Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Mercapto Carbenes – New Precursor Strategies

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Introduction

Schreiner's group was able to synthesize various hydroxy carbenes by thermal extrusion of CO_2 from *α*-keto carboxylic acids (Fig. 1). The corresponding esters of *α*-keto carboxylic acids are also capable of extruding CO_2 and the carbene after the ester is cleaved during high vacuum flash pyrolysis (HVFP) producing ethylene or isobutene in the case of ethyl- or *t*-butyl-esters, respectively.

Methods

The precursor molecules get evaporated in high vacuum together with a stream of a host gas (mostly noble gases). This stream passes an oven where the precursor decomposes. All the fragments get caught on a CsI window which is cooled to 3 K. The fragments are now frozen and separated by host gas molecules or atoms and get investigated spectroscopically (UV/IR). The experimental results will be investigated theoretically with high performance computations.

Results

After hydroxy methylene and derivatives were detected under cryogenic conditions, it was expected that the S and Se congeners would be detectable as well. Computational studies suggest that tunneling in these derivatives would be very slow so that they should be readily observable. A matrix isolation study by Schreiner and coworkers showed that high vacuum flash pyrolysis (HVFP) of 1,3 dithietane 1,3-dioxide delivers thioformaldehyde *S* oxide **2** which, upon irradiation, forms the

species shown in blue in Scheme 1, but not carbene **8**. Upon HVFP of thionated diethyl oxalate **7** we obtained CSO, ethylene, **5**, **6**, and evidence for the desired mercapto hydroxy methylene **8**.

Outlook

As shown in Figure 2 we will synthesize different precursor molecules for various mercapto carbenes and investigate them with matrix isolation spectroscopy and computational methods. The latter provide powerful tools to investigate properties of reactive intermediates such as tunneling reactions and half-lives. Furthermore, meta-dynamics simulations give insight to thermal decomposition reactions to predict thermolysis products.

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