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# Destabilized Vinyl Cations. An MO Study of the Influence of Electron-Withdrawing Substituents

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**Abstract**: Ab initio (6-31G* and MP3/6-31G*//6-31G*) calculations show that vinyl cations substituted with $\alpha$-CN, $\alpha$-CHO and $\alpha$-$CF_3$ groups are by 15-18 kcal/mol less stable than their saturated analogues and are among the least stable carbenium ions generated to date via solvolysis.

'Destabilized' carbenium ions, i.e., carbenium ions substituted with electronegative groups, such as CN, CHO and $CF_3$ have recently become the focus of much attention,[1] from a theoretical[2] as well as from a synthetic[3] point of view. Until very recently,[4] this attention was directed to destabilized saturated cations and the corresponding vinyl cations were not studied.[1-3]

Vinyl cations are now widely accepted intermediates in solvolysis,[5] as well as in superacid media.[6] Due to their inherent low stability relative to the corresponding alkyl cations (e.g., in the gas phase $H_2C{=}CCH_3^+$ is less stable than $(CH_3)_2CH^+$ by 10.5 kcal/mol[5]) their solvolytic generation requires the use of good leaving groups and/or of strongly stabilizing $\alpha$-substituents.[5] The generation of 'destabilized' vinyl cations therefore appeared to be highly unlikely.

Remarkably, we have found recently that the photosolvolysis at 254 nm of vinyl halides substituted with $\alpha$-electron-withdrawing groups leads to products which can be rationalized as derived from $\alpha$-cyano and $\alpha$-carbonyl substituted styryl cations ($PhCH{=}CR^+$, R=CN, CHO).[7] This intriguing observation led us to study the inherent stability of various 'destabilized' vinyl cations 1 by ab initio[8] and semiempirical methods (PM3[9a] and AM1[9b]). At the ab initio level we have fully optimized all structures with the 6-31G* basis-set[10a] and single point calculations were then carried out at the correlated MP3/6-31G* level[10b] (all energies quoted in the text are at MP3/6-31G*//6-31G*).

The effect of various α-substituents on the stability of the vinyl cations 1 (relative to hydride transfer) is given by the isodesmic[8] equation 1. For comparison we have calculated the effect of the same substituents on the corresponding 'saturated' carbenium ions, (2).[11] The relative stabilities of the two families of carbenium ions are compared in equation 3. The calculated energies at both 6-31G* and MP3/6-31G*//6-31G* for all three equations are reported in the Table.

$H_2C{=}CHR + H_2C{=}CH^+ \quad \text{----->} \quad H_2C{=}CR^+\ (\mathbf{1}) + H_2C{=}CH_2 \qquad (1)$

$H_3CCH_2R + H_3CCH_2^+ \quad \text{----->} \quad H_3CCHR^+\ (\mathbf{2}) + H_3CCH_3 \qquad (2)$

$H_3CCH_2R + H_2C{=}CR^+\ (\mathbf{1}) \quad \text{----->} \quad H_3CCHR^+\ (\mathbf{2}) + H_2C{=}CHR \qquad (3)$

Equation 3 shows that the α-cyano and α-carbonyl vinyl cations which are produced in the photolysis of PhCH=CRX (X=Cl, Br)[7] are less stable than the corresponding saturated cations by ca. 17 kcal/mol and they are therefore among the least stable (most 'destabilized') cations generated to date in solution (in particular **1**, R=CN which is less stable than **1**, R=CHO by 9.8 kcal/mol).

$H_2C{=}CRCl + H_2C{=}CH_2 \quad \text{----->} \quad H_2C{=}CHR + H_2C{=}CHCl \qquad (4)$

Calculations for equation 4 show that the ground state of $H_2C{=}C(CN)Cl$ is destabilized by 5.3 kcal/mol at MP3/6-31G*//6-31G* relative to $H_2C{=}CHCN$ and $H_2C{=}CHCl$, while for R=CHO the destabilization is only 0.4 kcal/mol. Thus, the thermal solvolysis of PhCH=C(CN)Cl will be strongly accelerated by ground state destabilization effects.[12] So will probably its photosolvolysis, since

**Table** Calculated Energies (kcal/mol) for Equations 1, 2 and 3.[a]

| R | Eq. 1 | | Eq. 2 | | Eq. 3 | |
|---|---|---|---|---|---|---|
| | 6-31G* | MP3/6-31G* //6-31G* | 6-31G* | MP3/6-31G* //6-31G* | 6-31G* | MP3/6-31G* //6-31G* |
| H | 0 | 0 | 0 | 0 | -23.4 | -20.5 |
| $CH_3$ | -32.3 | -26.9 | -22.8 | -18.8 | -14.0 | -18.7 |
| $HC\equiv C$ | -29.3 | -24.4 | -21.7 | -18.9 | -15.9 | -15.0 |
| $H_2C{=}CH$ | -45.5 | -38.3 | -38.0 | -32.6 | -16.0 | -14.6 |
| F | -4.2 | -7.3 | 10.2 | 8.0 | -37.8 | -35.8 |
| Cl | -9.5 | -9.8 | -5.8 | -8.6 | -19.7 | -19.4 |
| CN | 11.0 | 14.9 | 17.3 | 18.4 | -17.1 | -17.0 |
| CHO | 0.7 | 5.1 | 6.1 | 9.0 | -16.7 | -16.6 |
| $CF_3$ | 13.3 | 20.6 | 18.7 | 23.1 | -18.0 | -18.0 |

[a] In all calculations $CH_3CH_2^+$ and $H_2C{=}CH^+$ were taken in their H-bridged structures.

substituent effects in the photogeneration of vinyl cations from vinyl halides parallel the effects observed in ground state chemistry.[7b,c]

Examination of equation 1 and 2 reveals that the two cation families respond similarly to $\alpha$-substitution. $\pi$-Electron-donating substituents such as $CH_3$ and $CH{=}CH_2$, as expected, stabilize substantially both the vinyl and the alkyl carbenium ions while electron-withdrawing groups destabilize them considerably. CN, CHO and $CF_3$ substitution is strongly destabilizing, following the order: $R{=}CF_3$ (most destabilizing) > R=CN > R=CHO (least destabilizing). This order does not follow the order of the inductive electron-withdrawing effect of these groups (i.e., the corresponding $\sigma_I$ values are: 0.45, 0.56, and 0.45 respectively[13]). This points to the involvement of other effects, e.g., $\pi$-conjugation.

Although the behaviour of the two cation families is similar there is one important difference. For the electron-withdrawing groups, especially for R=CN and CHO the degree of destabilization is significantly smaller in the vinyl cations than in the corresponding ethyl cations. Thus, an $\alpha$-cyano destabilizes **2** by 18.4 kcal/mol compared to only 14.9 kcal/mol in **1**. Similarly, an $\alpha$-formyl group destabilizes **1** by only 5.1 kcal/mol compared with 9.6 kcal/mol in **2**. As electron-donating substituents, such as methyl and vinyl, stabilize the vinyl cation more effectively than they stabilize the ethyl cation (see Table), equation 3 is most exothermic for R=H and the differences in stability between the two families is smaller for all substituted cations in the Table, except for fluorine. An $\alpha$-fluorine substituent destabilizes the vinyl cation by 7.3 kcal/mol but it stabilizes the ethyl cation by 10.3 kcal/mol, so that for R=F the difference between the two cation families is the largest; i.e., 35.8 kcal/mol.

In conclusion, $H_2C{=}CH^+$ is better stabilized than (the more stable) $CH_3CH_2^+$ by stabilizing groups, but it is less effected than $CH_3CH_2^+$ by destabilizing groups.

An interesting observation is that **1**, R=CHO, adopts a planar conformation, i.e., conjugation between the carbonyl group and the $\pi(C{=}C)$ bond is more efficient than its conjugation with the cationic $2p(C^+)$ orbital. This points to the relative unimportance of $\pi$-conjugation effects of the formyl group in stabilizing the vinyl cation. The barrier to rotation around the $(C{=}C^+)$-(CHO) bond is 3.5 kcal/mol. Bridging by oxygen is not found in **1**, R=CHO, in contrast to $^+CH_2CH({=}O)$ which is found to be bridged.[1]

Finally, we find that for some of the ions under study, the PM3 and AM1 semiempirical methods gave results which are substantially different from the ab initio results. For example, using PM3 the destabilizing effect of the CN group is calculated to be much smaller than with ab initio methods: equation 1 and equation 2 for R = CN, are calculated at PM3 to be endothermic by 8.5

kcal/mol and 1.9 kcal/mol respectively, compared to 14.9 and 18.4 kcal/mol respectively at MP3/6-31G*//6-31G*. On the other hand, PM3 strongly overestimates the stabilizing effect of chlorine; at PM3 equation 1 for R = Cl is exothermic by 27.7 kcal/mol while at MP3/6-31G* it is exothermic by only 9.8 kcal/mol (at AM1 it is exothermic by 8.9 kcal/mol).

Work in progress concentrates on the effects of other destabilizing R substituents, on the effect of various leaving groups, as well as on a detailed study of the electronic structure of destabilized vinyl cations.

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