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LASER FLASH PHOTOLYSIS OBSERVATION OF THE 1-p-METHOXYPHENYLVINYL CATION BY PHOTOPROTONATION OF p-METHOXYPHENYLACETYLENE. COMPARISON WITH THE 1-p-METHOXYPHENETHYL CATION.

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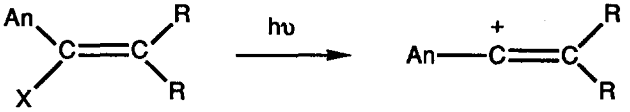
Summary. Photolysis of p-methoxyphenylacetylene in trifluoroethanol results in the transient 1-p-methoxyphenylvinyl cation **7** which has been detected by laser flash photolysis (λ = 248 nm). This cation shows remarkably similar behavior to the 1-p-methoxyphenethyl cation **4**: λ_{max} - 335 nm (**7**) and 340 nm (**4**) and rate constants for decay - 1.3×10^{6} s^{-1} (**7**) and 3.9×10^{5} s^{-1} (**4**).

We have recently reported the direct measurement of rate constants for the reactions of short-lived carbenium ions with nucleophiles, using the technique of laser flash photolysis to generate the cations.[2] 1-p-Methoxyphenyl-2,2-(disubstituted)vinyl cations **2** have been investigated in a similar way by other groups, the cation in each case being observed on photolysis of a halide **1** (An = p-methoxyphenyl).[3]



1; X = Cl, Br; R = Me, Ph, An

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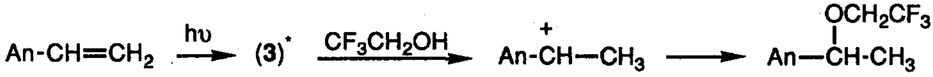
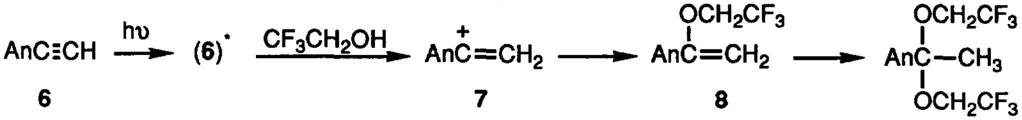
These studies however are such that it is not possible to make a comparison of a carbenium ion and a vinyl cation bearing similar substituents. In this paper we report such a comparison, for 1-p-methoxyphenylvinyl and 1-p-methoxyphenethyl cations. This study also reports the first observation of a vinyl cation obtained in a flash photolysis experiment by photoprotonation of an alkyne rather than by photoheterolysis.

The possibility of generating carbocations by photoprotonation was suggested by studies of Yates and coworkers, who demonstrated that styrenes and phenylacetylenes undergo Markovnikov hydration upon photolysis in aqueous acids.[4] Using trifluoroethanol, a solvent where carbocations are expected to be longer lived than in water,[5] we have found that p-methoxystyrene **3** undergoes photoaddition without the need for added acids.[2b] Figure 1a shows the results of a laser flash photolysis study. The laser pulse results in bleaching of the styrene absorbance at wavelengths less than 300 nm, and the appearance of a transient with λ_{max} at 340 nm which can been assigned to the 1-p-methoxyphenethyl cation **4**.[2b] The decay of this transient is exponential, there are rate accelerations on adding azide or water that are characteristic of carbenium ions, and oxygen, a typical radical and triplet scavenger, has no effect. In addition the same transient signal with the same rate constant for decay is obtained on photolysis of 1-p-methoxyphenethyl acetate,[2b] the cation arising in this case via photoheterolysis. Analysis of the product after 254 nm Hg lamp photolysis of the styrene shows essentially quantitative conversion to the trifluoroethanol adduct **5**. The observation in the flash photolysis experiment that there is little change at the lower wavelengths as the cation decays implies that, once formed, **4** proceeds on to product and there is little, if any, deprotonation to return to styrene.



$$\underset{\mathbf{3}}{\text{An-CH=CH}_2} \xrightarrow{h\nu} (\mathbf{3})^* \xrightarrow{CF_3CH_2OH} \underset{\mathbf{4}}{\text{An-}\overset{+}{\text{C}}\text{H}\text{—CH}_3} \longrightarrow \underset{\mathbf{5}}{\text{An—}\overset{\text{OCH}_2\text{CF}_3}{\overset{|}{\text{C}}}\text{H-CH}_3}$$

We have now found that very similar behavior occurs with p-methoxyphenylacetylene **6** in trifluoroethanol (Figure 1b), with the transient now centered at 335 nm. The spectrum of this transient is similar to that of the previously observed **1** (see later), and there are rate accelerations with added nucleophiles and no effect of oxygen. We therefore attribute this transient to the vinyl cation **7** arising from protonation of excited acetylene. Support for this is from product analysis following lamp photolysis, which shows the formation of the vinyl ether **8** (although this is not stable and undergoes a slower conversion to the acetal **9**). It can be noted in the flash photolysis experiments that there are increases in absorbance in the region below 300 nm as the cation decays (Figure 1b). This is different from the situation with the styrene and is associated with the formation of the vinyl ether chromophore as **7** reacts with solvent. The net result after the laser photolysis is a bleaching from 220 - 260 nm, and an increase in absorbance from 260 - 280 nm. This can be explained by the differences in the spectra of **6** and **8**.



$$\underset{\mathbf{6}}{\text{AnC≡CH}} \xrightarrow{h\nu} (\mathbf{6})^* \xrightarrow{CF_3CH_2OH} \underset{\mathbf{7}}{\text{An}\overset{+}{\text{C}}\text{=CH}_2} \longrightarrow \underset{\mathbf{8}}{\text{An}\overset{\text{OCH}_2\text{CF}_3}{\overset{|}{\text{C}}}\text{=CH}_2} \longrightarrow \underset{\mathbf{9}}{\text{An}\underset{\text{OCH}_2\text{CF}_3}{\underset{|}{\overset{\text{OCH}_2\text{CF}_3}{\overset{|}{\text{C}}}}}\text{—CH}_3}$$

There have been flash photolysis investigations of substituted phenylacetylenes in aqueous acids. In this case the product of solvent addition to the vinyl cation is an enol, and this intermediate is detected, this route offering an excellent way for the photogeneration and subsequent kinetic study of enols of this type.[6] However the vinyl cations could not be observed in these experiments. This is not surprising, since our present results show that even the p-methoxy derivative is too short-lived to be detected in water. For example in 1:4 water:trifluoroethanol we can observe the cation **7**, but the rate constant for its decay is ca 10^7 s^{-1}, approaching the limit of our apparatus. In a 1:1 mixture cation is not observed at all, even though the overall spectral change indicates that the photolysis reaction is occurring.

Figure 1. Transient absorption spectra following 248 nm excitation (20 ns pulses) of p-methoxystyrene (A) and p-methoxyphenylacetylene (B) in trifluoroethanol. The points indicated by squares were obtained 30 - 50 ns after the laser pulse, circles at 500 μs (A) and 200 μs (B). Data could not be obtained near 250 nm because of interference from the laser pulse.

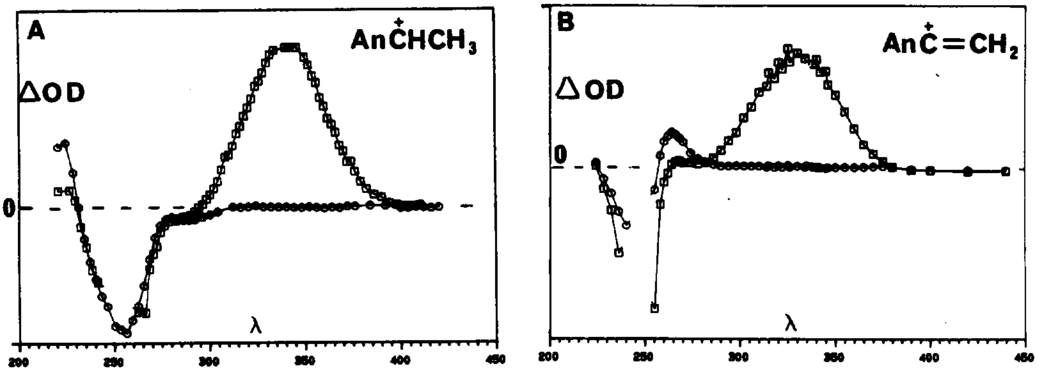
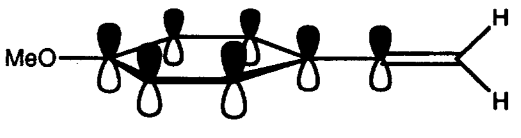


Table 1. 1-p-Methoxyphenylvinyl and 1-p-Methoxyphenethyl Cations in Trifluoroethanol.

Cation	λ_{max}	k(decay), s^{-1}
$An\overset{+}{C}{=}CH_2$	335 nm	$1.3 \times 10^6 s^{-1}$
$An\overset{+}{C}HCH_3$	340 nm	$3.9 \times 10^5 s^{-1}$

Table 1 provides a comparison of the two cations, showing how little the differences are in both the spectral characteristics and reactivities. The similar spectra can be explained in terms of the structure **10** for the vinyl cation,[7] with the π systems of the benzene and alkene orthogonal, and the formally empty p orbital conjugated with the former in essentially the same manner as in the benzylic carbenium ion (**11**). The conclusion is that the substituents attached to the benzylic carbon have little effect on the electronic transition, regardless of whether they are H, CH_3 or $=CH_2$. Substituents on the β carbon of the vinyl cation also have little effect , λ_{max} of **1** in acetonitrile being 340 nm (R = Me), 345 (Ph) and 350 (An).[3b] This is also explained by the structure **10**; in particular the β substituents are orthogonal to the benzylic portion.



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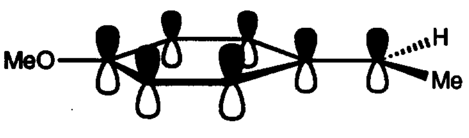

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It is tempting to propose the similar structures as an explanation behind the reactivities, but this is likely an oversimplification. Richard has found that lifetimes of 4-methoxybenzyl carbenium ions are remarkably insensitive to the nature of substituents at the α carbon (for example CH_3 versus CF_3).[8] Whatever the explanation for this, it now appears as if the phenomenon extends to the vinyl cation.

Indirect comparisons of the reactivities of carbenium ions and vinyl cations have been considered previously, using selectivity ratios (k(halide)/k(solvent)) calculated from common ion rate depressions. There was in fact one comparison involving cations with similar substituents, the 1-(9-anthryl)vinyl and 1-(9-anthryl)ethyl cations, with the conclusions that the selectivities were similar.[9] The results of this study indicate that this situation likely arises from similar absolute reactivities.

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References

1. (a) University of Toronto. (b) Max-Planck-Institut.
2. (a) R. A. McClelland, N. Banait and S. Steenken J. Am. Chem. Soc. *108*, 7023 (1986). (b) R. A. McClelland, V. M. Kanagasabapathy and S. Steenken ibid. *110*, 6913 (1988). (c) R. A. McClelland, N. Banait and S. Steenken ibid. *111*, 2929 (1989). (d) R. A. McClelland, V. M. Kanagasabapathy, N. S. Banait and S. Steenken ibid. *111*, 3966 (1989).
3. (a) W. Schnabel, I. Naito, T. Kitamura, S. Kobayashi and H. Taniguchi Tetrahedron, *36*, 3229 (1980). (b) S. Kobayashi, T. Kitamura, H. Taniguchi, W. Schnabel Chem. Lett. 1117 (1983). (c) F. I. M. Van Ginkel, R. J. Visser, C. A. G. O. Varma and G. J. Lodder J. Photochem. *30*, 453 (1985). (d) S. Kobayashi, Q. Q. Zhu and W. Schnabel Z. Naturforsch. *43b*, 825 (1988).
4. (a) P. Wan, S. C. Culshaw and K. Yates J. Am .Chem .Soc. *104*, 2509 (1982). (b) P. Wan and K. Yates J. Org. Chem. *48*, 869 (1983). (c) J. McEwan and K. Yates J. Am. Chem. Soc. *109*, 5800 (1987).
5. J. P. Richard, M. E. Rothenberg and W. P. Jencks J. Am. Chem. Soc. *106*, 1361 (1984).
6. (a) Y. Chiang, A. J. Kresge, M. Capponi and J. Wirz Helv. Chim. Acta *69*, 1331 (1986). (b) Y. Chiang, A. J. Kresge, J. A. Santabello and J. Wirz J. Am. Chem. Soc. *110*, 5506 (1988). (c) T. Hochstrasser, A. J. Kresge, N. P. Schepp and J. Wirz ibid. *110*, 7875 (1988).
7. P. J. Stang, Z. Rappoport, M. Haneck and L. R. Subramnian "Vinyl Cations" Academic Press, New York, 1979, p. 16.
8. Richard, J. P. J. Am. Chem. Soc. *108*, 6819 (1986); ibid. *111*, 1455 (1989).
9. Reference 7, p. 355 -373.

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