A MOLECULAR ORBITAL STUDY OF ALKOXY ALLYL AND VINYL ANIONS

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An adequate description of the electronic structure of anions poses an important challenge for the computational chemist.[1] The purpose of the present work is to explain how substituted vinyl anions (1,X=OR) can be stabilized relative to the isoelectronic substituted allyl anions
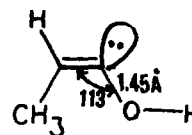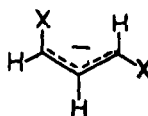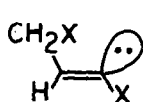
(2,X=OR). Recent experimental results on substituted alkoxyalkenes[2] produced methylation exclusively at the α-vinyl position rather than yielding an allyl-alkylated product. On the other hand, calculations on unsubstituted propenyl and allyl anions (1,2,X=H) have shown that the allyl anion is significantly more stable than the propenyl anion for a variety of geometrical distortions.[3] In this work it will be shown how this trend can be modified by the substitution of an alkyoxy group for a hydrogen. The approach that we have followed in describing differences in stability and reactivity is the use of qualitative molecular orbital bonding concepts buttressed by symmetry arguments[4] as well as quantitative calculations on selected anions.[5]

The substitution of an alkoxy group for hydrogen is to stabilize by inductive effects both the vinyl and allyl anions. Since the vinyl carbanion center is more localized, substitution of an OR group adjacent to this center produces a more dominant stabilizing effect than for the allyl system. Superimposed upon the inductive stabilization is a trend of destabilization of the π system of the allyl moiety and to a lesser extent the carbanion center of the vinyl anion by the oxygen lone pair orbitals. An interaction diagram for the π orbitals of an allyl fragment interacting with oxygen lone pair orbitals of the -OR group is shown in Figure 1. The lower molecular orbitals of S and A symmetry are localized predominantly on the oxygen lone pair orbitals while the high energy orbitals are essentially on the allyl fragment with some oxygen lone pair character mixed in an antibonding manner. The overall effect is a four-electron destabilizing interaction between the π-donor orbitals on the oxygen with the filled π orbitals of the allyl moiety.

The OR group also has a destabilizing effect in the vinyl anion. In 3 is shown an alkoxy vinyl anion along with optimized values for some of the important structural parameters. The optimized value of 1.45 Å for the C-O bond length in the alkoxy vinyl anion represents an increase
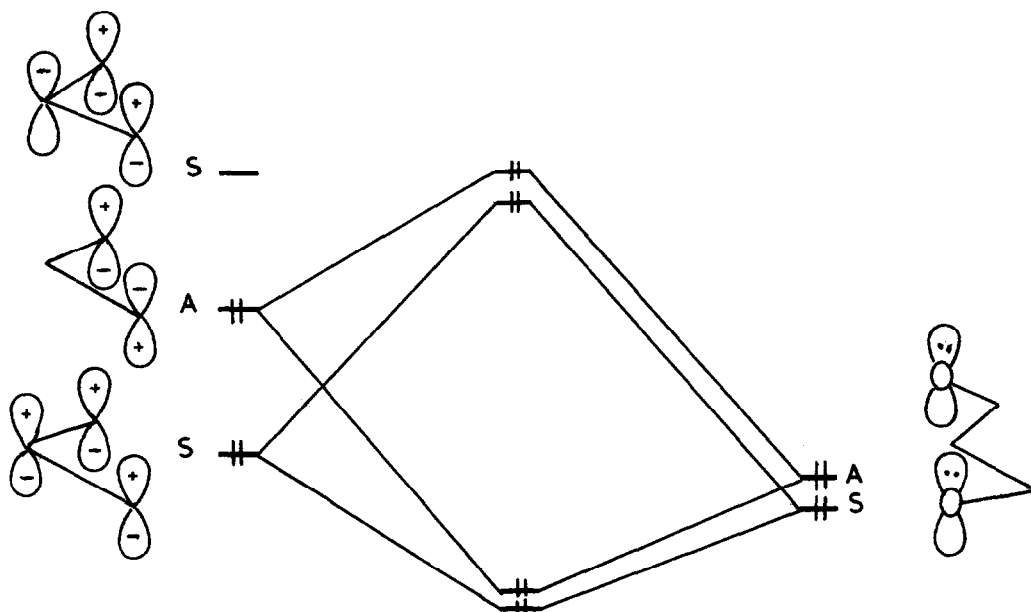
Figure 1. An interaction diagram for the lone pair orbitals on the OR group with the allyl π
orbitals.

			ΔE (KCAL/MOLE)
-116.2260		-116.1865	24.8
-190.9691		-190.9639	3.3
-229.9330		-229.9296	2.1
-265.7101		-265.7083	1.1

Figure 2. Total energies (au) of selected allyl and vinyl anion pairs calculated using the STO
4-31G Basis Set.[6] For the substituted allyl anions, the OR group is rotated 90° out of
the plane of the anion and corresponds to the most stable structure. The value under
ΔE indicates the stability of the allyl anion compared to the partner vinyl anion.

of 0.06 Å over the neutral $\underline{6}$[7] and indicates a repulsive interaction between the localized anion
orbital and the lone pair orbital on the oxygen. The decrease in the <CCO angle from 120° to 113°

allows an increase in s character and consequently stabilizes the localized anion orbital.

The extent of destabilization operative in substituted allyl anions is greater than for alkoxy vinyl anions as can be seen in Figure 2. Inspection of Figure 2 indicates that an energy difference of 25 kcal/mole between the unsubstituted allyl and vinyl anions is reduced substantially to about 2-3 kcal/mole for the monosubstituted alkoxy anions. The energy difference for the dihydroxy anions is about the same indicating that a second OR group does not have as great a destabilizing influence as the first. It is important to emphasize that the values of energies given in Figure 2 should be taken as indicative of a _trend_, since the treatment of anions at the SCF level is a difficult problem, and quantitative differences of these species can be obtained only by including correlation effects. As expected there is a decrease in charge on the alkoxy vinyl anion relative to the unsubstituted vinyl carbanion ($\Delta Q=0.47$), indicative of a stabilizing inductive effect by the electronegative oxygen substituent.

In order to explain why the alkoxy vinyl anion is formed exclusively, we have also considered factors contributing to the kinetic acidities of the alkoxy vinyl and allyl hydrogens. Since there may be other factors influencing the relative activation energies, it was decided to perform calculations on propene $\underline{4}$ and vinyl alcohol $\underline{5}$ to determine if the vinyl carbon-hydrogen bond is weakened by the introduction of an OR substituent.[7]
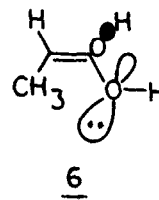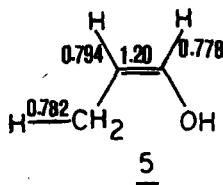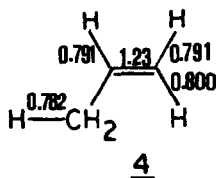
It can be seen from a comparison of the Mulliken Overlap Population[8] of the vinyl C-H bond _trans_ to the methyl group with the methyl C-H bond in $\underline{4}$ and $\underline{5}$ that the vinyl C-H bond is weakened by the introduction of the O-H group. This seems to indicate that a hyperconjugative interaction[9] as shown in $\underline{6}$ is playing a role to weaken the C-H bond. The decrease in overlap population of the C-C bond in going from propene $\underline{4}$ to the vinyl alcohol $\underline{5}$ is mainly due to the π system and is not directly related to the weakening of the vinyl C-H bond.

Finally, it should be noted that the most stable geometry of the neutral molecule $\underline{6}$ is the planar one shown with the O-H bond eclipsing the vinyl C-H bond. The energy required to rotate the O-H group 90° out of the plane to obtain the preferred conformation of the allyl anion, is about 3 kcal/mole.[7] On the other hand, the most stable conformation of the alkoxy vinyl anion is still planar (c.f. Fig. 2). The formation of a vinyl alkoxy anion from the neutral molecule involves a smooth transition with simple cleavage of the vinyl C-H bond whereas formation of the alkoxy allyl anion involves breaking the methyl C-H bond as well as rotation about the C-O bond. The additional rotational constraint for the formation of the alkoxy allyl anion could increase the activation energy and allow faster formation of the substituted vinyl anion.

In summary, the calculations presented in this paper provide a plausible explanation for the preferred formation of alkoxy vinyl anions over alkoxy allyl anions. However, it is not sufficient to explain the experimental results by solely invoking the relative thermodynamic stabilities of of the anion intermediates as obtained by these calculations. Additional explanation of the experimental results may lie in understanding the effects of ion pairing in solution, an effect

neglected by MO calculations of this type which find better correlation with gas phase reactions. Finally, it is also necessary to compare kinetic acidities of propene with methoxy vinyl ether to obtain a theory which is totally consistent with experiment.

References.

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5. Quantitative results were obtained using the GAUSSIAN 70 series of programs: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, QCPE, 10, 236 (1973); in addition, qualitative calculations were also performed using the extended Huckel program, FORTICON8, J. Howell, A. Rossi, D. Wallace, K. Haraki, and R. Hoffmann, QCPE, 10, 344 (1977).

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7. The geometrical parameters used for both 4 and 5 were: C=C: 1.31; C-H: 1.08 Å; C-C: 1.52 Å; C-O: 1.386Å; O-H: 0.97 Å; all angles about the C=C double bond were idealized to 120° and those about the methyl group were given a value of 109.47°. The C-O and O-H bonds were obtained by optimizing the neutral molecule with the STO 4-31G basis for these parameters.

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