Chemical Physics Letters 556 (2013) 35–38

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

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

Concerted and sequential pathways of proton-coupled electron transfer in hydrogen halide elimination

Aimable Kalume, Lisa George, Nicole Cunningham, Scott A. Reid *

Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881, USA

A R T I C L E I N F O

Article history:
Received 27 September 2012
In final form 20 November 2012
Available online 29 November 2012

A B S T R A C T

Proton-coupled electron transfer (PCET) is a key reaction in a diverse array of chemical and biochemical processes. *Concerted* PCET, a single step process where no intermediates are expected, is often difficult to distinguish from *sequential* electron transfer/proton transfer (or proton transfer/electron transfer) events that involve one or more reactive intermediates. Here we demonstrate that in an apparently simple and fundamental organic reaction, hydrogen halide elimination (dehydrohalogenation), both mechanisms occur, with concerted PCET kinetically favored over sequential ET/PT. The latter involves a well-defined reactive intermediate, the corresponding iso-halon.

1. Introduction

Proton-coupled electron transfer (PCET) reactions, where an electron and proton are transferred in the same kinetic step [1–4] and thus bypass high energy reactive intermediates, are key reactions in a diverse array of biochemical [5–8], catalytic [9–11], and solar energy conversion processes [12,13]. While recent progress has been made [14,15], in many systems it has proven difficult to experimentally distinguish *concerted* PCET, a single step process where no intermediates are expected, from *sequential* electron transfer/proton transfer (ET/PT, or PT/ET) events that involve one or more reactive intermediates. In this work, we describe an apparently simple and fundamental organic reaction, hydrogen halide elimination (or dehydrohalogenation), where both concerted and sequential mechanisms of proton coupled electron transfer are operative. Dehydrohalogenation reactions of haloalkanes have been extensively studied [16–22], and the role of charge transfer has previously been implicated [20]. For example, in the series of monohaloethanes C_2H_5X ($X = F, Cl, Br, I$), it was shown that the barrier to HX elimination correlates more strongly with the heterolytic $(C-X \rightarrow C^{+} + X{:}^{-})$ than homolytic $(C-X \rightarrow C^{\cdot} + X^{\cdot})$ bond dissociation energy [21]. However, these reactions have not yet been described within the general framework of PCET. Here we make this connection, showing that in the dehydrohalogenation reaction of a gem-dihalide, 1,1-dibromoethane, concerted PCET is kinetically favored over a sequential ET/PT mechanism that involves a well-known reactive intermediate, the corresponding iso-halon.

This work originated in studies of the isomerization reactions of simple polyhalomethanes (e.g., formation of $H_2C{-}Br{-}Br$ from CH_2Br_2) [23–35], fascinating reactions that feature isomerization as electron transfer, in that bonding in the iso-halon is best described as an ion-pair interaction between a halide anion and halocarbocation [25,34]. In condensed phases, these isomers are readily formed in geminate recombination of the nascent radical pair produced following cleavage of a carbon–halogen bond in polyhaloalkanes [36]. Working with groups at UW-Madison, we have recently examined the timescales for isomer formation and relaxation in a model system, CH_2ClI, using ultrafast spectroscopy in both solution and cryogenic matrices [35]. These studies reveal that the isomer is formed on the ps timescale, with vibrational relaxation of the hot isomer occurring on with a time constant of ~50 ps, largely invariant to the environment.

In extending our studies to a polyhaloethane, 1,1-dibromoethane (1,1-DBE), we were surprised to find no trace of the isomer in studies of the photolysis of 1,1-DBE in cryogenic Ar matrices at 5 K; rather, the dominant products were HBr and vinyl bromide (C_2H_3Br) [37]. In comparison, photolysis of matrix isolated 1,1-dibromo-2,2,2,-trifluoroethane yields the isomer as the only observable photoproduct [37]. To understand this result, we have conducted and report in this Letter an extended theoretical analysis using Density Functional Theory [M06-2x] and post-Hartree Fock [MP2, CCSD(T)] methods in combination with correlation consistent basis sets. These studies reveal the existence of distinct (concerted vs. sequential) proton coupled electron transfer mechanisms for dehydrohalogenation lying below the threshold for simple bond fission.

2. Computational methodologies

All calculations performed in this work used the Gaussian 09 and NBO 5.9 packages [38,39] and were run on the Marquette Pere high speed cluster. Geometry optimizations were performed using DFT

---

* Corresponding author. Fax: +1 414 288 7066.
E-mail address: scott.reid@mu.edu (S.A. Reid).

0009-2614/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2012.11.053

(M06-2x) and MP2 methods with correlation consistent basis sets, typically Dunning's aug-cc-pVTZ basis set [40–43]. Harmonic vibrational frequencies were calculated for the optimized structures to characterize the order of the respective stationary point, and to determine corrections for Zero-Point Energy (ZPE). To obtain a more quantitative description of the relative energies between selected stationary points, single point energy calculations were performed using a higher level single reference method [CCSD(T)/aug-cc-pVTZ] on the optimized DFT and/or MP2 structures. To check for the effects of solvation on the barrier heights, calculations were performed in solvent (dichloromethane) using the Polarizable Continuum Model.

3. Results and discussion

Our theoretical characterization of the 1,1-DBE PES began with relaxed scans of the C–Br–Br angle at the MP2/aug-cc-pVTZ and M06-2x/aug-cc-pVTZ levels, shown in the upper panel of Figure 1. In the polyhalomethanes, such scans have been shown to closely approximate the isomerization reaction coordinate [34]. A plot of the partial (MK) charge on the isomerizing Br atom, derived from the MP2 wavefunction, shows the maximum charge build up at a C–Br–Br angle of 80° (Figure 1, middle panel) [34], which as we show below lies very close to that found in the optimized structure of the isomerization transition state (TS). Importantly, the partial charge on a Hydrogen atom on the adjacent methyl group increases during the scan, and abruptly changes at an angle near 85°, which coincides with a rotation of the methyl moiety that leads to a sudden decrease of that H–Br distance (Figure 1; lower panel). *This led us to hypothesize the existence of a sequential ET/PT pathway for HBr elimination in 1,1-DBE, involving the isomer as reactive intermediate.*

To investigate this hypothesis, we characterized stationary points on the 1,1-DBE Potential Energy Surface using M06-2x and MP2 methods with an aug-cc-pVTZ basis set [44], followed by single point calculations at the CCSD(T)/aug-cc-pVTZ level, with corrections for zero-point energy and thermal corrections to the Gibbs energy calculated at the M06-2x/aug-cc-pVTZ level. The structure of the isomer (Figure 3) is similar to that of related systems [27,34], and vibrational frequency analysis (Table S1, Supporting information) confirms that the isomer is a minimum on the PES. However, a TS for HBr elimination from the isomer was found, which vibrational frequency analysis (Table S1) confirms is a first-order saddle point on the PES. Intrinsic Reaction Coordinate (IRC) calculations (Figure 2) verify that this TS connects the isomer with the elimination products. Importantly, the energy of this TS lies below the energy of the isomerization TS at the CCSD(T)//M06-2x/aug-cc-pVTZ level (Figure 3). *Thus, a sequential ET/PT mechanism for HBr elimination in 1,1-DBE exists along the isomerization coordinate.* The first, and rate-limiting, step involves formation of the isomer, featuring electron transfer and formation of an ion pair. A second step of proton transfer leads to the final set of products (HBr and vinyl bromide), as illustrated in Figure 3.

Additional insight is gleaned from Natural Resonance Theory analysis, [45,46] details of which are provided in Figure S1 in the Supporting information. The TS to HBr elimination from the isomer shows significant (~60%) ion-pair character, as expected, while 8% of the overall resonance description corresponds to a H^+/Br^- ion pair (Figure 4). The presence of the HBr elimination pathway shown in Figure 3 accounts for our failure to trap the isomer of 1,1-DBE in matrix isolation experiments. Ultrafast studies of this system should be particularly revealing; such studies can follow the formation and decay of the isomer via its intense near-UV ($S_0 \rightarrow S_3$) absorption band, calculated to lie at 356 nm with an oscillator strength of 0.41 (TDM06/aug-cc-pVTZ). This is very close to the observed position (360 nm) of this absorption in iso-CH_2Br_2 [23]. The HBr elimination product can be probed most conveniently in the mid-infrared.

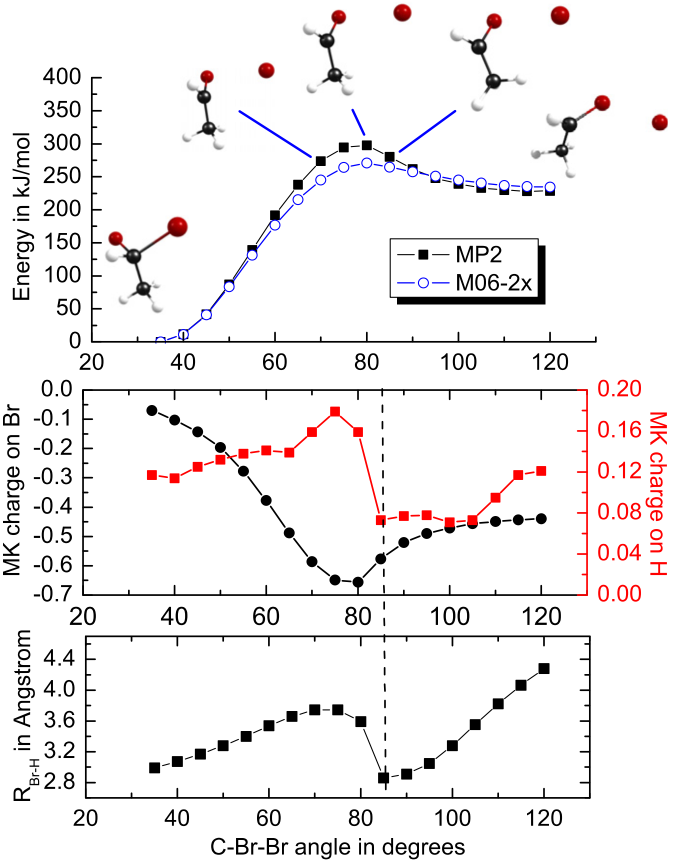

Figure 1. Upper panel: scans along the C–Br–Br bond angle in 1,1,-dibromoethane at the M06-2x and MP2 levels of theory with an aug-cc-pVTZ basis set. Middle panel: partial atomic (MK) charges on adjacent H and Br atoms at each scan point, calculated at the MP2/aug-cc-pVTZ level. Lower panel: distance between adjacent H and Br atoms at each scan point, calculated at the MP2/aug-cc-pVTZ level.

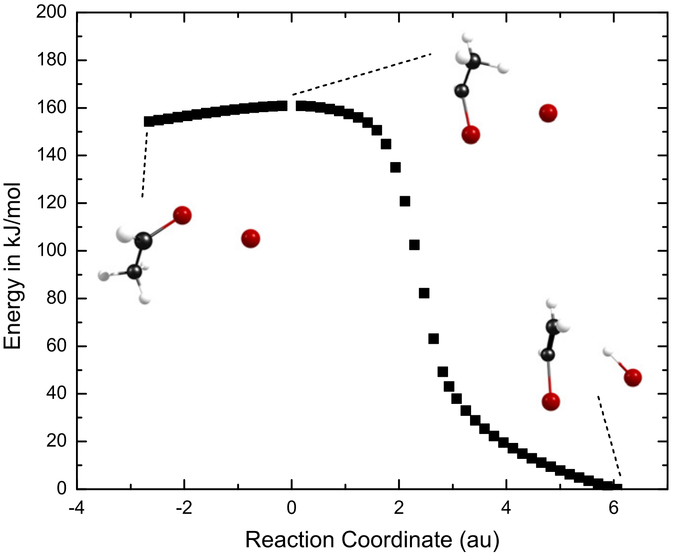

Figure 2. Intrinsic Reaction Coordinate calculation of the reaction path linking iso-1,1-dibromoethane with the elimination products HBr + C_2H_3Br, performed at the M06-2x/aug-cc-pVTZ level.