

Absolute reactivity of arylallyl carbocations

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A series of α -vinyl arylmethyl cations were generated and studied using nanosecond laser flash photolysis. Rate constants for the decay of the substituted α -vinyl arylmethyl cations were determined under solvolytic conditions in pure solvents and solvent mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) and 2,2,2-trifluoroethanol (TFE). In addition the absolute reactivity of the carbocations with added nucleophiles were obtained. The reactivities of the α -vinyl arylmethyl cations were then compared to the reactivities of the corresponding α -methyl, α -phenyl, and α -cyclopropyl arylmethyl cations. Hammett σ^+ plots of each of the series of carbocations were obtained and the substituent effects on carbocation reactivity analyzed. These data show that the influence of substituent on the reactivity of the α -vinyl carbocations was different from the substituents effects on the reactivity of the α -methyl, α -phenyl, and α -cyclopropyl series. Copyright © 2008 John Wiley & Sons, Ltd.

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INTRODUCTION

In recent years, a number of studies have reported on the use of nanosecond laser flash photolysis to examine the absolute reactivity of a wide range of structurally diverse carbocations. Many of these studies have focused on the reactivity of arylmethyl cations with different groups attached to the carbocation center, including electron-donating alkyl, aryl, and cyclopropyl groups,^[1–6] as well as electron-withdrawing acyl^[7,8] and trifluoromethyl^[9] groups. As a result of these studies, the effect of a wide range of substituents on the absolute reactivity of arylmethyl cations is now well established.

One type of arylmethyl cation whose absolute reactivity has not yet been investigated in detail by nanosecond laser flash photolysis is the α -vinyl arylmethyl (or arylallyl) cation.^[10–12] Like other hydrocarbon substituents such as alkyl, phenyl, and cyclopropyl groups, a vinyl substituent is thought to have a significant thermodynamic stabilizing effect on carbocations.^[13] For example, a recent computational study indicates that a vinyl group provides almost 32 kcal mol⁻¹ of stabilization to the ethyl cation, which is slightly less than the 37 kcal mol⁻¹ provided by a phenyl group, but more than the 19 kcal mol⁻¹ of stabilization provided by a methyl group.^[14] The thermodynamic stabilization is reflected in faster solvolysis reactions of substrates that give allyl cations compared to substrates that give alkyl-substituted carbocations.^[15,16] In addition, because the vinyl group is a stabilizing feature, the reactivity of α -vinyl methyl cations is expected to be lower than the analogous alkyl-substituted carbocations. This expectation has been demonstrated in a small number of studies that report on the absolute reactivity of vinyl-substituted carbocations in comparison with alkyl-substituted analogs. For example, the α -methyl- α -vinylbenzyl cation has been estimated to react in water with a rate constant of $k_w \approx 7 \times 10^8 \text{ s}^{-1}$ that is about sevenfold slower than the cumyl cation ($k_w \approx 4 \times 10^9 \text{ s}^{-1}$).^[17]

Despite all that is known about allyl cations, there has been no systematic study using nanosecond laser flash photolysis into how the absolute rate constants for the reactions of these cations

compare to the rate constants for the reactions of similar alkyl or phenyl-substituted cations. In the present work, such a systematic study is described in which the absolute reactivities of substituted arylallyl cations with solvent and selected nucleophiles were measured using laser flash photolysis, and then compared to the rate constants for the same reactions of substituted α -methyl, α -phenyl and α -cyclopropyl arylmethyl cations, Scheme 1.

Each of the substituted arylallyl cations was generated by laser irradiation of substituted cinnamyl acetates **1a–1c** and in one case the cinnamyl chloride **3a**, Scheme 2. These materials were chosen as precursors on the basis of recent results^[18,19] showing that irradiation of substituted cinnamyl acetates leads to efficient formation of arylallyl cations by photoheterolysis.

RESULTS AND DISCUSSION

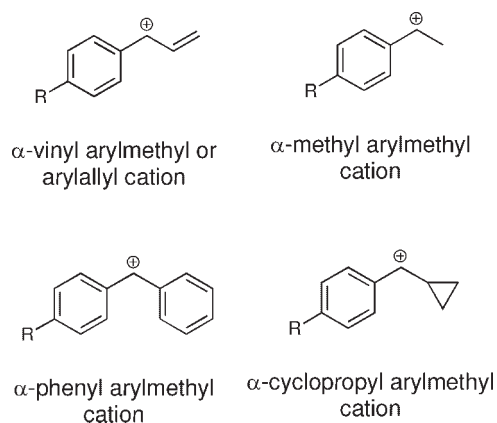
Laser irradiation of substituted cinnamyl acetates

Laser irradiation of 4-methoxycinnamyl acetate **1a** and 4-methylcinnamyl acetate **1b** in 2,2,2-trifluoroethanol (TFE) gave rise to the time-resolved transient absorption spectra shown in Fig. 1(a) and (c). The spectra are dominated by a single absorption band at 390 nm for the transient generated from 4-methoxycinnamyl acetate and 380 nm for the transient from 4-methylcinnamyl acetate. Both transients decayed in a first-order manner with rate constants of $7.1 \times 10^3 \text{ s}^{-1}$ and $1.2 \times 10^6 \text{ s}^{-1}$ for the 4-methoxy and 4-methyl derivatives, respectively.

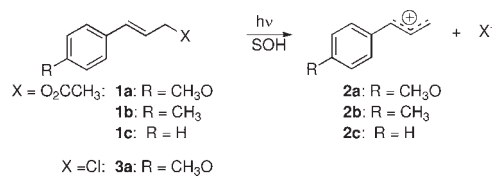
Laser irradiation of cinnamyl acetate **1c** gave no distinct transient species in TFE, but in 1,1,1,3,3,3-hexafluoro-2-propanol

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Scheme 1.



Scheme 2.

(HFIP) did give a single transient with an absorption maximum at 380 nm, Fig. 1(d), that decayed in a first-order manner with a rate constant of $7.0 \times 10^4 \text{ s}^{-1}$.

Laser irradiation of the 4-methoxycinnamyl chloride **3a** in TFE led to the formation of a transient with an absorption maximum at 390 nm, Fig. 1(b), and a decay rate constant of $4.9 \times 10^3 \text{ s}^{-1}$ that were closely similar to those for the transient obtained

upon laser irradiation of 4-methoxycinnamyl acetate **1a**, indicating that the same transient species was generated from both 4-methoxycinnamyl derivatives. It is worth noting that 4-methoxycinnamyl chloride **3a** decomposed after several minutes in TFE, and several fresh samples were used to generate the absorption spectra shown in Fig. 1(b). The differences evident between the spectra of the transient species generated using the 4-methoxycinnamyl acetate **1a** and 4-methoxycinnamyl chloride **3a**, such as the lower absorption intensity of the transient generated from the chloride and the residual absorption at 390 nm after decay of the transient, are likely due to the instability of the chloride in TFE.

The first-order decays of the transient species shown in Fig. 1 remained unchanged in the presence of molecular oxygen, but did become significantly more rapid upon the addition of nucleophiles like bromide, water, and methanol (*vide infra*). These kinetic data are consistent with the transient species being an electrophilic species like the desired arylallyl cations **2a–2c** generated by photoheterolysis, Scheme 2. Furthermore, the absorption maximum of each transient is located at longer wavelengths than the absorption maxima for arylyethyl cations ($\text{abs}_{\text{max}} = 320\text{--}360 \text{ nm}$)^[1] and at shorter wavelengths than diarylmethyl cations ($\text{abs}_{\text{max}} = 440\text{--}500 \text{ nm}$).^[4] Since the charge in the arylallyl cations is presumably delocalized over more bonds than in arylyethyl cations but over less bonds than in the diarylmethyl cations, and since charge delocalization tends to shift the absorption maxima of arylmethyl cations to longer wavelengths,^[20] the location of the observed absorption bands near 380–390 nm is consistent with identification of the transient species as the arylallyl cations. The results from product studies also provided good evidence that arylallyl cations were generated upon irradiation of the cinnamyl acetates in TFE. Steady-state irradiation of the precursors in TFE with 10% methanol gave 3-aryl-3-methoxy-1-propene and

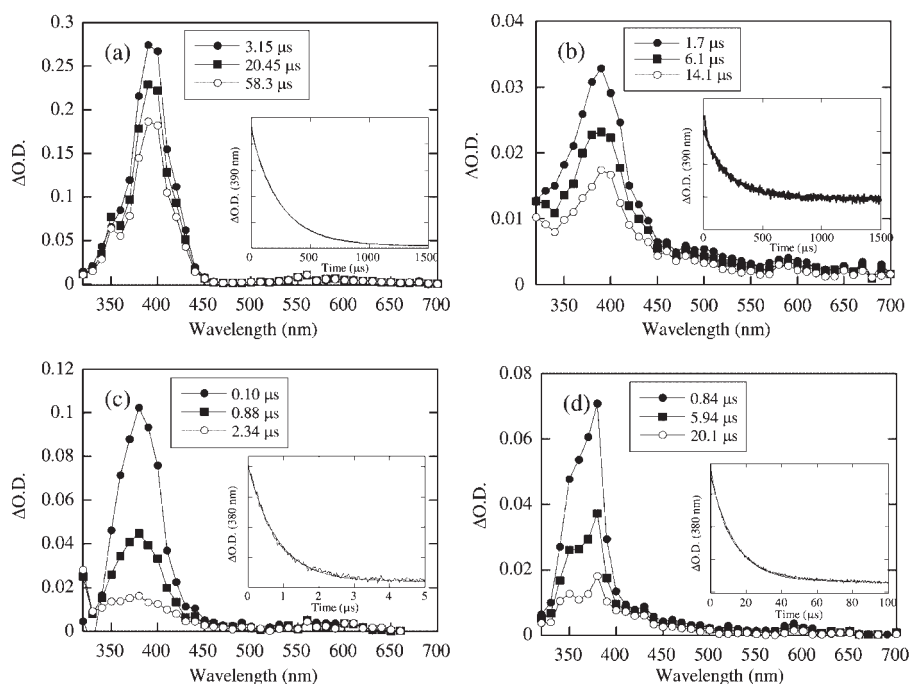
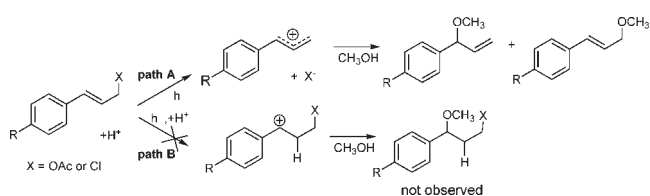


Figure 1. Time resolved absorption spectra obtained upon 266 nm laser irradiation of (a) 4-methoxycinnamyl acetate **1a** in TFE, (b) 4-methoxycinnamyl chloride **3a** in TFE, (c) 4-methylcinnamyl acetate **1b** in TFE, and (d) cinnamyl acetate **1c** in HFIP, at 22 °C. The insets show the change in absorbance at the maximum absorbance of the transient as a function of time. Legend gives time interval between laser pulse and acquisition of spectral data

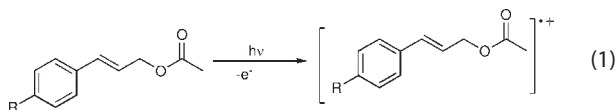


Scheme 3.

1-aryl-3-methoxy-1-propene as the sole methanol-addition products, Scheme 3, path A. These results are identical to those obtained by nucleophilic addition of methanol to arylallyl cations generated by irradiation of cinnamyl acetates in neat methanol.^[19]

The results outlined above also argue against the transient species being aryloxy-type carbocations that would be generated by photoprotonation, Scheme 3, path B. In particular, reaction of these carbocations with methanol would lead to products different from those observed. In addition, the aryloxy-type cations would likely have absorption maxima near 320–360 nm,^[11] which is considerably different from the maxima at 380–390 nm for the observed transients. Furthermore, the kinetic data given in Table 2 (*vide infra*) illustrate that the transient species observed in the present work are considerably less reactive than previously studied aryloxy cations.^[11]

The possibility that the transients observed were radical cations generated by photoionization of the precursors, Eqn (1), was also considered.



To address this possibility, these radical cations were generated by photoinduced electron transfer using chloranil as the sensitizer. The cinnamyl acetate radical cations generated by these methods showed two absorption bands, one near 380 nm and a second, weaker one near 610 nm, Fig. 2, as is typical for radical cations of substituted styrenes.^[21,22] Since the transients generated by laser irradiation in TFE showed no band near 600 nm, the possibility that the observed transients were the radical cations was also ruled out.

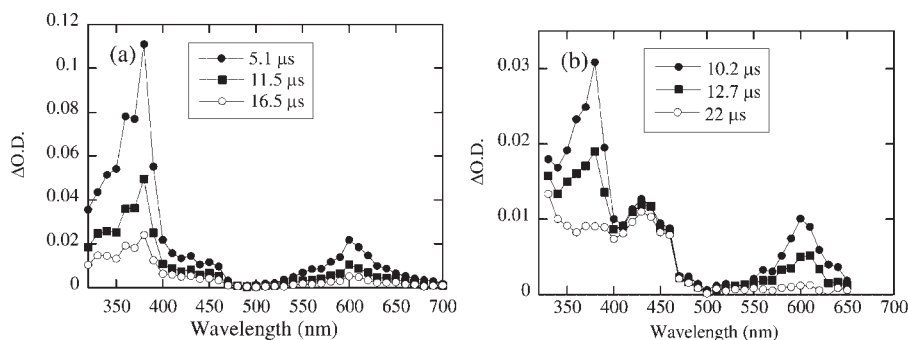


Figure 2. Time-resolved absorption spectra obtained upon 355 nm laser irradiation of chloranil with (a) 4-methoxycinnamyl acetate (4.1×10^{-4} M) and (b) 4-methylcinnamyl acetate (3.2×10^{-4} M) in nitrogen-saturated acetonitrile. Legend gives time interval between laser pulse and acquisition of spectral data

Absolute reactivity of allyl carbocations

In previous work where aryloxy cations were generated by photoprotonation of styrenes in TFE or HFIP,^[11] the observed rate constants for the decay of some of those carbocations depended on the concentration of the styrene, with the styrene acting as a nucleophile. In those cases, the rate constants for reaction of the carbocations with solvent, k_{TFE} or k_{HFIP} were determined with Eqn (2) using observed rate constants measured at various precursor concentrations.

$$k_{\text{obs}} = k_{\text{HFIP}} + k_{\text{precursor}}[\text{Precursor}] \quad (2)$$

In the present work, the observed rate constant for the decay of the phenylallyl cation **2c** in HFIP was found to depend on the concentration of the precursor used to generate the cation. The relationship between the observed rate constant and precursor concentration was linear (Fig. 3), and treating these data using Eqn (2) led to the pseudo-first rate constant for reaction of the phenylallyl cation in neat HFIP, $k_{\text{HFIP}} = (2.2 \pm 0.2) \times 10^4 \text{ s}^{-1}$, and the rate constant for addition to its precursor, $k_{\text{precursor}} = 3.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

The rate constants for the decay of the 4-methoxy- and 4-methylphenylallyl cations in TFE did not change with the concentrations of their precursors. Thus, the observed first-order rate constants determined directly from the decay of these cations in TFE of $k_{\text{TFE}} = 7.1 \times 10^3 \text{ s}^{-1}$ and $k_{\text{TFE}} = 1.2 \times 10^6 \text{ s}^{-1}$ for

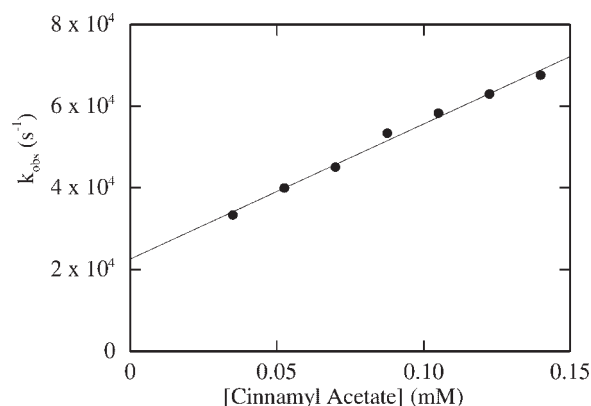


Figure 3. Relationship between the observed rate constant for the decay of the phenylallyl cation and the concentration of cinnamyl acetate in HFIP at 22 °C

Table 1. Rate constants for the decay of the substituted arylallyl cations in TFE or HFIP at 22 °C

	k_{TFE} (s^{-1})	k_{HFIP} (s^{-1})	$k_{\text{MeOH}}^{\text{a}}$ ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{Water}}^{\text{a}}$ ($\text{M}^{-1} \text{s}^{-1}$)	$k_{\text{Br}^-}^{\text{a}}$ ($\text{M}^{-1} \text{s}^{-1}$)
	$7.1 \times 10^{3\text{b}}$	—	5.4×10^4	2.2×10^3	3.0×10^8
	$1.2 \times 10^{6\text{b}}$	—	8.5×10^6	9.6×10^5	7.3×10^9
	$\approx 5 \times 10^{7\text{c}}$	$2.2 \times 10^{4\text{d}}$	$1.8 \times 10^{6\text{e}}$	$9.5 \times 10^{4\text{e}}$	$1.5 \times 10^{10\text{e}}$

^a In TFE unless otherwise indicated.
^b Average of seven measurements, standard deviation $\approx 10\%$.
^c Estimated as described in text.
^d Determined as described in text.
^e In HFIP.

the 4-methoxy and 4-methyl derivatives, respectively, represents the rate constants for their reactions with solvent. These rate constants are summarized in Table 1.

As mentioned above, the unsubstituted phenylallyl cation **2c** was not observed upon irradiation of cinnamyl acetate in neat TFE, presumably because the cation was too short-lived in that solvent. This generally would mean that the cation decayed within the ~ 10 -ns laser pulse width, but in the present case intense luminescence lasting for 50 ns after the laser pulse broadened the time-window during which the transient was undetectable, leaving a lower limit estimate for the decay of the phenylallyl cation of $k_{\text{TFE}} > 2 \times 10^7 \text{ s}^{-1}$.

In order to obtain a better estimate, observed rate constants for the decay of the phenylallyl cation were obtained in TFE:HFIP mixtures. The cation was readily observed in these mixtures up to 60% TFE:40% HFIP. In solutions containing 70 and 80% TFE, the cation was observed, but kinetic data for the decay of the cation could not be reliably obtained due to the strong luminescence, and at higher TFE contents luminescence appeared to completely obscure absorption due to the cation. The data obtained in these mixed solvents up to 60% TFE are shown in Fig. 4(a) (closed squares). The slight downward curvature as the % TFE content increased is similar in shape to the plot of $k_{\text{TFE}/\text{HFIP}}$ versus % TFE content for the 4-methylcumyl cation,^[23] Fig. 4(a) (closed circles) and also similar to other plots of nucleophilicity versus % content of the more nucleophilic component in other alcohol mixtures.^[24–26] Moreover, since the curvature is generally maintained as the content of the more nucleophilic component reaches 100%,^[24–26] the data were extrapolated to 100% TFE to give an estimate for the rate constant for the decay of the phenylallyl cation in TFE of $k_{\text{TFE}} \approx 5 \times 10^7 \text{ s}^{-1}$.

The decays of all three carbocations in TFE or HFIP accelerated in the presence of nucleophiles such as methanol, water, and bromide ion. In each case, the rate constants for the decay of the carbocations increased in a linear manner with respect to nucleophile concentration, which led to the rate constants for addition of the nucleophiles to the carbocations summarized in Table 1. These rate constants are all in the range expected for the reaction of reactive electrophiles with nucleophiles. The rate constants for reaction with bromide ion are large, being at or near

the diffusion limit for the 4-methyl and 4-H substituted arylallyl cations. The reactivities of the cations toward methanol and water are considerably lower, with the more nucleophilic methanol adding slightly faster to the cations than water. The lower reactivity of water and methanol toward the unsubstituted phenylallyl cation in HFIP compared to their reactivity toward the 4-methylphenylallyl cation in TFE is presumably due to the effects of solvent on nucleophilicities.

Absolute reactivities of α -vinyl, α -cyclopropyl, and α -phenyl arylmethyl cations

Table 2 provides data that allow for a direct comparison between the absolute reactivities of the substituted α -vinyl arylmethyl carbocations with previously measured reactivities of α -methyl, α -cyclopropyl, and α -phenyl arylmethyl carbocations. Several comments can be made about these data. First, by looking at the relative rate constants for reaction with solvent in TFE or HFIP, the data show that the α -vinyl-substituted carbocations are 20–50-fold less reactive than the α -methyl derivatives, and 4–15 times more reactive than the diarylmethyl carbocations, with the range of reactivity differences caused by differential effects of substituents. These results definitively show that the kinetic stabilizing ability of the α -vinyl group lies between that for the α -methyl and α -phenyl group, but considerably closer to the latter.

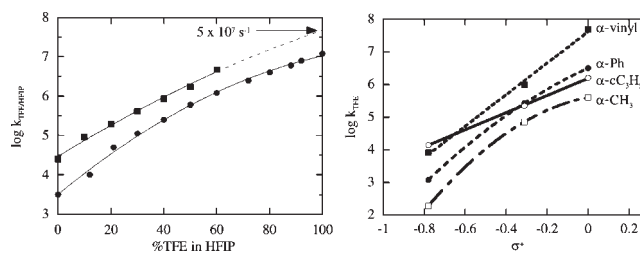
The observation that the α -vinyl group leads to a substantial decrease in reactivity with solvent is consistent with previous analysis^[27,28] of the effect of α -substituents on carbocation reactivity. In that work, it was recognized that α -substituents like $-\text{CF}_3$ and $-\text{OCH}_3$ cause very large changes in thermodynamic stability, but have little effect on carbocation reactivity. On the other hand, α -substituents like aryl groups in which delocalization of positive charge occurs over a more extended π -system provide a decrease in reactivity that correlates with the effect of the α -aryl groups on thermodynamic stability. Since delocalization of positive charge into the α -vinyl group is more similar to delocalization into the α -aryl group, it would be expected that the α -vinyl group should cause a decrease in reactivity that follows its effect on carbocation stability in a manner analogous to an α -aryl group.

Table 2. Rate constants (k_{SOH}) for the decay of the α -methyl, α -vinyl, α -phenyl, and α -cyclopropyl arylmethyl cations in TFE or HFIP at 22 °C

	k_{SOH} (s^{-1}) ^a	$\frac{k_{\text{SOH}}^{\alpha\text{-X}}}{k_{\text{SOH}}^{\alpha\text{-vinyl}}}$
	$3.9 \times 10^{5\text{b}}$	55
	7.1×10^3	
	$1.5 \times 10^{3\text{c}}$	$\frac{1}{4.7}$
	$1.4 \times 10^{4\text{c}}$	2
	$>5 \times 10^{7\text{b}}$	>50
	1.2×10^6	1
	$2.8 \times 10^{5\text{c}}$	$\frac{1}{4.3}$
	$2.2 \times 10^{5\text{c}}$	$\frac{1}{5.4}$
	$>>5 \times 10^{7\text{b}}$ ($4 \times 10^{5\text{b,d}}$)	— (18) ^d
	$\approx 5 \times 10^7$ ($2.2 \times 10^{4\text{d}}$)	1
	$3.4 \times 10^{6\text{c}}$	$\approx \frac{1}{15}$
	$1.6 \times 10^{6\text{c}}$	$\approx \frac{1}{30}$

^a SOH = TFE unless indicated otherwise.
^b Data taken from Reference.^[1]
^c Data taken from Reference.^[5]
^d SOH = HFIP.

Plots of $\log k_{\text{TFE}}$ versus σ^+ for the α -vinyl, α -phenyl, and α -cyclopropyl arylmethyl cations in TFE, and the α -methyl analog in HFIP are shown in Fig. 4(b). While the data in the Hammett plots are admittedly limited, enough information is available to identify some interesting differences in the manner by which the different groups attached to the methyl cation center affect the influence of substituents at the 4-position of the aromatic ring. First, while the ρ^+ value for the α -vinyl series ($\rho^+ = 4.8$) is similar to those for the α -methyl ($\rho^+ = 4.4$) and α -phenyl ($\rho^+ = 4.4$) series, the shapes of the plots are different, with the Hammett plot for the α -vinyl series being nicely linear and the plots of $\log k_{\text{SOH}}$ versus σ^+ for the

**Figure 4.** (a) Relationship between the rate constants for the decays of the (■) phenylallyl cation and (●) 4-methylcumyl cation^[23] and % TFE (by vol) in HFIP. (b) Hammett plots for the decay of (■) α -vinyl, (●) α -phenyl^[5] and (○) α -cyclopropyl^[5] in TFE and the (□) α -methyl arylmethyl cation^[1] in HFIP

α -phenyl and α -methyl arylmethyl cations displaying distinct downward curvature.^[1,6] The downward curvature observed for the latter two series has previously been attributed to the fact that σ^+ values do not adequately account for the extensive delocalization of positive charge between the cationic center and π -donor substituents, like a 4-methoxy group.^[1,6] In contrast, σ^+ values do appear to accurately reflect the ability of π -donors to stabilize the charge in the α -vinyl series, which in turn leads to the conclusion that delocalization of charge to π -donors attached to the aromatic ring is less important for the α -vinyl series than for the α -phenyl and α -methyl series of arylmethyl cations. One possible reason for these different substituent effects is that the vinyl group can readily maintain a planar relationship with the cationic center, which allows the positive charge to be effectively delocalized into the vinyl group and lowers the need for the positive charge to delocalize extensively into the aryl ring, while the positive charge cannot be delocalized into α -methyl group and also is not thoroughly delocalized into the α -phenyl group that is rotated out of planarity due to steric effects. This increases the opportunity for delocalization into the aryl ring bearing the substituent, and enhances the sensitivity of the reaction to good π -donors like 4-methoxy.

The Hammett plot for the α -cyclopropyl series is also linear due to the ability of the cyclopropyl group to donate charge by resonance to the cationic center, just like the α -vinyl group. However, the substituent sensitivity parameter for the α -cyclopropyl series ($\rho^+ = 2.4$) is considerably smaller than that for the α -vinyl series ($\rho^+ = 4.8$). As discussed by Kirmse *et al.*,^[5] the shallow slope for in the α -cyclopropyl plot is due to the strong cation stabilizing ability of the cyclopropyl group that reduces the effectiveness and the importance of electron-donating aryl substituents.^[5] Clearly, while the α -vinyl is able to interact by direct resonance with the positive charge, the fact that the Hammett plot for the α -vinyl series is much steeper clearly indicates that the α -vinyl group does not possess the same ability to stabilize carbocations as the α -cyclopropyl group.

EXPERIMENTAL

Materials

TFE (>99.5%) and HFIP (>99.8%) were used as received. 2,3,5,6-Tetrachloro-*p*-benzoquinone (chloranil) was purified by recrystallization with 95% ethanol prior to use. (*E*)-Cinnamyl acetate (**1c**) was commercially available and used as received.

(*E*)-4-Methoxycinnamyl acetate (**1a**), (*E*)-4-methylcinnamyl acetate (**1b**) and (*E*)-4-methoxycinnamyl chloride (**3**) were prepared following previously published methods.^[19,29]

Laser flash photolysis

The nanosecond laser flash photolysis system at Dalhousie University is of standard design and has been previously described.^[30] Samples for laser experiments were prepared in $7 \times 7 \text{ mm}^2$ quartz laser cells made in house of Suprasil quartz tubing. Each sample contained 2 ml of solvent (TFE or HFIP) to which was added 5–10 μl of a cinnamyl acetate or chloride stock solution (made in CH_2Cl_2). The final concentration of the precursor was in the range of 0.1–0.4 mM, with absorption at the excitation wavelength near 0.4. The sample was capped with a rubber septum and, unless otherwise indicated, deaerated by purging the sample with a low flow of ultrahigh purity (UHP) nitrogen for 15 min. For most experiments, the excitation source was 266 nm from a pulsed Nd:YAG laser ($\leq 8 \text{ ns/pulse}$; $\leq 25 \text{ mJ/pulse}$). The third harmonic, 355 nm, from a pulsed Nd:YAG laser ($\leq 8 \text{ ns/pulse}$; $\leq 50 \text{ mJ/pulse}$) was used as the excitation source in the chloranil photosensitized experiments. In the cation quenching experiments, small amounts of neat methanol (0–300 μl), neat water (0–300 μl), or a stock solution of tetrabutylammonium bromide in TFE or HFIP (0–50 μl) were added to the sample cells. All experiments were carried out at room temperature ($22 \pm 1^\circ\text{C}$).

Product studies

Steady-state photolysis was conducted by irradiating a sample containing 25 mg of the cinnamyl acetate or chloride (**1a–1c** or **3a**) dissolved in 2 ml of TFE containing 200 μl of methanol. The solution was placed in a $7 \times 7 \text{ mm}^2$ quartz laser cell, capped with a rubber septum, purged under N_2 for 15 min to deaerate the solution and continuously irradiated for 20 min. The light source was a Rayonet photochemical reactor using 16 lamps (75 W, 254 nm). The resultant photoproducts were examined by GC/MS. Products were identified by comparing retention times and mass spectral data of the products generated in the present work with data obtained previously by Fleming *et al.*^[19] using the same GC/MS instrument.

Acknowledgements

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