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AB INITIO CALCULATION OF THE STABILITIES OF THE OXETENYL ANION AND CATION

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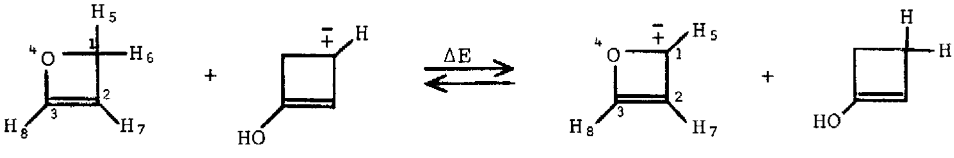
ABSTRACT: *Ab initio* calculations show a cyclic resonance stabilization of ~20 kcal/mol for the 6-pi electron oxetenyl anion. The 4-pi electron cation is destabilized by ~50 kcal/mol.

Molecular orbital calculations not only serve to rationalize experimental data, but also to calculate quantities that are experimentally unavailable as well as to provide theoretical guidance for future experimentation. In this regard, we are interested in whether the stabilities of the oxetenyl anion and cation, 1a,b, will be unusual since they are formally composed of 6-pi and 4-pi electrons, respectively. Furthermore, the results of the calculations are of more than just theoretical interest, since we should be able to prepare these species from their parent oxetene, 2.[1]

We have chosen the isodesmic[2] reaction (1) shown below in order to relate the stability of the ions 1a or 1b to those ions of a suitable model system. The model compound 4 we chose has a cyclic four-membered ring whose allylic system is linearly conjugated to an oxygen atom.



(1)

2　4a,b　1a,b　3

We first calculated by simple Hückel methods the ΔE for the two isodesmic reactions. Standard Coulomb and resonance integrals were used with zero overlap.[3] At this simple MO level, the anion 1a appears to be stabilized by 0.28β whereas the cation, 1b, has the same proton transfer energy as the model.

To obtain a better estimate of the ΔE, *ab initio* calculations were carried out. The geometries of 1-4 were determined by minimizing the total energy of each species. In all cases, the heavy atoms were assumed to be in one plane. Carbon-hydrogen and oxygen-hydrogen bond lengths were held at constant values while all other bond angles and bond distances were varied. The geometry calculations were done with the Gaussian 70 program[4] at the STO-3G level.[5] Each parameter was ultimately optimized[6] over a structural grid of 0.01Å or 1° which results in an error in the calculated energy of <0.0125 kcal/mol/parameter.

Single point calculations at the 4-31G level[7] were then done using the STO-3G geometries. In addition, we also wanted to know what the "vertical" ΔE is, in which the geometries of 2 and 3 were fixed at values corresponding to the relaxed geometries of 1 and 4. The only relaxation given to 2 and 3 were the parameters associated with the CH_2 groups. Relaxed geometries were assigned to the ions rather than to 2 and 3 because the 4-pi or 6-pi resonance effect applies to the ions 1a,b. The results are as follows:

Energies for Optimized Geometries, au

System	Neutral	Anion	Cation
Oxetene			
STO-3G	-188.298198	-187.458358	-187.433867
4-31G	-190.412044	-189.716134	-189.492126
Cyclobutenol			
STO-3G	-226.885842	-226.015931	-226.096486
4-31G	-229.416626	-228.689394	-228.576749

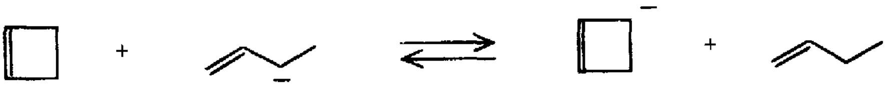
ΔE (kcal/mol) for Isodesmic Reaction (1)

System	STO-3G	4-31G
Anion	-19(-24)	-20(-22)
Cation	+47(+63)	+50(+58)

The excellent agreement between the 4-31G and STO-3G results was expected since the calculated ΔE's are for an isodesmic reaction in which errors substantially cancel. The vertical ΔE's are in parentheses and show the same relative effects.

The ΔE for the anion reactions implies that there is a substantial amount of stabilizing resonance energy. In perspective, however, this does not imply that the oxetene would be unusually acidic relative to, for example, propene. The STO-3G energies of propene[8] and propenyl anion[8] are known from which it can be calculated that the ΔE of proton transfer from oxetene 2 to propenyl anion is uphill by 11 kcal/mol. Oxetene should therefore be less acidic than propene even though anion 1a benefits by about 20 kcal/mol over the model system 4a. The results suggest that were the anion 1a not stabilized by cyclic conjugation, there would be a very small acidity to the allylic hydrogens.

This discovery is supported by MINDO/3 calculations which also show a low acidity of cyclobutene allylic hydrogens.[9] Indeed, experimental evidence suggests that the vinyl hydrogens of cyclobutene are exchanged by base before the allylic hydrogens.[10]



ΔE = 22.8 kcal/mol

The calculated energy of the cation reaction of 1b is surprisingly large. Classically, cation 1b should be unusually stable due to neighboring oxygen and double bond groups. Theoretically, however, an isodesmic reaction with propene[8] shows that the primary propenyl cation[11] should be 10 kcal/mol more stable than cation 1b. As a result, we expect that an NBS allylic bromination of oxetene 2 should give a reasonably stable bromide with much less reactivity than normal allylic bromides located alpha to oxygen.

The structural differences among oxetene 2 and its ions 1a,b are shown as follows:

Geometry	Oxetene 2	Anion 1a	Cation 1b
C_1—C_2	1.526Å	1.383	1.397
C_2—C_3	1.312	1.383	1.397
C_3—O_4	1.424	1.432	1.448
$\angle C_1C_2C_3$	88.3°	90.3	86.5
$\angle C_2C_3C_4$	98.1	91.7	95.4
$\angle H_5C_1C_2$	140.6	142.8	140.1
$\angle H_5C_1H_6$	110.6	-	-
$\angle H_7C_2C_3$	137.3	134.9	136.7
$\angle H_8C_2C_3$	139.0	142.8	140.1
C_1—H_5 (fixed)	1.089Å	1.10	1.10
C_1—H_7 (fixed)	1.082	1.10	1.10
C_3—H_8 (fixed)	1.082	1.10	1.10

Our structural data for oxetene is similar to that previously calculated by van der Meer and Mulder.[12] It is interesting to note that the cation 1b has a four-membered ring in which $C_{1,3}$ distance is slightly shorter and the perimeter is slightly longer than those of anion 1a. Presumably, these features serve to limit the resonance destabilization of the cyclic 4-pi conjugation in the cation.

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