining stage of the reaction is the RA unimolecular decay through fluoride ion elimination [1], which is the main channel of RA decay in polar media.

Experimental investigations of polyfluorinated RAs are complicated by the extremely short lifetime of these particles. Currently, such investigations are possible owing to advanced high-sensitive methods for radical-ionic pairs detection such as Optical Detection (OD) EPR and Time-Resolved Magnetic Field Effect (TR MFE) [4]. While the electronic and spatial structure of fluoroarene RAs have been thoroughly studied [5] by now, the reactivity of these RAs remains unexplored.

In a gas phase, fluoroarene RAs are usually stable to fragmentation. Their decay becomes possible in polar media due to the large solvation energy of the fluoride ion. For planar π-type RAs the reaction is symmetry forbidden [6] because of the RA π and σ term crossing in the course of reaction. The crossing avoidance is realized by the out-of-plane shift of the leaving fluorine atom. The transition state (TS) for fluoride ion elimination has a noticeably nonplanar structure [7]. It is essential that RA stability decreases drastically under fluorine accumulation in the aromatic nuclei [8] while C–F bond energy increases [9].

As has been shown earlier [7,10], the reaction mechanism depends on the electronic state of the breaking RA. When the halide ion eliminates from the ring position bearing zero or low density of an odd electron, the reaction coordinate includes not only C–Hal bond stretching and out-of-plane deviation but also an aromatic ring in-plane distortion (pseudorotation) resulting from the avoided crossing of π terms. More detailed information about pseudorotation and usage of this term for low-symmetric molecular systems may be found in recent review [5] and references herein. Pseudorotation serves as a mechanism of electron density transfer between the ring positions. These concepts allowed us to interpret the experimental data on relative stability of chlorobenzonitrile RAs [11] and on regioselectivity of octafluoronaphthalene RA fragmentation [12]. However, there is still neither systematic theoretical research of polyhaloarene RA cleavage nor the analysis of reaction position selectivity. Corresponding experimental investigations of precursor defluorination are few and far between [1–3,13,14].

---

[*] Corresponding author.
E-mail addresses: mashkantsev01@mail.ru (D.E. Mashkantsev), ivb@nioch.nsc.ru (I.V. Beregovaya), sln@nioch.nsc.ru (L.N. Shchegoleva).

http://dx.doi.org/10.1016/j.jfluchem.2016.07.002
0022-1139/© 2016 Elsevier B.V. All rights reserved.

Consequently, the detailed experimental study of a full set of fluorinated benzoate RAs [8] is still relevant today. However, the interpretation of the decay rate constant variation with the number and relative position of fluorine atoms in [8] was based on semi-empirical INDO calculations without taking into account the solvation effects, except for the strongly required CO_2^- group local solvation. It was the only accessible level of calculations for such systems at that time. Since the σ term is not dissociative in the gas phase, the reaction TS does not exist in this phase; it could only be modeled. Regioselectivity of C–F bond cleavage in polyfluoroarene RAs was not considered theoretically at all.

This work presents a new insight into the problem of fluorinated benzoate RAs reactivity based on the up-to-date level of experience. We have located the true TSes for fluoride ion elimination from various ring positions and have built respective sections of RA potential energy surfaces (PESs). The calculated barriers for RA fragmentation are in line with the experimental trends in the rate constant behaviour within the series of RAs and account for the regioselectivity of reductive defluorination for their precursors.

2. Calculation details

Calculations of the electron structure and PES sections for fluorinated benzoate RAs were performed within spin-unrestricted DFT theory with the CAM-B3LYP functional and 6-31 + G(d) basis set. Stationary PES points were located and their types and interrelations were determined by the normal vibrations analysis accompanied by intrinsic reaction coordinate (IRC) calculations. All calculations were done with the GAMESS package [15]. Molecular orbital (MO) images were constructed by MOLDEN [16] program, using the isosurface contour value that corresponds to electron density of 0.05 a.u.

The polar media influence was taken into account within the polarizable continuum model (PCM) using built-in parameters for H_2O. The CO_2^- group local solvation was modeled by the direct inclusion of two H_2O molecules into calculations (the so-called supermolecular approach). Note that H_2O molecules simulating local solvation of the CO_2^- group form a hydrogen bond between them as well (see Fig. 1 in Results and discussion).

The heights of energy barriers (E^a) for the studied RA fragmentation were estimated as total energy differences between the TSes for the C–F_i bond cleavage and the PES minimum corresponding to the initial RA.

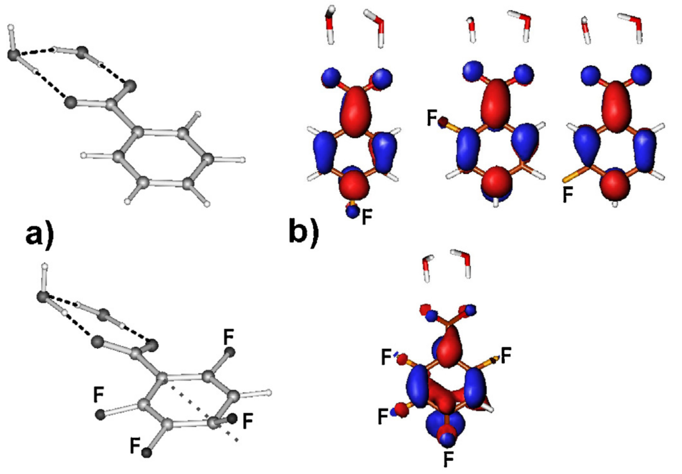

Fig. 1. Geometrical structures of the benzoate and 2,3,4,6-tetrafluorobenzoate RAs adjusted for the CO_2^- group local solvation (a) and SOMO images for RAs of monofluorinated benzoates and 2,3,4,6-tetrafluorobenzoate (b).

We performed additional calculations of the gas phase PESes for a set of polyfluorinated benzoate RAs, for whose precursors there are available experimental data on monodefluorination.

3. Results and discussion

3.1. Spatial and electronic structure of initial radical anions

Geometry optimization of the fluorobenzoate RAs studied within the solvation model described above showed the RAs of this family to differ noticeably in their spatial structure. Mono- and difluorinated benzoate RAs that contain no fluorine atom in *para*-position to the CO_2^- group (except for 2,3-difluorobenzoate) are π-type radicals possessing a nearly planar structure (Fig. 1). This is also true for 2,3,5-trifluorobenzoate RA. The rest of the polyfluorinated RAs display out-of-plane distortions that are mostly C–F bond deviations from the ring plane. When *ortho*-F atoms are present, the planes of the ring and CO_2^- group become non coplanar. An example of such a nonplanar RA is shown in Fig. 1a.

The singly occupied MO (SOMO) structure for the RAs considered is determined by the CO_2^- group, the major SOMO density located in *para*- and *ipso*-positions to the group (Fig. 1b).

3.2. Unimolecular fragmentation of monofluorinated benzoate RAs

The PES sections of isomeric mono-fluorobenzoate RAs along the reaction coordinates corresponding to fluoride ion elimination are shown in Figs. 2 and 3. In the case of *para*-isomer the reaction coordinate is a superposition of the C–F bond stretching and its out-of-plane deviation. The respective TS structure is given in Fig. 2 together with the SOMO image that shows an increase in the antibonding σ^*_{C-F} orbital contribution during the π-σ crossing avoidance. The reaction barrier height is estimated to be 4.1 kcal/mol.

For *ortho*- and *meta*-fluorobenzoate RAs the reaction coordinate becomes more complicated (Fig. 3). The C–F bond stretching is preceded by odd electron density transfer to the bond, which is realized through moving along the pseudorotation way. The contribution of pseudorotation to the reaction coordinates comes to light as a result of comparison of SOMO evolution (Fig. 3b) when moving along these coordinates with the SOMOs of the benzene RA structures involved in pseudorotation (see [17] for details). To

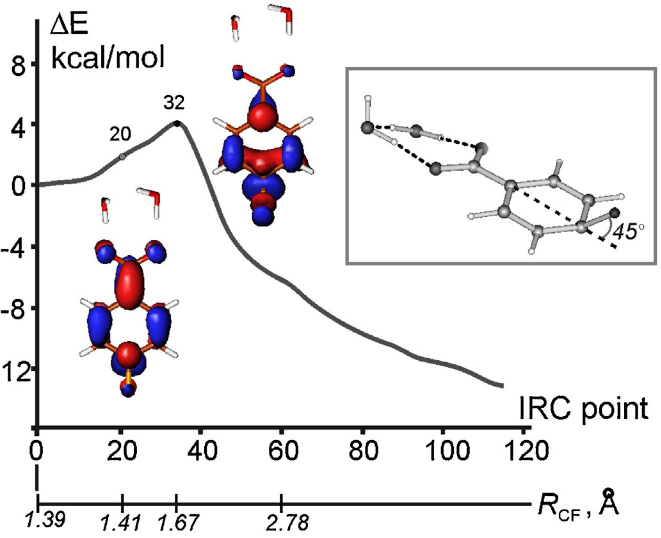

Fig. 2. PES section of the *para*-fluorobenzoate RA along the C–F bond cleavage coordinate. The IRC points accompanied by respective SOMO images are marked by their numbers. The TS structure (point 32) is shown in a frame.