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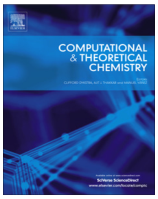

Computational study of carbon–hydrogen bond deprotonation by alkali metal superbases

Daniel B. Pardue [a,*], Samantha J. Gustafson [b], Roy A. Periana [c,*], Daniel H. Ess [b,*], Thomas R. Cundari [a,*]

[a] Department of Chemistry, Center for Advanced Scientific Computing and Modeling (CASCaM), University of North Texas, Denton, TX 76203, United States
[b] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, United States
[c] The Scripps Energy & Materials Center, Department of Chemistry, The Scripps Research Institute, Jupiter, FL 33458, United States

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ABSTRACT

Deprotonation of hydrocarbon C–H bonds by alkali metal amide “superbases” is analyzed with the use of density functional theory calculations. The role of alkali metal, amide substituents (NH_2 versus NH(cyclohexyl)), solvent (implicit and explicit), and substrate (methane versus toluene) are probed. Additionally, Hammett and energy decomposition analyses are utilized to assess the nature of the charge distribution in these transition states. Implications of the present study for the cleavage of strong C–H bonds found in natural gas, such as methane and ethane, are discussed.

1. Introduction

The exploitation of acidity or electrophilicity is a vital aspect of many chemical reactions as well as catalysis. Olah and coworkers were pioneers in the study of superelectrophiles [1–4]. These researchers showed that such compounds, also known as “superacids,” possess the ability to accomplish chemistry that “normal” acids are unable to accomplish. A shining example includes Olah’s work in which he was the first to effectively stabilize carbocations and permit direct experimental characterization of many of their properties. These strong electrophiles/acids have the ability, for example, to react with weakly nucleophilic/basic sites such as the π-electrons of alkenes or small hydrocarbon C–H bonds [1,2]. Strong acids are vital in the transformation of typically inert hydrocarbon feedstocks into materials of economic importance. For example, “superacid” systems are able to crack or isomerize alkanes [5]. Superacidic systems play a vital role in the production of valuable industrial compounds, e.g., ethylene, propylene and hence compounds derived from these olefins.

Although not as well studied as superelectrophilic/superacidic compounds, supernucleophilic/superbasic compounds mediate interesting and important chemical transformations. A substantial body of work has been published by Streitwieser and coworkers concerning the kinetic acidities of alkanes, cycloalkanes and other very weak carbon acids using cesium cyclohexylamide (CsCyNH) as a “superbase” [6–21]. Proton exchange kinetics have been reported for reactions of alkanes with CsCyNH in cyclohexylamine solvent [9,12]. From this it was concluded that CsCyNH was monomeric in solution [9]. Streitwieser et al. evaluated dissociation constants derived from conductivity studies of alkali metal ion pairs in THF [27]. This study indicated that these dissociation constants for lithium ion pairs are 10^2 to 10^3 times greater than those of cesium salts. They reasoned that lithium salts of delocalized carbanions exist as solvent separated ion pairs in which dissociation is favored by weak metal–anion interactions and long interionic separations [28]. In contrast, the cesium salts exist as contact ion pairs [29]. The stronger metal–anion interactions and shorter interionic separations make dissociation less favored for cesium salts verses lithium salts. Although not d-block metal complexes, cesium amides hold considerable interest in the context of hydrocarbon activation [11,22]. Specifically, cesium amides permit deprotonation of very strong C–H bonds including those of methane, the primary component of natural gas. Acid/base properties of transition metal organometallics have been demonstrated to be important in CH activation of methane [23–26]. Study of cesium amides thus allows testing of one extreme in ligand basicity/nucleophilicity (and hence metal acidity/electrophilicity) as it pertains to the factors that control metal-mediated cleavage of C–H bonds.

Herein are reported the results of density functional theory (DFT) calculations of cleavage of the CH bonds of methane by $CsNH_2$ as well as derivatives with a larger hydrocarbyl substituent,

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* Corresponding authors.
E-mail address: danielpardue@my.unt.edu (D.B. Pardue).

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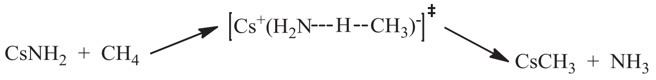

Scheme 1. Depiction of proposed cleavage of the CH bonds of methane by a model cesium amide complex [30].

Scheme 1, cyclohexyl (Cy). Also, Cs is replaced with other alkali metals. The influence of varying the acidity of the substrate was also studied with smaller model complexes. Although studied experimentally [7–12], the extreme reactivity of superbasic compounds has hindered the elucidation of some aspects of their chemistry requiring special experimental techniques. A computational study on the thermodynamics and barriers of hydrocarbon C–H bond cleavage by these and related alkali metal compounds may provide important insight into harnessing superbasic properties of related transition metal complexes without the complications that may arise from the redox non-innocence of d-block metals.

2. Computational methods

DFT within the Gaussian 09 package [31] was used for geometry optimization and vibrational frequency calculations. B3LYP functional was employed. Also, an effective core potential basis set (LANL2DZ) was used for the alkali metals [32]. All other atoms were calculated using the all-electron, 6-31+G(d,p) basis set. Tests with the M06 [33] functional [M06/LANL2DZ/6-31+G(d,p)] did not yield significantly different calculated geometries or free energies.

The energies quoted are free energies that were calculated at 298.15 K and 1 atm. Stationary points were defined as minima or transition states (TSs) by the presence of 0 or 1 imaginary frequencies, respectively, as obtained from calculated energy Hessians. The vibration associated with the single imaginary frequency confirmed that the calculated TS associated with C–H bond cleavage involved the transfer of hydrogen between the carbon (of the substrate) and nitrogen or oxygen of the alkali metal complex. All compounds are in the singlet spin state, unless stated otherwise. Implicit solvation calculations were performed with the SMD [34] method. Geometries were optimized in the presence of the continuum solvent, butylamine, as this was the SMD-parameterized solvent deemed closest to the cyclohexylamine solvent used by Streitwieser and coworkers [6].

Transition state energies were dissected using the general Morokuma/Ziegler and Rauk [35] approach within the Kohn–Sham density functional formalism. This type of analysis for C–H bond activation reactions has been popularized by Bickelhaupt [36] and Ess [37]. Within this approach the total energy (ΔE, Fig. 1) results from the energy to deform ground-state reactants (ΔE_{DIST}) into their transition-state geometry and the energy of the fragments interacting (ΔE_{INT}, Eq. (1)).

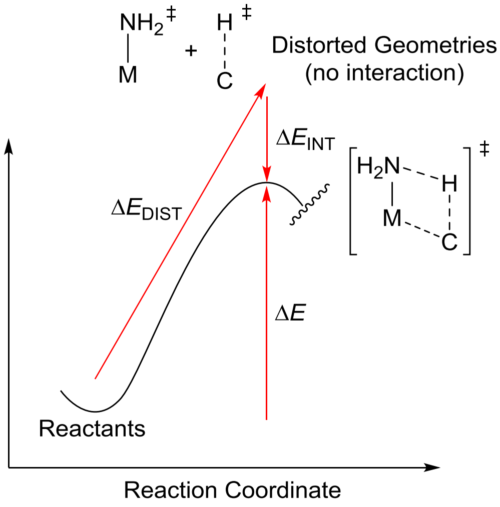

Fig. 1. Illustration of distortion, interaction, and total transition-state energy.

$$\Delta E = \Delta E_{DIST} + \Delta E_{INT} \tag{1}$$

Two different energy decomposition analysis (EDA) schemes were used to further dissect ΔE_{INT} into chemically meaningful terms. The first method used the BLYP functional with Slater-type double-ξ quality orbitals and zero-order regular approximation (ZORA) basis sets in the Amsterdam Density Functional (ADF) package [38]. In this scheme, referred to as ADF-EDA, ΔE_{INT} is dissected into three terms (Eq. (2)).

$$\Delta E_{INT} = \Delta E_{ES} + \Delta E_{PAULI} + \Delta E_{ORB} \tag{2}$$

The full details of ADF-EDA can be found elsewhere [39]. The first term is the electrostatic energy (ΔE_{ES}), which is the result of overlapping transition-state fragment electron densities. This includes nuclei–nuclei, nuclei–electron, and electron–electron quasi-classical Coulombic interactions. The second term is the quantum mechanical closed-shell or Pauli repulsion (ΔE_{PAULI}). The third term is orbital or charge-transfer stabilization (ΔE_{orb}), which results from filled-empty orbital interactions. ΔE_{orb} includes both intermolecular and intramolecular (polarization) orbital stabilization.

The second method used the absolutely localized molecular orbital (ALMO)-EDA developed by Head-Gordon co-workers [40]. ALMO-EDA calculations used the B3LYP density functional with the 6-31+G(d,p) basis set for H, Li, C, and N and the HWMB basis set for Na, K, Rb, and Cs. ALMO-EDA calculations were carried out in Q-Chem 4.0 [41]. The ALMO-EDA method is useful because it has a small basis set dependency and is compatible with hybrid density functionals. In addition, the method can provide an estimate of stabilization for directional donor–acceptor orbital interactions. In the ALMO-EDA scheme the total energy is partitioned according to Eq. (1). However, ΔE_{INT} is dissected into the terms given in the following equation:

$$\Delta E_{INT} = \Delta E_{FRZ} + \Delta E_{POL} + \Delta E_{CT} + \Delta E_{HO} \tag{3}$$

The ΔE_{FRZ} term is a combination of electrostatic and exchange (Pauli) repulsion. This is similar to the ΔE_{ES} and ΔE_{PAULI} energy terms in the ADF-EDA scheme. ΔE_{POL} is intramolecular orbital stabilization. ΔE_{CT} is strictly the energy stabilization gained by allowing intermolecular filled-empty orbital interactions, which can be directionally determined. ΔE_{CT1} is defined as energy stabilization for electron transfer from MNH_2/M(NHCy) (M = Li, Na, K, Rb, Cs) to methane/toluene. ΔE_{CT2} is defined as energy stabilization for electron transfer from methane/toluene to MNH_2/M(NHCy). The higher-order charge transfer term (ΔE_{HO}) is small and cannot be assigned to a specific direction of electron transfer.

3. Results and discussion

3.1. Cleavage of methane CH bonds

The computational methods described above were first employed to model the reaction coordinate for C–H cleavage of methane by $CsNH_2$. The reaction, $Cs(CH_4)NH_2 \rightarrow Cs(CH_3)NH_3$, was calculated to be endergonic by 11.7 kcal/mol (ΔH = 11.0 kcal/mol). Within the adduct, $Cs(CH_4)NH_2$, methane was only weakly bonded to Cs (Cs–C = 3.92 Å), Fig. 2. The calculated Cs-amide nitrogen distance in the adduct was 2.92 Å. Upon C–H cleavage, Cs–C shortens by ~0.6 Å to 3.28 Å, relative to this distance in the