



Negative ion Wolff rearrangement of some diazoketones: A theoretical mechanistic study



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ABSTRACT

The mechanism of the Wolff rearrangement of some deprotonated diazocarbonyl compounds has been studied using density functional calculations, for both the gas and aqueous phases. The anionic rearrangement of the deprotonated analogues proceeds in a similar manner to the neutral counterparts. In the gas phase, the *syn* and *anti* conformers form the deprotonated ketene product concertedly. In certain analogues, the reaction of the *anti* conformer occurs non-concertedly, involving a deprotonated carbene-like intermediate. The migratory aptitude is similar to that in the neutral rearrangement, except that methoxy and amino substituents exchange positions.

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1. Introduction

The rearrangements of organic compounds and their cations in the gas phase have been studied extensively, but studies on the corresponding anionic rearrangements are rare. However, negative ion mass spectrometry [1,2], which involves resonance capture of electrons, has made it possible to study anionic rearrangements. The chemical ionization experiment in the presence of a strong base (such as hydroxide or amide) can result in the organic molecule getting deprotonated. Deprotonation can also take place in the fast atom bombardment technique or secondary ion mass spectrometry. The compound that is fed into the spectrometer is in the gas phase. The primary fragmentations of the deprotonated ions are often simple, but sometimes lead to thermodynamically unstable anions. In such a case, molecular skeletal rearrangement of the initially formed anion may take place under conditions of collisional activation in the mass spectrometer [3–13].

Undoubtedly, negative ions play an important role in many condensed-phase reactions of organic and organometallic systems, and it is equally fascinating to study the corresponding gas-phase chemistry that takes place in the mass spectrometer. Two reviews [14,15] detail the comparison of such skeletal rearrangement pro-

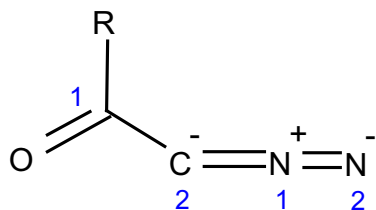
cesses of even-electron anions in the gas phase and the solution phase. Anionic rearrangement reactions like acyloin [16], anionic Wolff, benzoic acid [17], Dieckmann [18,19], Lossen [20–22], nitrogen Wittig [23,24], Smiles [25] and Wittig [26,27] rearrangements can occur both in solution as well as in the gas phase. It is also suggested that some rearrangements, including Favorskii [28–30] and Tiemann [31], occur only in the condensed phase. On the other hand, negative ion pinacol/pinacolone [32] and Beckmann [33] rearrangements have no condensed phase analogy.

Since we have already investigated the Wolff rearrangement [34], which involves the skeletal rearrangement of diazocarbonyl compounds, in this work we proceed with their deprotonated analogues. Diazo compounds are the main precursors of the Wolff rearrangement reaction, and they are ambiphilic in nature, as is obvious from their resonance structures [34]. The partial negative charge on the carbon atom attached to the diazo group renders nucleophilic character to it, and makes it open to electrophilic attack. However, diazo compounds generally degrade under acidic conditions, but are comparatively stable when treated with bases [35]. They can form detectable deprotonated species with a strong base [36]. The results demonstrate that a hydrogen atom is lost mainly from the original diazocarbonyl portion [37,38], i.e. specifically from the methine (C₂) position (Scheme 1).

The deprotonated diazocarbonyl compounds are thought to follow a Wolff type rearrangement (Scheme 2) under collisional activated decomposition, except that the reactant and product are

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Scheme 1. Structure of the deprotonated diazocarbonyl compounds.

deprotonated, and therefore the rearrangement reaction is termed as *negative ion* or *anionic Wolff rearrangement* (Scheme 3).

Deprotonated precursors are also suspected to be involved in the metal catalyzed Wolff rearrangement. The following mechanism (Scheme 4) was proposed [39] for the Wolff rearrangement of α -diazacetophenone (I), where R = Ph) in basic solution of silver benzoate and triethylamine.

The reaction is suspected to form the deprotonated ketene (II) via two different mechanisms, i.e. concerted mechanism or two-step mechanism. The latter involves a deprotonated carbenic intermediate complexed with the catalyst (III).

Primarily, the gas phase negative ion Wolff rearrangement was first reported by the Lebedev group. The product ion studies conducted by them showed that the collision-induced loss of dinitrogen from deprotonated aryl diazomethyl ketones yields a deprotonated ketene derivative [11]. Later, in the same year, they proposed a direct analogy between the behavior of deprotonated diazo species in the gas phase and that of the neutral precursor under basic conditions in solution [40]. They found that 2-diazo-2-cyanoacetamide anion **A** cyclizes to **B** both in the gas and condensed phases; **B** then fragments to form a ketene derivative **D** as the major ionic product rather than the alternate product **C**, as shown in Scheme 5.

However, the key question is whether the *anionic* or *negative-ion* Wolff rearrangement proceeds in a similar manner to its neutral counterpart or not. For this purpose, we need to gain insight into the mechanistic aspect of the anionic Wolff rearrangement reaction. Therefore, in this paper, we have investigated the key step of expulsion of molecular nitrogen (Scheme 3) for some deprotonated diazocarbonyl compounds.

2. Computational details

The geometries of all structures were fully optimized at the DFT B3LYP/6-311 + G(d,p) level [41–44] with respect to the energy, followed by harmonic vibrational frequency calculations at the same level, which were used to confirm the nature of all stationary point structures, and to account for zero-point energy and entropy corrections to the Gibbs energy [45]. The energy values reported here are all Gibbs energies at 298.15 K and 1 atm pressure. Intrinsic Reaction Coordinate (IRC) calculations [46,47] were performed to

confirm that the transition states connect the reactant to the desired product.

The NBO method [48] was used to identify the best Lewis structure representations of the equilibrium structures and transition states. The natural charges on the various atoms and Wiberg bond orders were also computed. All calculations were performed with the Gaussian 09W suite [49]. The universal implicit solvent model, SMD (solvation model based on density) [50] was used to study the influence of bulk solvent, with the dielectric constant (ϵ) taken as 78.39 for water at 298.15 K. The optimized gas-phase structures were taken as initial geometries for their complete optimization with respect to the energy using the SMD model.

3. Results and discussion

3.1. Structure of deprotonated diazoethanal

We first conducted an investigation of the potential energy profile of deprotonated diazoethanal. Similar to the neutral molecule, two conformations are possible for the deprotonated form: *syn* and *anti*, which are displayed in Fig. 1.

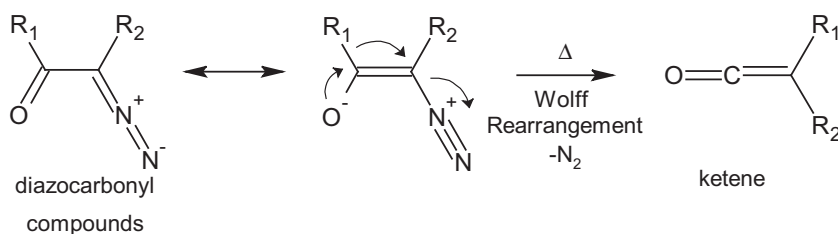
Table 1 gives the relative Gibbs energies of the structures on the energy surface of deprotonated diazoethanal with respect to the *syn* conformer. Unlike the neutral precursor, the *syn* conformer is computed to be higher in Gibbs energy than the *anti* conformer by 1.5 kcal mol⁻¹.

The structural bond parameters of the *syn* and *anti* conformers are given in Table S1.1 of the Supplementary Information (SI). The two conformers are planar, as confirmed by their dihedral angles. As compared to the neutral counterpart [34], there are only slight variations in the bond lengths.

The *syn* and *anti* conformers of deprotonated diazoethanal also have similar structures. Each is a hybrid of four possible resonating structures, as shown in Scheme 6 for the *anti* conformer.

The resonance causes delocalization of the unit negative charge over the diazo and carbonyl moieties, as evident from the computed natural charges given in Table 2. As compared to the neutral molecule, the negative charge on the oxygen atom increases by ~ 0.2 , whereas the natural charge on the hydrogen atom is halved. Surprisingly, the *anti* conformer carries a slight negative charge on the N₁ atom, though there is a positive charge on that nitrogen atom in all the possible resonance structures (Scheme 6).

The computed Wiberg bond orders are tabulated in Table 3. It is found that the C–C and C–N bond orders increase as compared to the neutral molecule [34]. The deprotonation also weakens the C₁–H bond. There is an overlap between the orbitals of the diazo carbon and the carbonyl oxygen as well, as seen from the C₂...O bond orders in both the conformers (Table 3). The carbonyl and C–N bond orders are ~ 1.5 , which indicates towards partial double bond character of these bonds, and also signifies contribution of resonance structure **C**, along with **A** (Scheme 6). In fact, resonance structures **B** and **D** are ruled out on the following grounds too. In structure **B**, the formal charge on C is -2 , which is highly unlikely because of its proximity to the more electronegative nitrogen



Scheme 2. Wolff rearrangement of diazocarbonyl compounds.

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