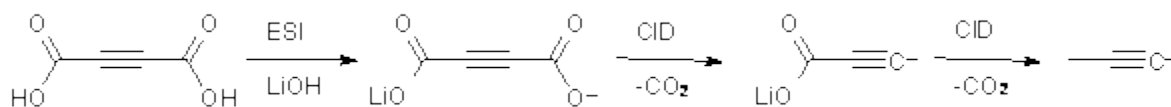


ACIDITY OF LITHIUM ACETYLIDE

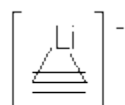
I have had a long-standing interest in organolithium compounds, dating back to my graduate student days. Thus, I was excited to read Kass and Radom's latest work on the computational and experimental evaluation of the acidity of lithium acetylide LiCCH .¹

The gas phase experimental acidity is accomplished by preparing the conjugate base of lithium acetylide through a procedure of collision-induced dissociation with loss of CO_2 , as in Scheme 1. By reacting this anion with a variety of different acids, they were able to bracket the acidity and determine that ΔH_{acid} is $391.0 \pm 1.3 \text{ kcal mol}^{-1}$. This is about 13 kcal mol^{-1} *less acidic* than acetylene itself. The reduction in acidity is understandable in terms of the C-Li being essentially ionic, and thereby loss of the proton builds up negative charge on a carbon adjacent to a carbon that already has a great deal of negative charge.

Scheme 1



Computations support this enthalpy for deprotonation. The G3, G4 and W1 values for the enthalpy deprotonation of lithium acetylide are 389.1, 388.9, and 390.4 kcal mol⁻¹, respectively. It should also be noted that the conjugate base of lithium acetylide possesses a non-classical bridging geometry **1**, which is well-known for organolithium species.²



1

Source: <http://comporgchem.com/blog/?p=1082>