Journal Club 2014.11.27 Kohei Hashimoto

The Highly Reactive Benzhydryl Cation Isolated and Stabilized in Water Ice

Paolo Costa, Miguel Fernandez-Oliva, Elsa Sanchez-Garcia and Wolfram Sander

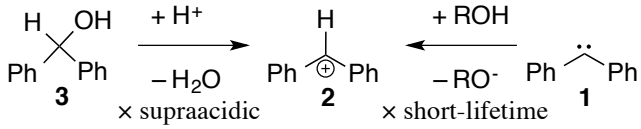
J. Am. Chem. Soc., **2014**, *136* (44), 15625-15630

1. Introduction

1-1. Carbenium Ion

- One of the most important reactive intermediate
- Only in superacidic condition cation**2** is stable for characterization (such as conc. H_2SO_4)
- Proton transfer to a singlet carbene **1** is general rout to cation **2**
- The life time scale of cation **2** in general solvent is in order of picosecond

Scheme 1. Formation of carbenium ion **2**



1-2. History of Charactlization of 1 and 2

- Methanol is efficient solvent for protonation of **1** (1963).[a]
- Formation of **2** by protonation of **1** was confirmed by picosecond UV-vis absorption spectroscopy (1990).[b]
- By femtosecond spectroscopy, in neat methanol, **2** is formed by protonation of singlet-**1** (**S-1**) with a time constant of 9 ps. And **2** is reacted with surrounding methanol with a time constant of 31 ps (2002).[c]

1-3. Matrix Isolation Spectroscopy

- Trapping the reactive chemical species with unreactive matrix, such as noble gases.
- The mixture of noble gas and dilute sample are deposited on the windows cooled to below the melting point of the host gas.
- These samples were used in various spectroscopic analyses.

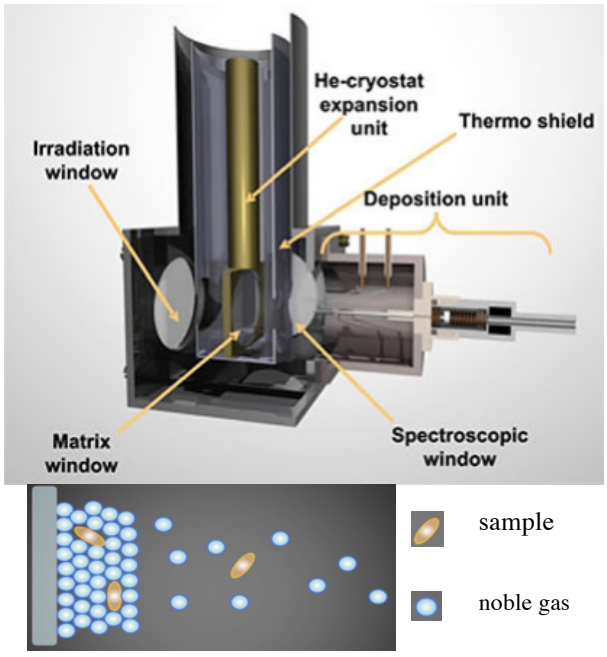


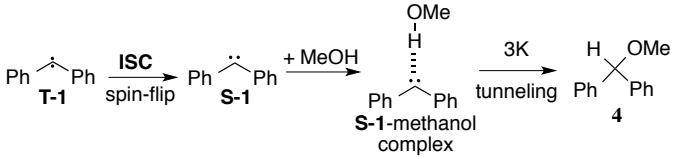
Figure 1. Structure of the matrix isolation machine

1-4. Authors' Previous Work[d]

- Reaction of **1** with single molecule of methanol in argon matrices doped with 0.5-1% of methanol was investigated by matrix isolation spectroscopy.
- **S-1** formed a very strong hydrogen bond with methanol, while **T-1** is weak hydrogen bond acceptor.

→ The spin ground state of carbene-methanol complex was shifted to singlet via spin-flip.

Scheme 2. Reaction of **1** and methanol



- Even in 3 K, this complex reacted to ether via quantum chemical tunneling.
- Expand the scope of solvent-induced spin-flip is necessary.

2. Results and Discussion

2-1. Reaction of 1 with Single Water Molecule

- **T-1** is obtained by photolysis of diphenyldiazomethane matrix in argon doped with 0.5-1% water at 3 K and **T-1** is obtained by photolysis .
- Then this matrix is annealed at 25 K, **S-1** – water complex is generated.

→ These species are characterized by IR spectrum and UV-vis absorption (Figure 2).

- 1327.8 cm^{-1}

→ asym. C-C-C str. vibration of the center (in agreement with DFT calculation and ^{13}C labeling)

→ Spin-flip is confirmed also in water

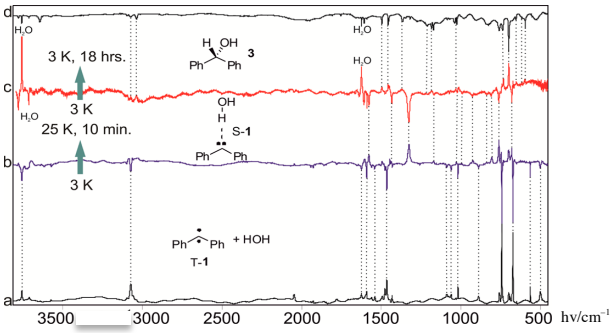


Figure 2. IR spectrum of the reaction between **1** and water

- These findings are corroborated by DFT calculation in gas phase and by QM/MM level of theory in argon matrices.
- In gas phase, the S-T gap of **1** is 3.3 kcal/mol.
- In argon, the S-T gap of **1** is 1.5 kcal/mol.

→ Suggest that stabilization by solvation

- The S-T gap of **1**-water complex is inverted, singlet state is more stable than triplet by 1.6 kcal/mol in the gas phase and even by 2.4 kcal/mol in argon(Figure 3).

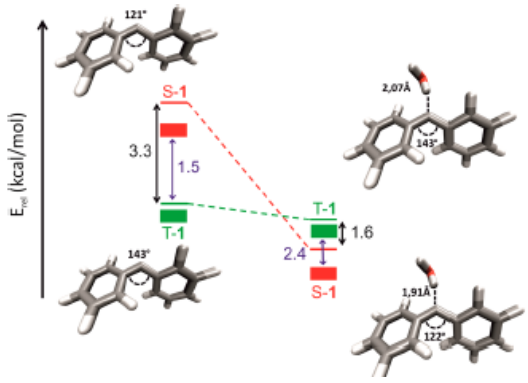


Figure 3. S-T gap of **1** and **1**-water complex

・Complex **S-1** – methanol is metastable and at temperature between 3-12 K rearranges with a rate of $5.8 \pm 0.2 \times 10^{-6}$ to **3** (independent of temperature) (Figure 4).

→ Indicate tunneling reaction.

・Activation barrier is 16.7 kcal/mol

→ Significantly larger than methanol complex.

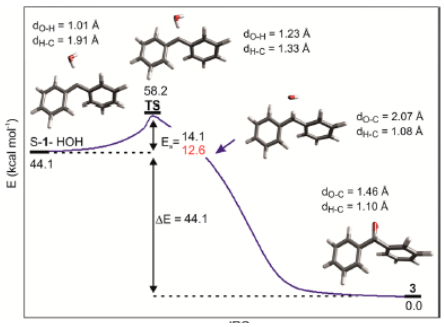


Figure 4. Intrinsic reaction coordinate

・ In argon, the ion pair **2** and OH^- is not obtained nor predicted by calculation.

→ More polar medium stabilize this ion pair? ⇒ Water matrix.

2-2. Reaction of 1 in Amorphous Water Ice

・ What is low density amorphous (LDA) water ice?

→ ・ absence of long-range periodic structure

・ Similar to liquid water formation than crystalline ice

・ Ultraslow reorientation even at temperature of glass-liquid transition

・ At 3 K, this motion is completely frozen.

・ Diphenyldiazomethane is sublimed and trap with water at 50 K. Then cooling to 3 K and LDA ice is formed.

・ Then photolysis with 530 nm is started and cation **2** was formed, and annealing above 40 K, **2** is disappeared alcohol **3** is formed.

・ In this process, singlet carbene **S-1** is not detected.

・ These reactions are confirmed by UV-vis absorption (Figure 5).

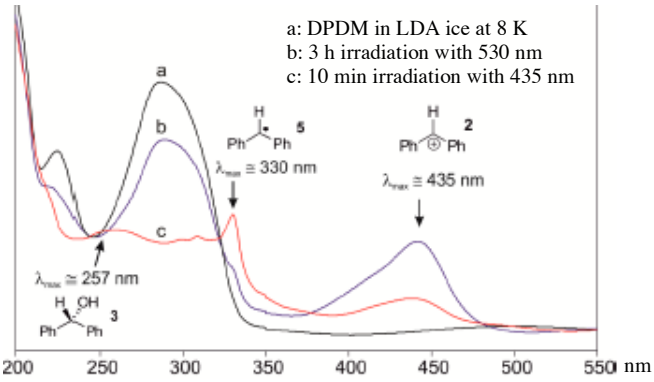


Figure 5. UV-vis absorption in LDA ice

・ The IR spectrum of cation **2** in LDA ice nicely matches the calculated gas-phase spectrum of **2** (Figure 6).

・ Calculation among cation **2** and surrounding water is carried out.

→ No hydrogen bonding is formed.

→ The reason why real situation matches in gas-phase calculation.

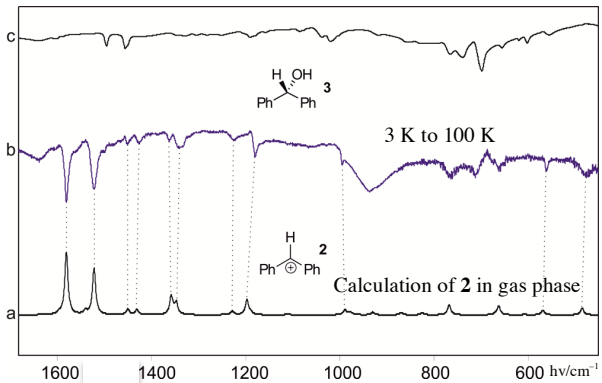


Figure 6. IR spectrum in LDA ice

・ Irradiation with 435 nm cause unexpected photochemistry.

→ Disappearance of cation **2** and, generate benzhydryl radical **5**.

→ Expected that photolysis of cation **2** and formed radical **5** with surrounding water molecule.

⇒ The high reactivity of cation **2** is remained.

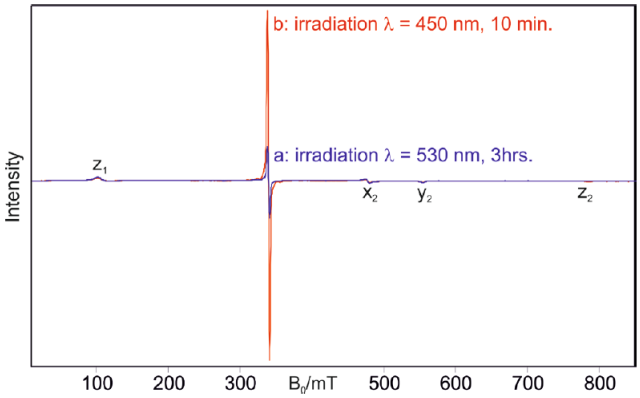


Figure 7. ESR spectrum after irradiation

・ These results reveale the reaction process between **1** and water molecule (Figure 8).

・

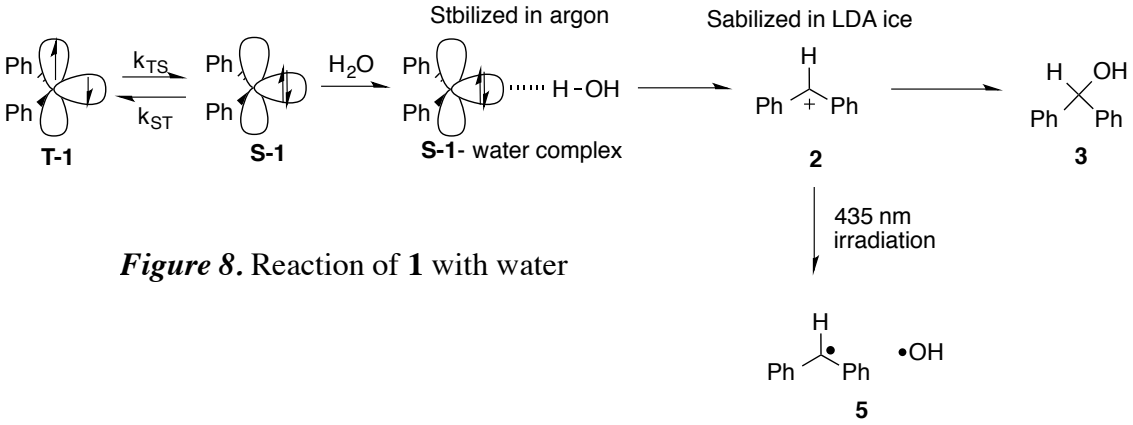


Figure 8. Reaction of **1** with water

3. Conclusion

・ The author achieve the characterization of reaction intermediate in the reaction between **1** and water by IR and UV-vis spectroscopy and theoretical calculations.

・ In argon, **S-1** water complex is stabilized by high polarity and the rate of the tunneling reaction is about 1 order slower in methanol case.

・ In LDA ice, cation **2** is entirely stable below 40 K.

・ This stabilization is derived from kinetic effect but not thermodynamic effect.

→ This LDA method allow us to synthesize and spectroscopically characterize some of unrevealed reactive intermediates.

4. Reference

a. Kirmse, W. *Angew. Chem.* **1963**, *75*, 678.

b. Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399.

c. Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428

d. Costa, P.; Sander, W. *Angew. Chem., Int. Ed.* **2014**, *53*, 5122