

Study of the Time-resolved IR Spectrum of α -Arylvinyl Cations Generated by Laser Flash Photolysis

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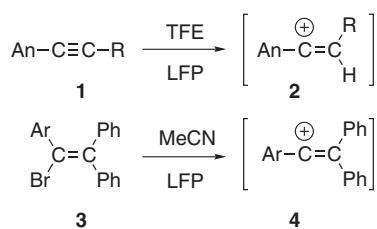
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The characteristic stretching band of the $C(sp^2)=C(sp)^+$ moiety in vinyl cations was observed for the first time around 1870 cm^{-1} by a time-resolved IR spectrometry with 266 nm or 308 nm laser flash irradiation of (4-methoxyphenyl)alkynes in TFE and α -arylvinyl bromide in acetonitrile. The ultraviolet-visible and the IR absorption maxima were affected by the β -substituents.

Laser flash photolysis (LFP) have been shown to be one of the most useful methods for the observation of reactive transient species and for the direct measurement of the rate constants of their decay under the reaction conditions. Most detection methods involve the measurement of the electronic spectrum of the transient species. Vinyl cations generated by photoprotonation of arylalkynes or by photolysis of haloalkenes have been detected by the UV-vis spectrometry¹⁻⁹ but time-resolved IR spectrometry, which was recently developed, had not been used yet for measuring the IR spectra of vinyl cations.

We report here the first example of measurement of time-resolved IR spectra of vinyl cations. The transient species were generated by applying the nanosecond laser flash of Nd:Yag (266 nm) or Excimer (308 nm) to a solution of arylalkynes **1** in 2,2,2-trifluoroethanol (TFE) or to a solution of bromoalkenes **3** in acetonitrile (Scheme 1). The samples had flown into a calcium fluoride cell at room temperature and the generated transient species were detected by using the time-resolved IR spectrometer.¹⁰



In the case of 4-methoxyphenylethyne (**1a**) in TFE, a transient species was detected at 1914 cm^{-1} (Figure 1). Since it is known that the 1-(4-methoxyphenyl)vinyl cation (**2a**) was generated and detected at 328 nm by 266 nm laser flash irradiation of **1a** in TFE^{4,9} the transient species which has an absorption maximum at 1914 cm^{-1} could be assigned to the vinyl cation **2a**. Similarly, a 266 nm laser flash irradiation of 1-(4-methoxyphenyl)prop-1-yne (**1b**) in TFE gave the 1-(4-methoxyphenyl)-2-methylvinyl cation (**2b**) as the only transient species with an absorption maximum at 333 nm in the UV-vis spectrum.¹¹ The β -

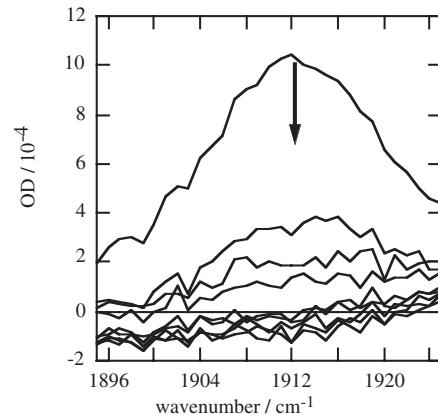


Figure 1. Time-resolved IR spectra of 1-(4-methoxyphenyl)vinyl cation (**2a**) generated by laser flash photoprotonation of **1a** in TFE. The spectra are the averages of data collected every 400 ns.

methyl-substituted vinyl cation **2b** have an absorption maximum at 1903 cm^{-1} , a closely similar position to that of the β -unsubstituted vinyl cation **2a**. In the case of the laser flash photoprotonation of 1-(4-methoxyphenyl)-2-phenylethyne (**1c**), the transient species has an absorption maximum at 1885 cm^{-1} , which could be assigned to 1-(4-methoxyphenyl)-2-phenylvinyl cation **2c** which has a UV-vis absorption maximum at 342 nm and is more stable than its 2-(4-methoxyphenyl)-1-phenyl cation

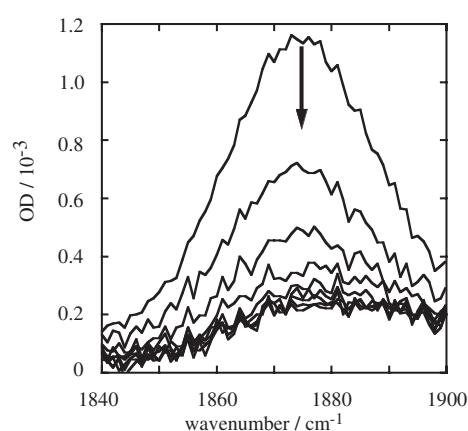


Figure 2. Time-resolved IR spectra 1-(4-methoxyphenyl)-2,2-diphenyl vinyl cation (**2a**) generated by laser flash photolysis of triaryl bromoethene **3a** in acetonitrile. The spectra are the averages of data collected every 400 ns.

Table 1. IR absorption maxima of the vinyl cations

Precursor	Cation	R ₁	R ₂	R ₃	Detected/cm ⁻¹	Calculated/cm ⁻¹ ^a
1a	2a	CH ₃ O	H	H	1914 ^b	1945
1b	2b	CH ₃ O	CH ₃	H	1903 ^b	1937
1c	2c	CH ₃ O	Ph	H	1885 ^b	1901
3a	4a	CH ₃ O	Ph	Ph	1868 ^c	1871
3b	4b	CH ₃	Ph	Ph	1862 ^c	1857
3c	4c	CH ₃ S	Ph	Ph	1867 ^c	1868

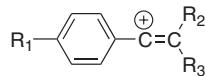
^a Calculated at the B3LYP/6-31G* level.^b Detected in TFE.^c Detected in acetonitrile.

isomer.

The laser flash photolysis of triarylbromoethenes **3** gave transient species which were clearly detected in the IR spectrum. It was reported that the laser flash photolysis of **3a** in acetonitrile gave the 1-(4-methoxyphenyl)-2,2-diphenyl cation with an absorption maximum at 350 nm as the only detectable transient species.⁸ Therefore, the generated transient species which display an absorption maximum at 1868 cm⁻¹ could be assigned to the vinyl cation **4a** (Figure 2). Similarly, the laser flash photolysis of 1-bromo-1-(4-methylphenyl)-2,2-diphenylethene (**3b**) gave the 1-(4-methylphenyl)-2,2-diphenylvinyl cation (**4d**) with an IR maximum absorption at 1862 cm⁻¹ and 1-(4-methylsulfanylphenyl)-2,2-diphenylvinyl cation (**4c**) was generated from 1-bromo-1-(4-methylsulfanylphenyl)-2,2-diphenylethene (**3c**) which was detected at 1867 cm⁻¹.

The decay rate constant of **4c** measured by following the change in its IR absorption with time was $7.1 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$. This value is reasonably close to the value measured by the UV-vis spectrophotometry ($9.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$).¹² The stretching bands of the C(sp²)=C(sp)⁺ bond of vinyl cations detected and calculated at the B3LYP/6-31G*(scale factor 0.9613) level are summarized in Table 1. The calculated values are in relatively good agreement with the observed values.¹³

We conclude that the vinyl cations **2** and **4** generated by the laser flash photolysis of 4-methoxyphenylalkynes **1** or of triarylbromoethenes **3** could be detected by their time-resolved IR spectra. The absorption maxima of vinyl cations are affected by the conjugation with the β -substituents.



References and Notes

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- 10 TRIR1000 in JASCO Co. Cf. T. Yuzawa, C. Kato, M. W. George, and H. Hamaguchi, *Appl. Spectrosc.*, **48**, 684 (1994).
- 11 The same vinyl cation was detected at 333 nm by 266 nm irradiation of 1-chloro-1-(4-methoxyphenyl)prop-1-ene in TFE.
- 12 The decay rate constants were measured in the presence of 1 M of ethanol as the nucleophile in TFE.
- 13 The stretching bands were calculated with Gaussian 98, Revision A.5.