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ABSORPTION SPECTRA OF VINYL CATIONS

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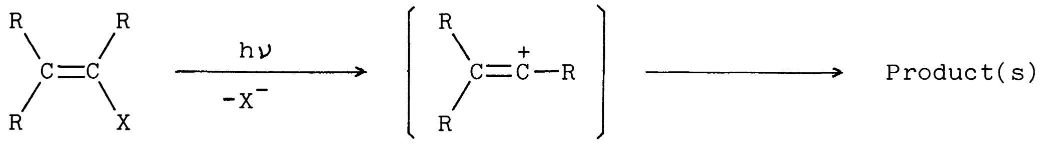
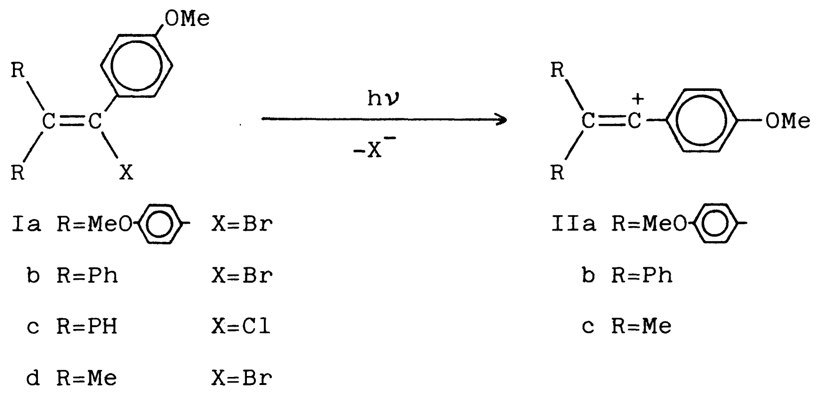
The absorption spectra of α-(p-methoxyphenyl)vinyl cations were measured by laser flash photolysis of the corresponding vinyl halides in acetonitrile and the nucleophilicity of several alcohols to the vinyl cations was evaluated by measuring the decay rates in the presence of the alcohols.

In spite of wide recognition of a vinyl cation as one of reactive intermediates1) there remain many difficulties to detect it.2) The detection of an α-ferrocenyl-substituted vinyl cation by nmr spectroscopy has been reported recently.3) It has been postulated that vinyl cations are formed by photolysis of substituted vinyl halides in solution.4-6) Recent photocurrent measurement by laser flash photolysis of 1,2,2-tris(p-methoxyphenyl)vinyl bromide gave dire evidence for formation of a cationic species, a vinyl cation.7) We wish here to report the first example of measurement of absorption spectra of vinyl cations and the nucleophilicity of alcohols to the vinyl cations.



Optical absorption measurement by irradiation of vinyl halides Ia-d in acetonitrile with 15 ns flashes of 265 nm light or 25 ns flashes of 347 nm light8) gave absorption spectra of the transient species shown in Fig. 2 immediately after the flashes. Oscilloscope traces of both optical absorption and photocurrent measured simultaneously after flash-irradiation of Ib were given in Fig. 1.9) The



detected species should be ions because the decay rates of optical absorption were equal to those of photocurrent. The transient species seem to be neither radicals nor radical anions because there was no difference between oxygen-bubbling and argon-bubbling into the acetonitrile solution on the oscilloscope traces of both formation and decay of the transient species. The absorption spectra obtained from bromide Ib and chloride Ic were identical. These results and the effect of alcohols as additives mentioned below show that the transient species should be vinyl cations IIa-c.

The decay rates of the vinyl cations in acetonitrile increased by addition of alcohols shown in Fig. 3 and a comparison of the effect of alcohols on decay of vinyl cations IIa and IIc was shown in Fig. 4. Decrease of the decay rates in the series MeOH > EtOH > i-PrOH > t-BuOH means decreasing nucleophilicity as well as increasing steric hindrance. Noteworthy is the low reactivity of water. This is probably caused by the fact that in acetonitrile H_2O molecules combine to clusters which are held together by hydrogen bonds. Cluster formation should weaken the nucleophilic character. The effect of alcohols on the decay of vinyl cations IIa

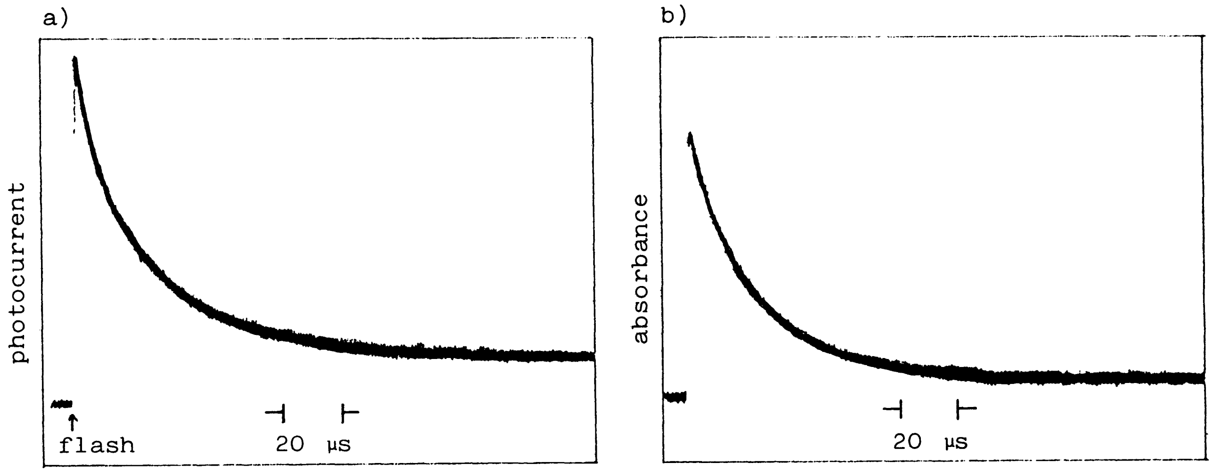


Fig. 1. Oscilloscope traces depicting the decay of a) photocurrent and b) optical absorption at 355 nm by irradiation of Ib in acetonitrile.

and IIc shown in Fig. 4 indicates that there is a reactivity-selectivity relationship. Vinyl cation IIc is more reactive than IIa and decay rate ratios, k_{MeOH}/k_{t-BuOH}, were 12 for IIc and 21 for IIa.

Further studies on vinyl cations by laser flash photolysis are in progress.

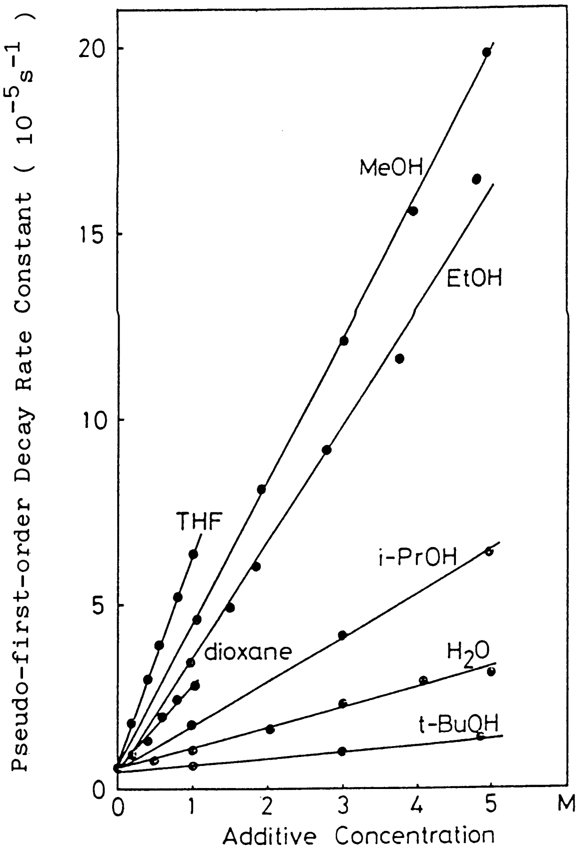


Fig. 3. The pseudo-first-order decay rate constants of the transient species by flash-irradiation of Ia in the presence of additives in acetonitrile.

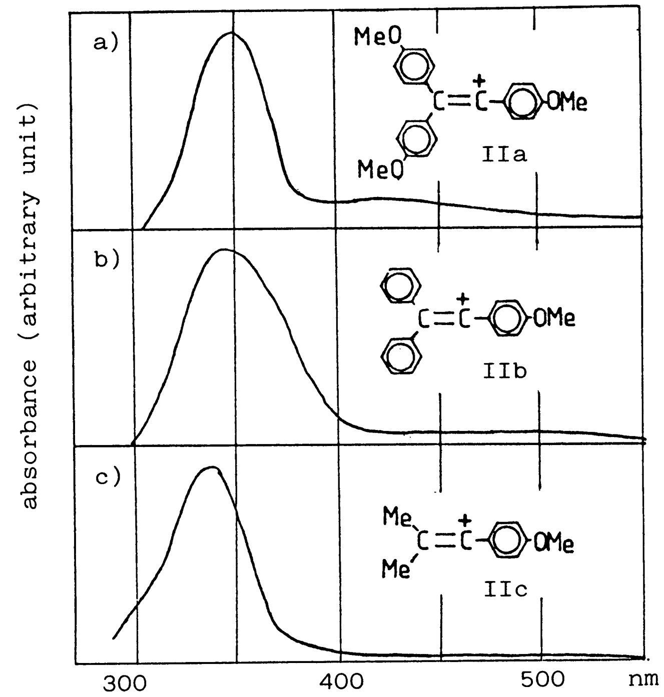


Fig. 2. Absorption spectra of the transient species just after flash-irradiation of a) Ia, b) Ib and Ic, and c) Id in acetonitrile.

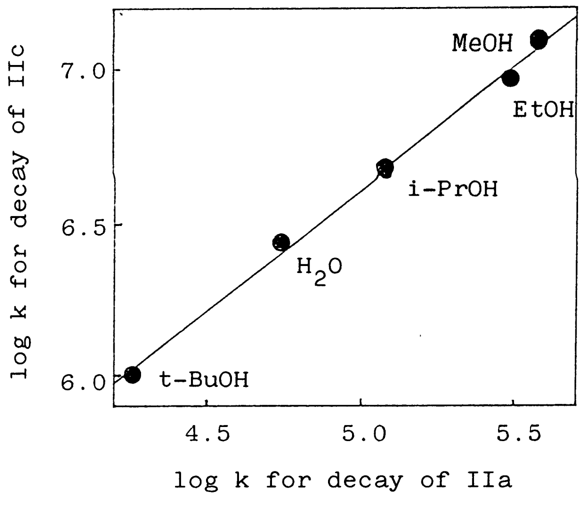


Fig. 4. The relationship between the effects of additives on the decay for the transient species by flash-irradiation of Ia and Id.

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8) Irradiation of vinyl halides Ia-d was done in air-, argon-, or oxygen-saturated acetonitrile solutions with 15 ns flashes of 265 nm light or 25 ns flashes of 347 nm light. The concentration of the solutions was kept constant, the absorbance of which showed 0.1 (light path: 1 cm) at the wavelength of the incident light.

9) Finding somewhat delayed photocurrent formation in Ref. 7 was based on an experimental error and its decay was as same as this work.

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