

Theoretical study of acid-catalyzed hydration of ground and excited state acetylenes

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Abstract - The proton affinities (PA), energies of protonation by hydronium ion (E_{PT}), and energies of hydration (E_H) of acetylene and several substituted acetylenes have been investigated by means of LCAO-MO-SCF calculations, mainly at the 3-21G level. Calculations were performed on the ground and low lying excited states of each species, and in the case of substituted acetylenes, the results of Markovnikov (M) and anti-Markovnikov (AM) protonation and hydration were compared. The calculated PA values show that the excited state cations are all significantly red shifted compared with the ground state cations, indicating strongly enhanced basicity of the acetylene group on electronic excitation. The results lead to the conclusion that hydration of both the lowest singlet and low lying triplet states should be much more facile than the corresponding ground state reactions, in accord with experimental observation on analogous systems. The results also lead to the conclusion that the S_0 and S_1 reactions should both be strongly regioselective in either the M or AM sense, depending on the nature of the substituent, but that the T_2 reactions should show little preference for either mode of addition, independent of substitution. The geometries and electronic distribution of the various excited species will be discussed, and the theoretical results will be compared with available experimental data on the rate profiles for this type of photohydration.

INTRODUCTION

The photohydrations of aryl-substituted acetylenes,¹ ethylenes¹ and alkenes² have been investigated experimentally over a range of aqueous acid solutions. The reactions are generally acid-catalyzed and facile in most cases, with maximum quantum yields in the $\phi = 0.6 - 1.0$ range. The rate constants for proton-transfer to the excited states have been measured for a variety of substrates and are in the $10^6 - 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ range, which represents a rate enhancement over the ground state analogues of $10^{11} - 10^{14}$. In the majority of cases the reactions take place via the lowest singlet state (S_1) and are regioselective in the M sense, as are the thermal reactions. In a few special cases, the analogous triplet state (T_1) reactions are also regioselective, but in the AM sense. Estimates of the ground and excited state basicities of the type of substrate indicate a pK shift ($\Delta pK = pK^* - pK^0$) on electronic excitation of at least 10 logarithmic units, which is believed to be primarily responsible for the greatly increased photochemical versus thermal reactivity of these systems.

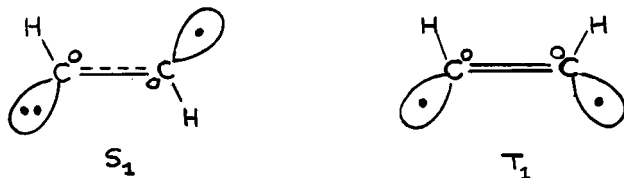
Previous LCAO-MO-SCF calculations³ on acetylene itself (in its S_0 and S_1 states) have indicated that the properties of greatly enhanced excited state basicity and reactivity are not uniquely characteristic of the aryl substituent in the systems investigated experimentally. It was therefore decided to extend the theoretical investigation to substituted acetylenes $Y-C\equiv C-H$ (where $Y = CH_3, H, CF_3, F, Cl, -CH=CH_2$) to determine the effects of both electron-donating and electron-withdrawing groups on the proton affinity, reactivity and regioselectivity in the hydration reactions of the ground and low lying excited states of these systems.

COMPUTATIONAL METHODS

Ab initio LCAO-MO-SCF calculations were performed utilizing the program MONSTERGAUSS⁴ on SEL 32/97 minicomputer. Basis sets used were the minimal STO-3G⁵, split valent 3-21G⁶ and split valent 6-31G**⁷ with double polarization. The RHF method was used exclusively for both open and closed shell systems. The geometries of S_0 and all excited states (S_n or T_n) under consideration were energy optimized, excluding the 6-31G** calculations, which were carried out on best 3-21G geometries. All gradient optimizations were terminated when the gradient length (g) was reduced to below 5×10^{-4} mdyne.

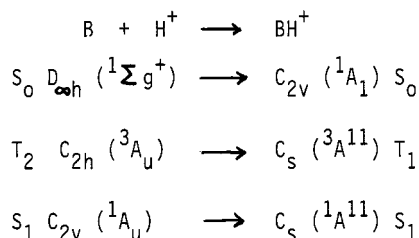
RESULTS

The optimized geometries of the S_0 (linear) and S_1 (trans-bent) states at the 3-21G level compared favourably with available experimental values for the C-H and C-C bond lengths, although the CCH bond angles for S_1 (125-130°) were somewhat large than that based on spectroscopic analysis (120.2°) of acetylene itself. The geometry of T_1 was found to be cis-bent, in agreement with expectations based on the Renner-Teller effect, although no experimental data are available on these states. By replacing the canonical MO's with localized hybrid orbitals, the S_1 and T_1 states can be represented pictorially as shown below, where the



carbons are "sp² hybridized". This leads to the qualitative conclusion that S_1 can be regarded as a polarized (or polarizable) species which should show regioselectivity depending on the nature of Y whereas T_1 can be regarded as a vinyl biradical and would not be expected to show marked regioselectivity.

However in considering the energetics of proton transfer only those processes occurring between directly correlating states should really be considered, as illustrated below for acetylene.

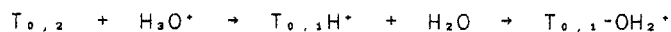
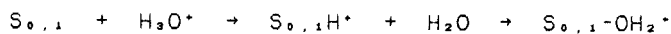


This means that the energetics of proton transfer to triplet states can involve states higher than T_1 , although the cation produced is the lowest triplet state in every case.

The overall results show that the excited states of cations of both \underline{M} and \underline{AM} types are significant red-shifted relative to those of the parent acetylenes, therefore substituted acetylenes should show enhanced basicity on electronic excitation. Also with respect both regiocentres (\underline{M} or \underline{AM}) and all three states (S_0 , T_2 or S_1) the calculated proton affinities are in the order $PA(\underline{CF}_3C\equiv CH) < PA(HC\equiv CH) < PA(\underline{CH}_3C\equiv CH)$.

However, a change in regioselectivity ($\underline{M} \rightarrow \underline{AM}$) is experienced in going from \underline{CH}_3 - to \underline{CF}_3 -substitution for both singlet states (S_0 and S_1), whereas the triplet states, irrespective of substituent, exhibit no significant regioselectivity. These conclusions also apply to other substituents ($Y = F, Cl, -CH=CH_2$) as will be shown graphically by plotting calculated $PA(\underline{M})$ values versus $PA(\underline{AM})$ values for all systems investigated (see Figure 1).

In terms of the overall process of hydration,



the S_0 reaction must involve a high activation barrier in the rate determining step since the first step is significantly endothermic for all $Y-C\equiv CH$. However both types of excited state hydrations are exothermic in the first step, and presumably would therefore have much lower activation barriers. This is particularly evident for the S_1 reactions. These theoretical conclusions based on simple acetylene models are in general accord with all experimental evidence to date on the reactivities of S_0 , S_1 and T_1 in aryl-substituted acetylenes and hence provide a rationale for the greatly enhanced photochemical reactivity observed in these and related aromatic systems.

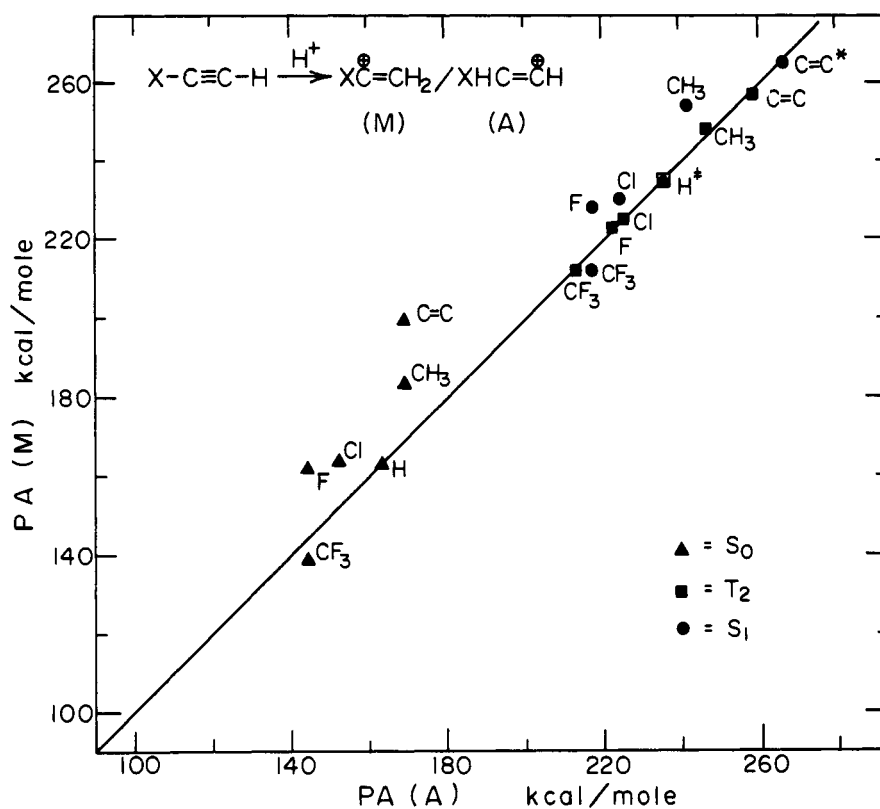


Figure 1. Correlation diagram of RHF-SCF 3-21G proton affinities (PA) for XCCH resulting in Markownikoff (M) and anti-Markownikoff (A) protonation products.

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