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A DFT proton affinity study of vinyl and allyl anions of cyclic vinyl ethers and cycloalkenes

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Abstract

Proton affinities of vinyl and allyl anions of cyclic vinyl ethers and cycloalkenes obtained at the B3PW91 level with Davidson's modification of basis set aug-cc-pVDZ are presented to further explore deprotonation reactions of cyclic vinyl ethers. The presence of an oxygen atom α to a vinyl anion has a clear acidifying effect. Relative proton affinities for 2,3-dihydrofuran and 2,3-dihydrooxepin are consistent with experimental results; however this is not the case for 2,3-dihydro-4*H*-pyran and 2,3,4,5-tetrahydrooxepin. Although gas-phase proton affinities may help to explain deprotonation of cyclic vinyl ethers with some alkyllithium reagents in solution, it clearly cannot be the only contributor. Other factors to consider include solvation, aggregation, and relative transition state energies.

Keywords: deprotonation; ethers; alkenes; acidity.

1. Introduction

In recent years, experimental[1–6,10] and computational[7–10] studies concerning deprotonation reactions of vinyl ethers and alkenes have been of interest. Our efforts in this area have examined allylic and vinylic deprotonation of vinyl ethers and alkenes with some alkyllithium reagents. Although attempts have been made to make estimates of the proton affinities of allyl and vinyl anions,[7,8] none of these studies have included more accurate electron correlated methods. It is known experimentally that 2,3-dihydrofuran (**3**), 2,3-dihydro-4*H*-pyran (**5**), and 2,3,4,5-tetrahydrooxepin (**7**) react with alkyllithium reagents in solution to form vinyl lithiated species.[5,6] Conversely, 2,3-dihydrooxepin (**9**) is deprotonated under the same reaction conditions to form 1-lithio-1-oxaheptatriene;[6] which may have formed from initial deprotonation at the allylic position and subsequent ring-opening to the experimentally observed product. For the purposes of this study, ab initio calculations were used to examine the proton affinities of **3**, **5**, **7**, **9**, oxete (**1**), cyclobutene (**2**), cyclopentene (**4**), cyclohexene (**6**), cycloheptene (**8**), and 1,3-cycloheptadiene (**10**).

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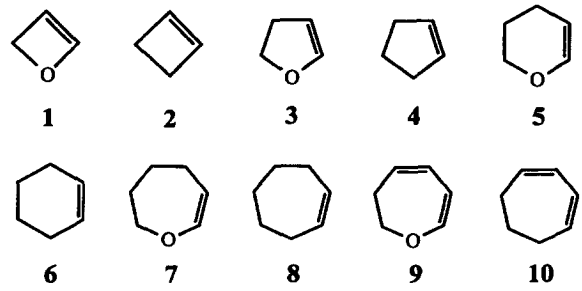


Figure 1. Structures

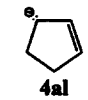
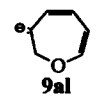
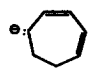
2. Computational details and methodology

Geometry optimizations were performed with Gaussian 94[11] on structures shown in Fig. 1 and Table 1 at the B3PW91[12,13] level of theory taking advantage of Davidson's[14] less contracted (modified) version of Dunning's aug-cc-pVDZ basis set[15–19] (aug-cc-pVDZ-*mod*). It has been well established with exhaustive testing that DFT proton affinity calculations performed at the B3PW91 level with the aug-cc-pVDZ basis set rival those results obtained with higher level calculations.[20] Using this methodology, Merril and Kass[20] were able to obtain a proton affinity value of 389.1 kcal/mol for the allyl anion and this is within the standard deviation of the gas phase experimental value (390.8±2.1 kcal/mol).[21] Using our slightly different methodology (B3PW91/aug-cc-pVDZ-*mod*) we were able to obtain 388.2 kcal/mol for the proton affinity of the anion. When compared to the experimental value, our calculated proton affinity (which is also within the limits of the value obtained experimentally) differs by less than one percent. This is very suggestive that the methodology employed here will give quite accurate results.[22] Unfortunately, and to the best of our knowledge, there are no experimental data at this time in the literature to compare proton affinity calculations of vinyl and allyl anions for the structures in Fig. 1. The allyl anion is the only example of an allylic anion for which there is an experimental comparison; there are no such examples of vinyl anions. Each stationary point was verified as a minimum using analytical second derivative vibrational frequency calculations. Proton affinities were computed with the incorporation of a zero-point correction energy, a finite temperature correction (298 K), and the pressure-volume work term.

3. Results and discussion

Proton affinities for vinyl and allyl anions of **1–10** are shown in Table 1. The presence of an oxygen adjacent to a vinyl anion has a clear acidifying effect in every case. The observation that an oxygen atom α to a vinyl anion lowers the proton affinity of the anion is consistent with previously reported computational findings.[7,8] Vinyl anions **1v**, **3v**, **5v**, **7v**, and **9v** are less basic than the vinyl anions **2v**, **4v**, **6v**, **8v**, and **10v** by 12.2, 9.8, 6.8, 4.4, and 7.5 kcal/mol, respectively. Also note that the difference in proton affinity between the corresponding vinyl and allyl anions is smaller for the cyclic vinyl ethers than it is for the cycloalkenes. With the exception of **9v**, the proton affinities of the vinyl anions increase with enlarging ring size such that 4<5<6~7. With the exclusion of **10v**, the cycloalkenes exhibit a moderately similar trend: 4~5<6~7. Regarding the allyl anions of the cycloalkenes, the calculated proton affinities decrease with increasing ring size. Examination of the proton affinities of the vinyl ether allyl anions as a function of ring size shows little resemblance to what is seen with the alkenes. Note that increasing the degree of conjugation within the seven-membered rings (allyl versus pentadienyl anion) decreases the proton affinities (**7al** and **8al** versus **9al** and **10al**, respectively). The vinyl anion **3v** and the allyl anion

Table 1
Proton affinities[a] (kcal/mol) calculated from B3PW91/aug-cc-pVDZ-*mod*

 **1v**	391.3	 **1al**	392.5	 **6v**	408.9	 **6al**	390.0
 **2v**	403.5	 **2al**	399.1	 **7v**	403.2	 **7al**	390.6
 **3v**	395.1	 **3al**	397.6	 **8v**	407.6	 **8al**	384.6
 **4v**	404.9	 **4al**	393.5	 **9v**	395.9	 **9al**	371.9
 **5v**	402.1	 **5al**	392.9	 **10v**	403.4	 **10al**	371.2

[a]All values have been zero-point, temperature, and pressure-volume work term corrected.

9al are both stabilized over the corresponding allyl anion **3al** and the vinyl anion **9v**, respectively, and this is consistent with the experimentally observed site of deprotonation in solution.[1,5,6] The allyl anions **5al** and **7al** are predicted to be less basic than the vinyl anions **5v** and **7v**, respectively. This is suggestive of allylic deprotonation of **5** and **7**. This conclusion is exactly opposite to what is seen experimentally when deprotonating with some alkyllithium reagents.[5,6] Although proton affinities may have something to do with directing deprotonation of cyclic vinyl ethers, it clearly cannot be the only contributor.

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