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The generation of vinyl cations and excited triplet states by laser flash irradiation of arylalkynes†

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ABSTRACT: Laser flash photolysis of 4-methoxyphenyl (anisyl) substituted alkynes **1** in protic and aprotic solvents was investigated in order to study the generation of the α-anisylvinyl cations **2** by laser flash photoprotonation of the arylalkynes. Cations **2** were generated in 2,2,2-trifluoroethanol, but the excited triplet state of arylalkyne **1** was detected in the aprotic solvents dichloromethane and acetonitrile. Reaction of the cations **2** with sodium azide was investigated and found to be diffusion controlled; reactions of **2** with cyclohexa-1,3-diene were also investigated and found to be appreciably affected by steric hindrance due to the β-substituents. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: laser flash photolysis; photoprotonation; vinyl cation; excited triplet state; arylalkyne

INTRODUCTION

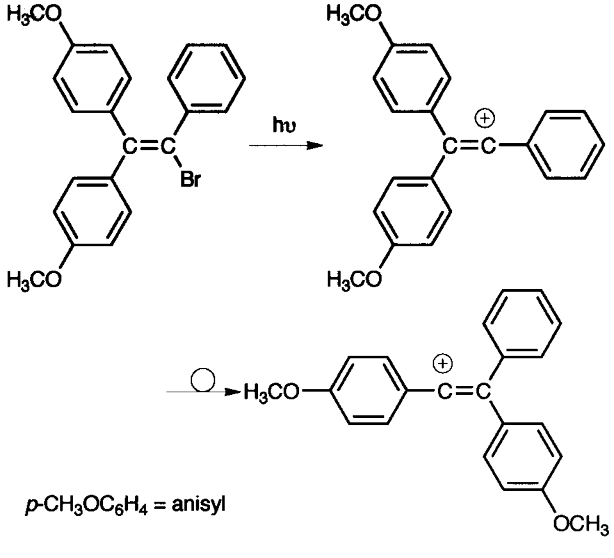
Laser flash photolysis (LFP) has been shown to be one of the most useful methods for the generation and observation of reactive transient species, and for the direct measurement of their decay rate constants under the reaction conditions of their generation. Photolysis of arylalkynes and haloalkenes has been used for generating vinyl cations as transient species, which can be detected by this technique.[1–7] We have previously reported the LFP of haloalkenes to generate the corresponding β,β-disubstituted cations, and have measured the rate constants for the subsequent migration of the β-aryl group (Scheme 1).[1–3]

McClelland *et al.* showed that laser flash photoprotonation of 1-ethynyl-4-methoxybenzene (**1a**) generated the α-(4-methoxyphenyl)vinyl cation (**2a**) in 2,2,2-trifluoroethanol (TFE) and reported the rate constant for the decay of **2a** in TFE that gave the vinyl trifluoroethyl ether (Scheme 2).[4] McClelland and coworkers presented a relationship between the nature of the substituent in the phenyl group and the absorption maximum of the vinyl cations generated.[8] Steenken and coworkers also reported the generation and reactivity of β-(2,2′-biphenyldiyl)-vinyl cations (Scheme 3).[6] We have reported the generation of 2,2-disubstituted 1-(4′-methoxyphenyl)vinyl cations by LFP of vinyl halides and the relationship between their stability and reactivity.[5]

In this report, we describe the generation of the vinyl cations **2** by laser flash photoprotonation of arylalkynes **1** (Scheme 4), and their subsequent reactions with olefins.

RESULTS AND DISCUSSION

The transient species were generated and detected with a nanosecond LFP system (Fig. 1). Irradiation by a 266 or a 308 nm laser flash of solutions of arylalkynes **1** in TFE,



Scheme 1

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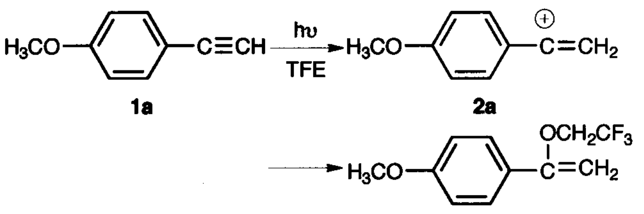
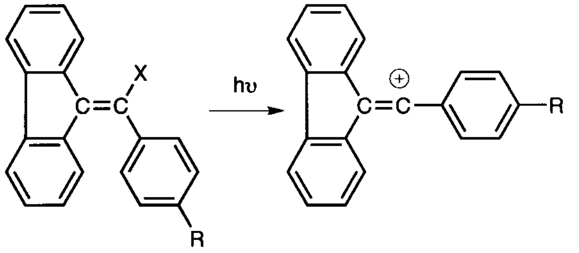


Scheme 2



Scheme 3

dichloromethane, and acetonitrile gave transient species that were detected by their time-resolved ultraviolet–visible absorption spectra.

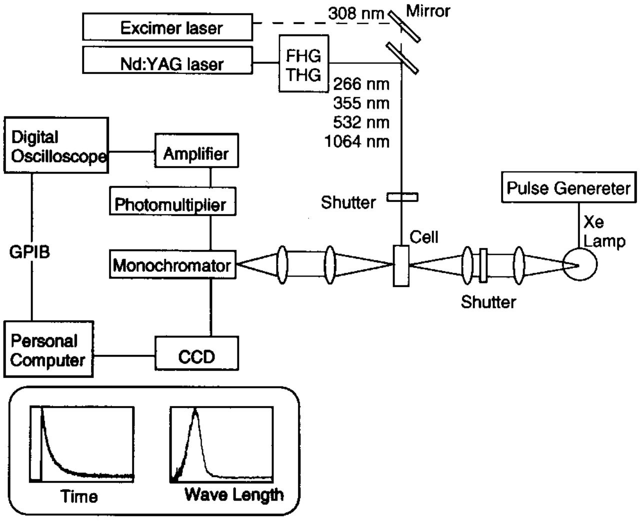


Figure 1. Time-resolved UV–vis LFP system

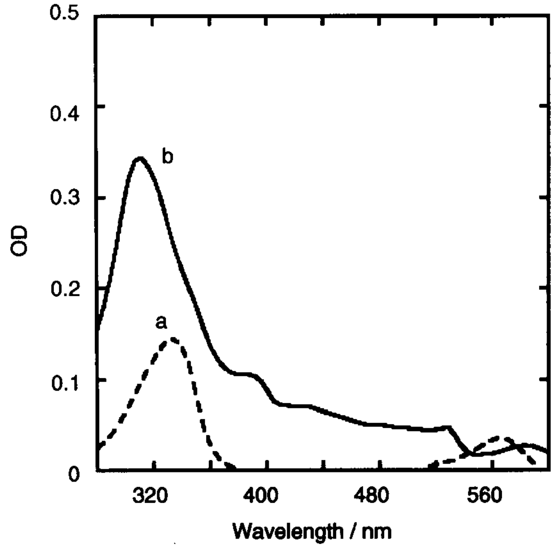
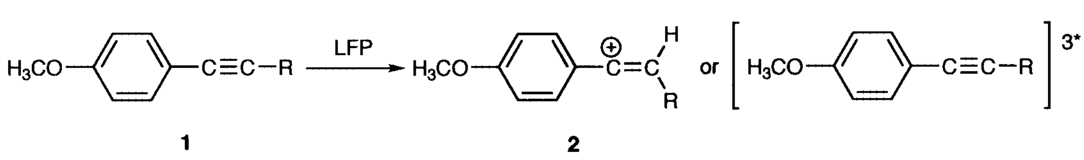


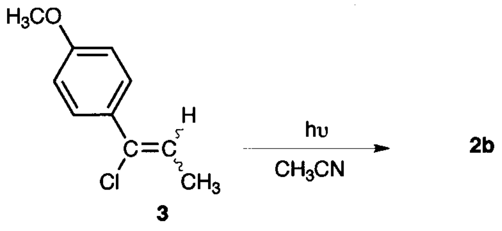
Figure 2. UV–vis spectrum of the transient species generated by the LFP of **1b**: (a) in TFE; (b) in dichloromethane

Generation of vinyl cations and the excited triplet state of arylalkynes

The 266 nm laser flash was applied to a solution of 1-methoxy-4-(propyn-1′-yl)benzene (**1b**) and the transient species generated was detected by its ultraviolet–visible spectrum, as shown in Fig. 2. In TFE and aqueous TFE it had an absorption maximum at 333 nm, and its second-order rate constant in the presence of $(0.2–1.2)\times10^{-4}$ M sodium azide in 1:1 TFE:H_2O was 6.2×10^{9} M^{-1} s^{-1}. This observed decay process is attributed to the diffusion-controlled reaction of a transient cationic species (**2b**) with azide. Additionally, LFP of 1-(1′-chloropropen-1′-yl)-4-methoxybenzene (**3**) gave a transient with an absorption maximum at 333 nm (Scheme 5), which we also propose is the vinyl cation **2b**. The spectra of vinyl cations **2** beyond 500 nm have not been reported previously; however, the transient species generated from anisylalkyne **1b** has an absorption at 570 nm, which could not be characterized unambiguously. Also, the energies of the lowest triplet excited states of simple alkynes are not known with certainty, although Evans assigned the triplet energies of some acetylenes from their enhanced singlet–triplet absorption spectra under a high pressure of dissolved oxygen,[8] and Brocklehurst *et al.* reported luminescence from the triplet state of diphenylacetylene.[9] The transient species generated from anisylalkyne **1b** in dichloromethane has an absorption maximum at 308 nm. In the presence of the triplet



Scheme 4



Scheme 5

quencher cyclohexa-1,3-diene ($E_T = 219$ kJ mol^{-1}),[10] the decay rate constant of the absorption at 308 nm increased linearly with the diene concentration, giving a second-order rate constant of 5.0×10^9 M^{-1} s^{-1}. Consequently, we propose that the transient species with an absorption maximum at 308 nm is an excited triplet state of the arylalkyne **1b** (Scheme 6).

Similarly, irradiation by a 266 nm laser flash of solutions of anisylalkyne **1a** in dichloromethane, TFE, and aqueous TFE gave a transient species (Fig. 3). In TFE, it had an absorption maximum at 328 nm, and reacted with sodium azide in aqueous TFE with a second-order rate constant of 8.45×10^9 M^{-1} s^{-1}. The reaction is clearly the diffusion-controlled capture of a cationic species whose absorption wavelength corresponds to that of the transient species reported by McClelland *et al.*, i.e. the vinyl cation **2a**. McClelland *et al.* detected the vinyl cation **2a** in TFE and in a 4:1 TFE:H_2O mixture, but reported that they could not detect it in a 1:1 mixture;[4] the α-anisylvinyl cations **2** are detectable in a 1:1 mixture. Furthermore, the decay rate constants of **2a** are not affected by the concentration of H_2O in the TFE (Fig. 4) as much as was reported by McClelland *et al.* The transient species generated in dichloromethane has an absorption maximum at 312 nm, but it could not be generated in the presence of excess cyclohexa-1,3-diene and hence is proposed to be the excited triplet state of anisylalkyne **1a**.

Irradiation of bis(4-methoxyphenyl)ethyne (**1c**) with a 308 nm laser flash in TFE gave a transient species that had an absorption maximum at 342 nm, whereas in dichloromethane or acetonitrile a transient absorbing at

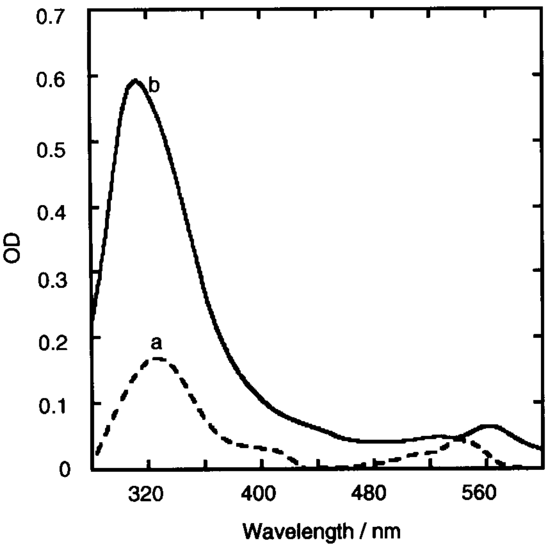


Figure 3. UV–vis spectrum of the transient species generated by the LFP of **1a**: (a) in TFE; (b) in dichloromethane

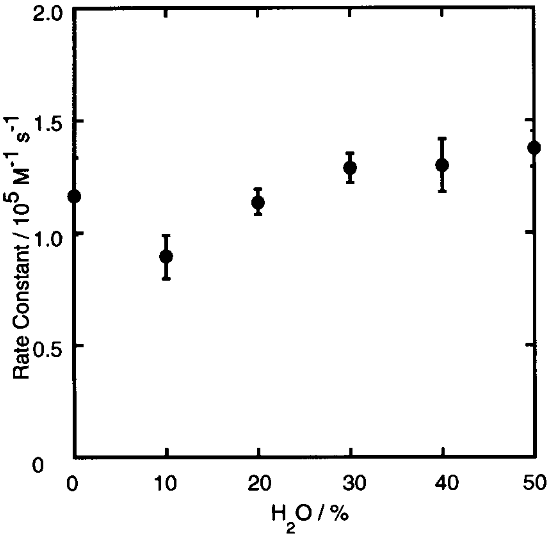
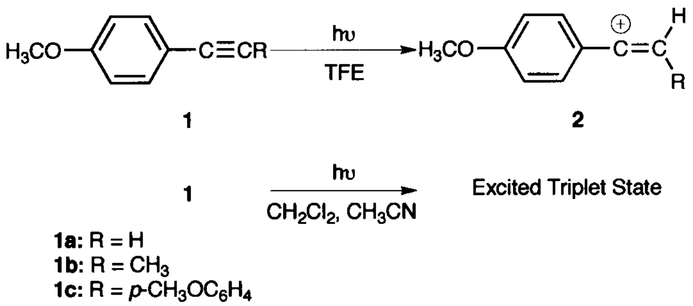


Figure 4. The effect of H_2O on the decay rates of the vinyl cation **2a** in TFE



Scheme 6

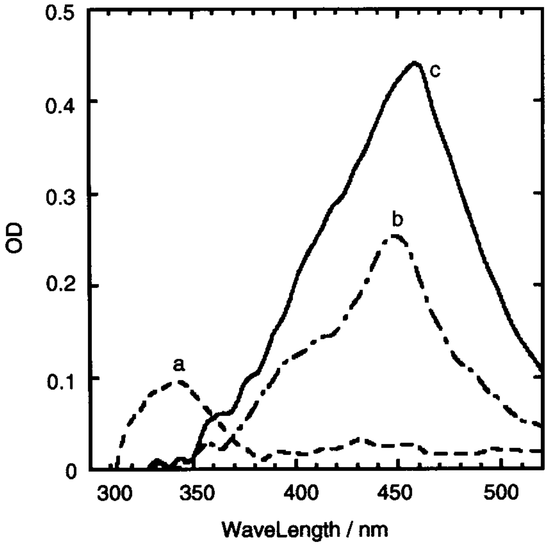


Figure 5. UV–vis spectrum of the transient species generated by the LFP of **1c**: (a) in TFE; (b) in dichloromethane; (c) in acetonitrile

450 nm was detected (Fig. 5). The latter species reacted with cyclohexa-1,3-diene with a rate constant of 7.88×10^9 M^{-1} s^{-1}; hence, it is proposed to be the excited triplet state of the dianisylalkyne **1c**, whereas the species generated in TFE is proposed to be the vinyl cation **2c**. The excited triplet states of anisylalkynes **1a** and **1b** display absorption maxima at 312 nm and 308 nm respectively, which are shorter wavelengths than those of the vinyl cations **2a** and **2b**. In contrast, the excited triplet state of dianisylalkyne **1c** has an absorption maximum at 450 nm, which is at a longer wavelength than that of the vinyl cation **2c**. In this case, the double bond of the vinyl cation is conjugated with the β-anisyl group, which contributes to the wavelength shift.

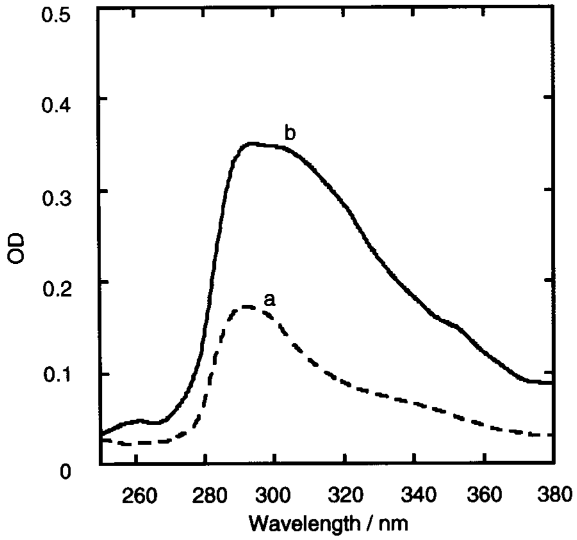
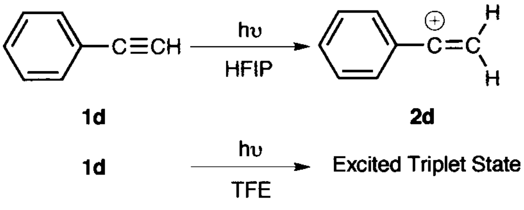
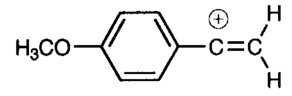
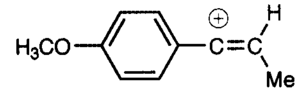
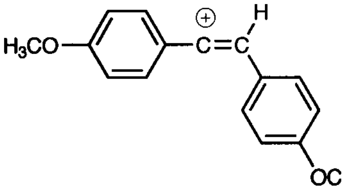


Figure 6. UV–vis spectrum of the transient species generated by the LFP of **1d**: (a) in TFE; (b) in dichloromethane



Scheme 7

Table 1. Rate constants for the reactions of α-anisylvinyl cations **2** with cyclohexa-1,3-diene

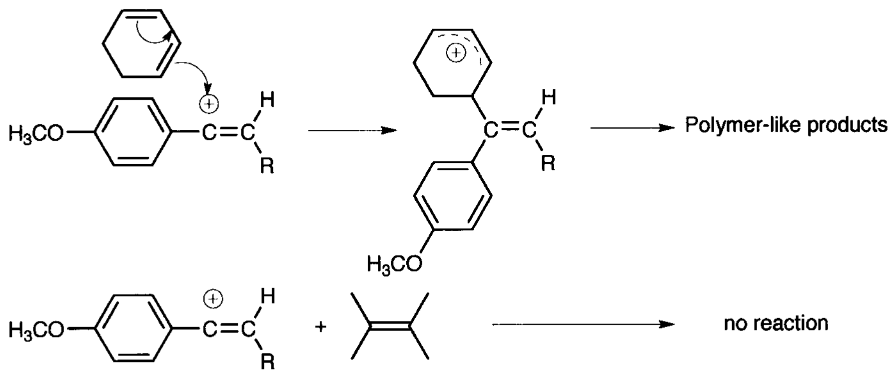
	k/M^{-1} s^{-1}
	4.99×10^9
	6.78×10^8
	6.37×10^7

McClelland *et al.* reported the generation of vinyl cation **2d** by the laser flash photoprotonation of ethynylbenzene (**1d**) in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP).[7] However, in our hands the LFP of arylalkyne **1d** both in TFE and in dichloromethane gave a transient species with an absorption maximum at 292 nm (Fig. 6); in neither case did the transient species undergo nucleophilic capture, but it did react with the triplet quencher. Hence, the transient species in both solvents is proposed to be the excited triplet state (Scheme 7).

Considering these results, we suggest that (a) an excited triplet state is generated by the LFP in an aprotic solvent, but a vinyl cation is generated in a protic solvent, and (b) an electron-donating group is required for generating the vinyl cations **2** in TFE.

Reaction of the vinyl cations with olefins

Reactions of vinyl cation **2c** and benzhydryl cation with 1-trimethylsilyloxycyclopentene (TMSOCP) or 1-trimethylsilyloxycyclohexene (TMSOCH) have been investi-



Scheme 8

gated.[11,12] Vinyl cations **2** also react with cyclohexa-1,3-diene (Table 1). The rate constant for the reaction of the β-unsubstituted vinyl cation **2a** with cyclohexa-1,3-diene is $4.99 \times 10^9\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, which appears to correspond to a diffusion-controlled process. However, for the reaction of β-methyl-substituted vinyl cation **2b**, $k_2 = 6.79 \times 10^8\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$; and for the β-anisyl-substituted vinyl cation **2c**, $k_2 = 6.37 \times 10^7\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$. The rate constant of vinyl cation **1c** with TMSOCP is $9.7 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and that with TMSOCH is $1.4 \times 10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[12] The reaction of **2c** with cyclohexa-1,3-diene was much faster than with TMSOCP or TMSOCH. Cations **2** did not react with 2,3-dimethylbut-2-ene, suggesting that the tetra-substituted alkene is too bulky for easy attack of vinyl cations, and the reaction products of vinyl cations **2** with 1,3-dienes are the stabilized allyl cation (Scheme 8).[13] Considering these limited data, the reactivity of cations **2** with cyclohexa-1,3-diene seems to be appreciably controlled by the steric hindrance exerted by the β-substituent of the vinyl cation **2**. The products of these reactions of **2a** and **2b** with cyclohexa-1,3-diene were not isolated, but brown polymeric material was obtained after 2×10^3 irradiation shots.

CONCLUSION

LFP of arylalkynes in the aprotic solvents dichloromethane and acetonitrile generate the excited triplet state, whereas vinyl cations are generated in the protic solvent TFE. The cations generated in TFE react with azide ion under diffusion control, but there is steric hindrance due to the β-substituent of the vinyl cations in their reactions with cyclohexa-1,3-diene.

EXPERIMENTAL

Materials

Dichloromethane and TFE (guaranteed reagent) were purchased from Nakalai Tesque. Acetonitrile (HPLC grade) was purchased from Kanto Chemical Co. Cyclohexa-1,3-diene was purchased from Tokyo Kasei Kogyo Co. Purified water (Japanese Pharmacopoeia) was purchased from Kozakai Seiyaku Co. 1-Ethynyl-4-methoxybenzene, 1-methoxy-4-(prop-1′-ynyl)benzene, and bis(4-methoxyphenyl)ethyne were prepared from the corresponding ketones (Aldrich Chemical Co.) with phosphorus oxychloride (Kishida Reagent Chemicals) and sodium hydroxide (Nakalai Tesque), and purified by vacuum distillation and silica gel column chromatography (>99% measured by JEOL JNM-A500 ^{1}H NMR). Solutions for the kinetics measurements of the reactions of vinyl cations with sodium azide were prepared by mixing the appropriate volume ratios of spectroscopic-grade TFE and purified water. The reaction with sodium azide was followed at *ca* 1 mM arylalkynes and $(0.2\text{–}1.2)\times 10^{-4}\,\mathrm{M}$ NaN_3.

Measurements

Irradiation by laser flash was carried out with a Continuum PL9010 Nd:YAG laser flash apparatus ($\lambda = 266$ nm; power/plus 80 mJ) or a Lambda Physik Lasertechnik COMPex 102 excimer laser flash apparatus (XeCl, $\lambda = 308$ nm; power/plus 40 mJ), and an Osram XBO 150 W xenon lamp was used as a light source for detection in the UV–vis region. Samples were irradiated in a quartz cell maintained at 25 °C. Rate constants are the averages of 8–16 kinetic runs carried out with each solution with Igor Pro 4.03J for Macintosh (Wave Metrics Inc.).

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