

NANOSECOND LASER FLASH PHOTOLYSIS OF 1-ANISYL-2,2-DIPHENYLVINYL BROMIDE IN ACETONITRILE AND ACETIC ACID

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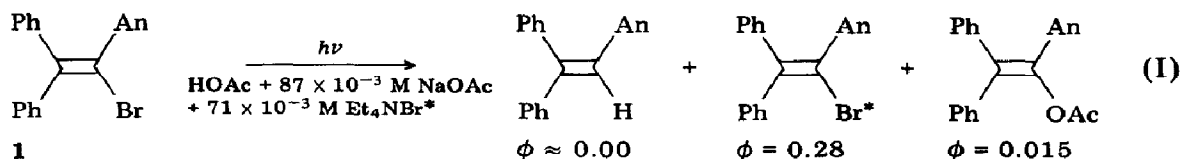
Summary

Nanosecond time-resolved spectroscopy shows that intermediates are produced upon laser flash excitation of 1-anisyl-2,2-diphenylvinyl bromide in acetonitrile and in acetic acid media. In acetonitrile optical absorption and electrical conductivity studies show the intermediacy of vinyl cations. In pure acetic acid no free ions are formed on laser flash excitation. The presence of polar additives in acetic acid is necessary for transient vinyl cations to appear. The cation is formed in parallel with a short-lived species, which is tentatively assigned as a radical pair or a tight ion pair. The least amount of additive necessary to produce a detectable quantity of vinyl cations depends on the nature of the additive. The quenching of the intermediate cations in acetonitrile and acetic acid media with bromide and acetate ions displays selectivity in agreement with the selectivity observed in steady-state irradiations.

1. Introduction

Both C—Br bond cleavage reactions and reactions characteristic of alkenes occur in the photolysis of vinyl bromides. In non-nucleophilic hydrogen-donating solvents the major C—Br bond cleavage process leads to reductive debromination; in nucleophilic media nucleophilic substitution occurs (for a review see ref. 1). It has been proposed that the latter reaction occurs via vinyl cations [2, 3]. In our laboratories we have studied the photochemical nucleophilic substitution reactions of a series of 1-arylvinyl bromides and have addressed the question of the mechanism of formation of the nucleophilic photosubstitution products by utilizing different probes.

Through studying nucleophilic capture ratios in systems such as that depicted in reaction (I) we have obtained clear chemical evidence for the involvement of cations identical with or very similar to those involved in thermal nucleophilic substitution reactions, *i.e.* free non-hot (thermally relaxed) vinyl cations [4].



(Ph \equiv phenyl; An \equiv *p*-methoxyphenyl; Br* \equiv ^{82}Br .) The determination of the quantum yield ratio of the bromide exchange reaction to the simultaneous acetate formation yields selectivity constants α equal or very similar to those for the corresponding thermal reactions. So, for example, in the photochemical reaction of 1-anisyl-2,2-diphenyl bromide (**1**) a selectivity $\alpha_{h\nu}$ towards bromide and acetate ions of 23 at 25 °C is found. On correcting for the temperature dependence of the selectivity, the factor would be 19 at 120 °C. The corresponding thermal reaction of **1** at 120 °C under otherwise identical conditions shows a selectivity $\alpha_{\Delta} = 19$ [5].

In experiments with continuous irradiation, the selectivity-determining rate constants of the reactive intermediate(s) cannot be obtained from the experimental data. We have used nanosecond time-resolved spectroscopy to observe reactive intermediates produced by laser flash excitation of vinyl halides and to monitor the kinetics of their reactions.

In this paper we report our investigation of the kinetics of the photochemical reactions of 1-arylviny bromides on a nanosecond time scale with the vinyl bromide **1** as a model compound [6] (for an extensive presentation see ref. 7). Studies of the lifetime of the transients as a function of the nature and concentration of added nucleophiles enabled us to determine directly both the reactivity and the selectivity of the intermediates.

Studies of laser-flash-induced optical absorption and electrical conductivity were carried out with **1** using two solvents, acetonitrile and acetic acid. Although the reaction looks very simple phenomenologically, the emerging mechanistic picture is complex and depends on the physical properties of the solvent. The results of the laser flash experiments in acetonitrile can be interpreted more easily than those in acetic acid. Therefore our experiments in acetonitrile will be described first. A knowledge of the nature and the properties of the observed intermediates in a solution of **1** in acetonitrile will serve as a basis for the interpretation of the experimental findings in acetic acid. Recently Schnabel *et al.* [8] reported a laser-flash-induced electrical conductivity study, and very recently Kobayashi *et al.* [9] reported a laser flash optical absorption study of 1,2,2-trianisylvinyl bromide in acetonitrile.

2. Experimental details

The transient absorptions and transient electrical conductivity of solutions of the vinyl bromide were studied by exciting the sample with a light pulse of wavelength 308 nm and time width 8 ns full-width at half

maximum (FWHM), using a Lambda Physik excimer laser (model EMG 500). For the observation of the light absorption, a wavelength-tunable monochromatic beam, derived from a pulsed xenon lamp, was crossed at 90° with the laser beam in the sample cell. The experimental details of the optical set-up and detection system have been described previously [10, 11]. The dimensions of the sample cell were $10\text{ mm} \times 20\text{ mm} \times 50\text{ mm}$. Typically the optical density OD of the vinyl bromide solution at 308 nm was 1.5 over a 1.0 cm path length. Photoinduced transient electrical conductivity measurements were performed as described by Visser *et al.* [12]. The signals were recorded using a Tektronix R 7912 transient digitizer and processed with a PDP 11/10 computer.

The vinyl bromide **1** was purified by repeated crystallization from ethanol [13]. The acetonitrile was spectrograde quality; the acetic acid was purified according to the method described in ref. 14.

3. Results

3.1. Experiments in acetonitrile

In the flash excitation (FWHM, 8 ns) of a $1.4 \times 10^{-4}\text{ M}$ solution of **1** in acetonitrile at 308 nm and at room temperature a transient X_1 having a UV absorption with a maximum optical density of 0.75 at 350 nm is observed. The presence of oxygen has no effect on the optical density. X_1 appears with a rise time identical with that of the integrated laser pulse (15 ns). This means that X_1 is formed within 5 ns of excitation of **1**. The absorption spectrum of X_1 is depicted in Fig. 1.

The decay of X_1 (Fig. 2(a)) can be very well described as a first-order process as is shown in Fig. 2(b) and less adequately by second-order kinetics. The lifetime of X_1 is $12\ \mu\text{s}$.

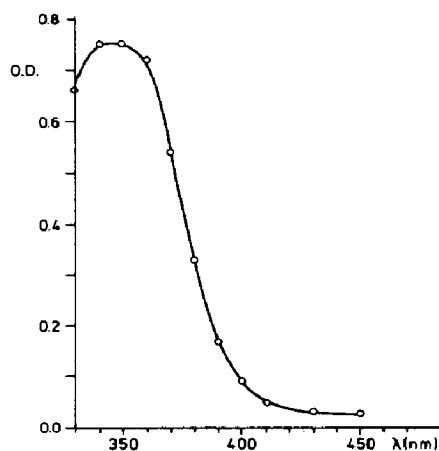


Fig. 1. UV spectrum of the transient X_1 observed upon flash photolysis of **1** in acetonitrile.

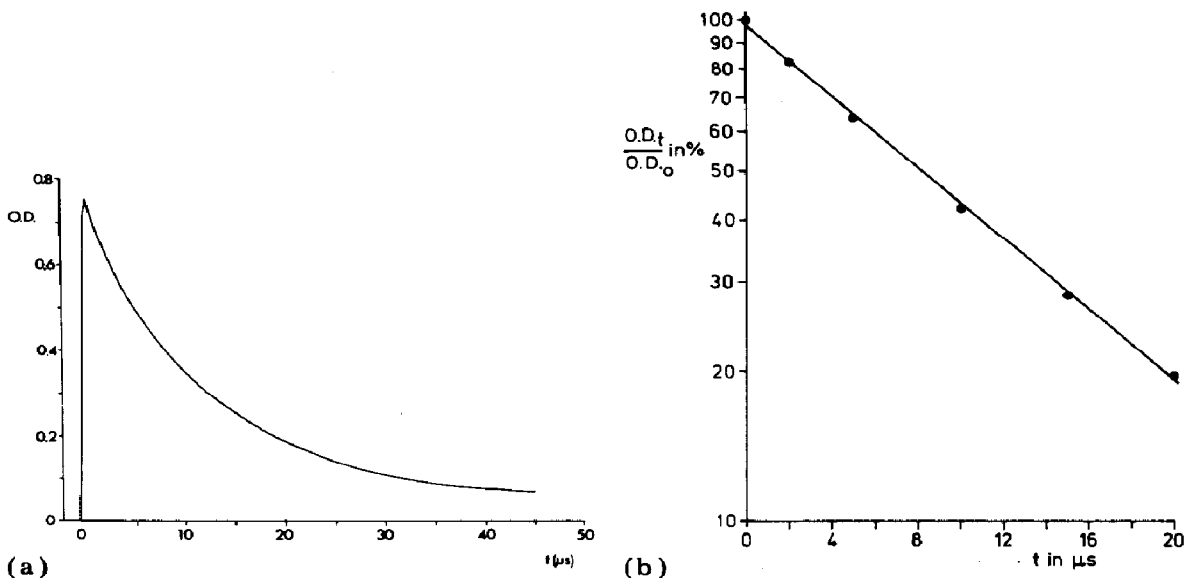


Fig. 2. The flash photolysis of 1 in acetonitrile: (a) decay curve of the optically detected transient X_1 ; (b) semi-logarithmic plot of the decay of the transient X_1 .

The lifetime of X_1 is not dependent on the intensity of the excitation light. In this experiment the laser flash intensity was varied from its maximum value to 2% of that level. The maximum optical density of the transient X_1 increases linearly with the intensity of the laser flash. At high flash intensity some deviation from this linear dependence occurs owing to saturation.

The nature of the intermediate X_1 was investigated via a study of the influence of various additives on its lifetime. The lifetime of the absorbance due to X_1 is not reduced by the presence of either oxygen or piperylene (10^{-1} M), but it is reduced by the presence of water, methanol, tetraethylammonium bromide (Et_4NBr) and tetraethylammonium acetate (Et_4NOAc). The lifetime of X_1 shows a first-order dependence on the concentration of the additives. This is illustrated in Fig. 3 for the nucleophile Et_4NBr . The quenching constants are given in Table 1.

The decay time constant of X_1 depends on the temperature of the solution: at 22°C the lifetime of X_1 is $12\ \mu\text{s}$, at 7°C it is $19\ \mu\text{s}$.

The lifetime of X_1 is also dependent on the concentration of 1. As shown in Fig. 4, gradually lowering this concentration from 1.4×10^{-4} M to 5.7×10^{-6} M gives an increase in the lifetime of X_1 .

Electronic excitation of a 2.4×10^{-5} M solution of 1 in acetonitrile also induces a transient (Y_1) in the electrical conductivity of the solution. Y_1 is formed within 5 ns. In ref. 8 it was reported that in the laser flash photolysis of 1,2,2-trianisylvinyl bromide, transient conductivity occurred with a delay. This was apparently due to an experimental error [9]. The decay of Y_1 is depicted in Fig. 5(a), which shows the presence of a constant signal at longer observation times. The transient photocurrent decays according

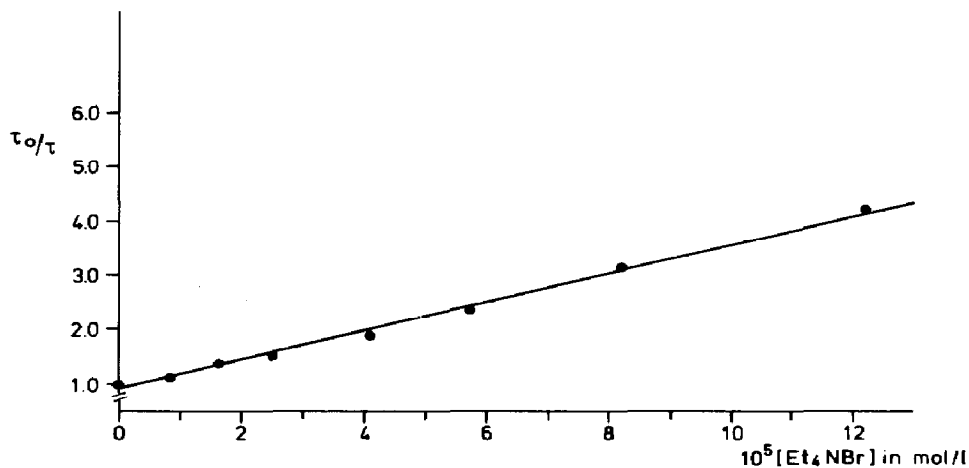


Fig. 3. The relative lifetime of the transient X_1 in the flash photolysis of 1 in acetonitrile as a function of the concentration of Et_4NBr .

TABLE 1

Rate constants for quenching of the transient X_1 by various additives in the flash photolysis of 1 in acetonitrile

Quencher	k_q ($\text{M}^{-1} \text{s}^{-1}$)
Water	6×10^4
Methanol	5×10^5
Et_4NBr	2×10^9
Et_4NOAc	3×10^9

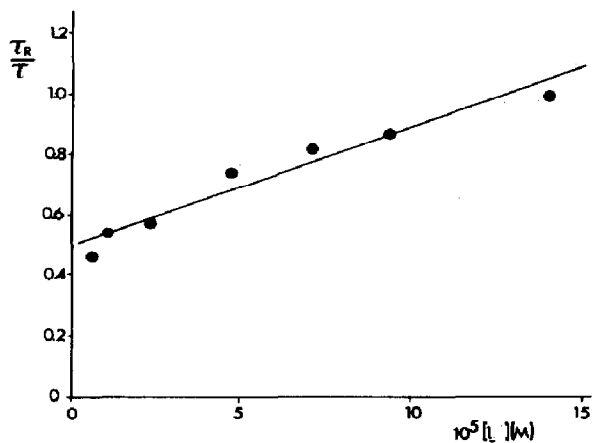


Fig. 4. The relative lifetime of the transient X_1 in the flash photolysis of 1 in acetonitrile as a function of the concentration of 1.

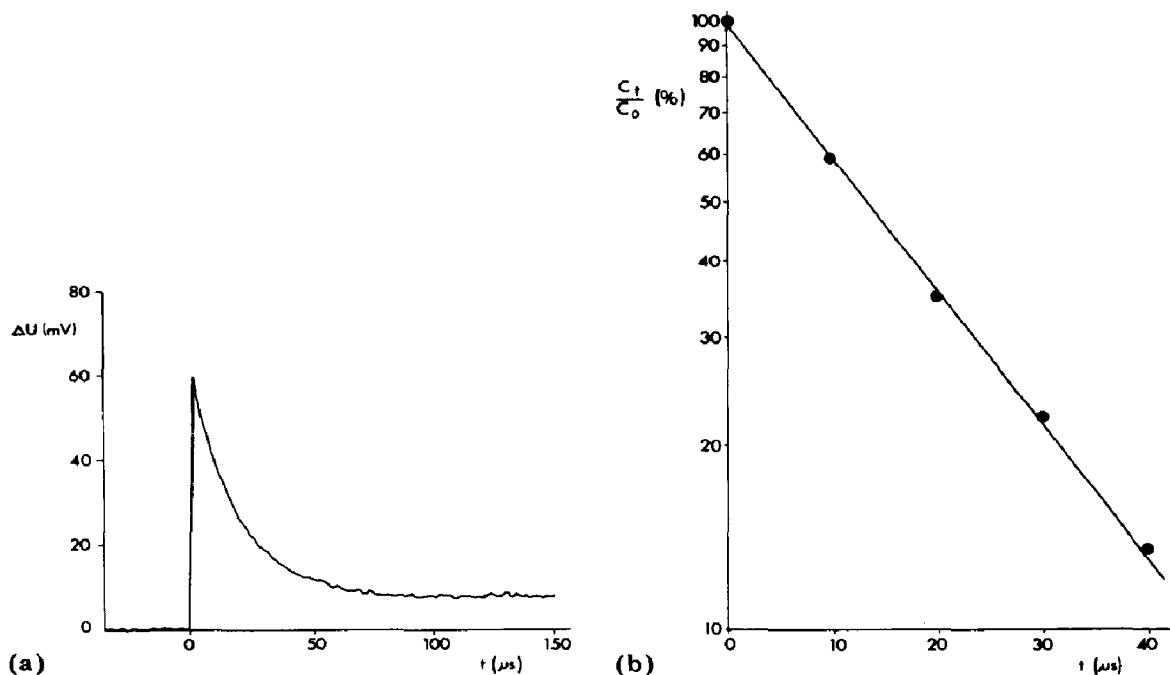


Fig. 5. The flash photolysis of 1 in acetonitrile: (a) decay curve of the transient Y_1 in the electrical conductivity of the solution; (b) semi-logarithmic plot of the decay of the transient Y_1 .

to first-order kinetics (Fig. 5(b)). The lifetime of Y_1 is $20 \mu\text{s}$. The maximum photocurrent increases linearly with the absorbed dose per laser pulse (Fig. 6) indicating that the electrical conductivity is not due to multiphotonic ionization. The lifetime of Y_1 is independent of the intensity of the laser flash.

In order to be able to answer the question whether or not the optically detected transient X_1 is the same species which is responsible for the appearance of the transient electrical conductivity, quenching experiments were carried out with Et_4NBr as the quencher. The results of these experiments are presented in Fig. 7. From the quenching data a rate constant k_q for quenching of Y_1 by Et_4NBr is calculated as $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

The presence of water in a solution of 1 in CH_3CN results in a quenching of the photocurrent that is analogous to the action of Et_4NBr , but produces an increase in the magnitude of the "constant" part of the signal. The rate constant of quenching of Y_1 by water is of the same order of magnitude ($k_q = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$) as the rate constant of quenching of X_1 by water (see Table 1).

3.2. Experiments in acetic acid

Excitation of the vinyl bromide 1 at room temperature in acetic acid ($[1] = 1.4 \times 10^{-4} \text{ M}$) yields a transient species X_2 . X_2 is formed within 5 ns and has an absorption spectrum similar to that of X_1 with a maximum at

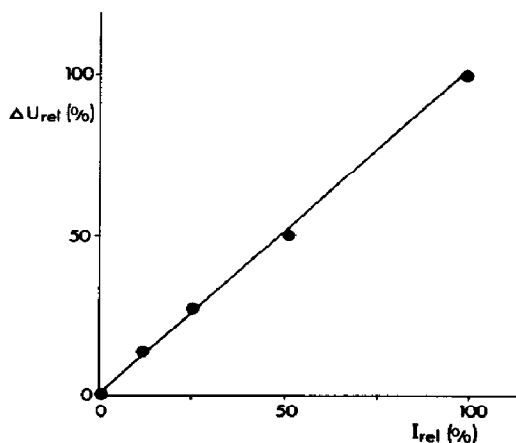


Fig. 6. Plot of the maximum value of the photocurrent observed as a function of the intensity of the laser flash.

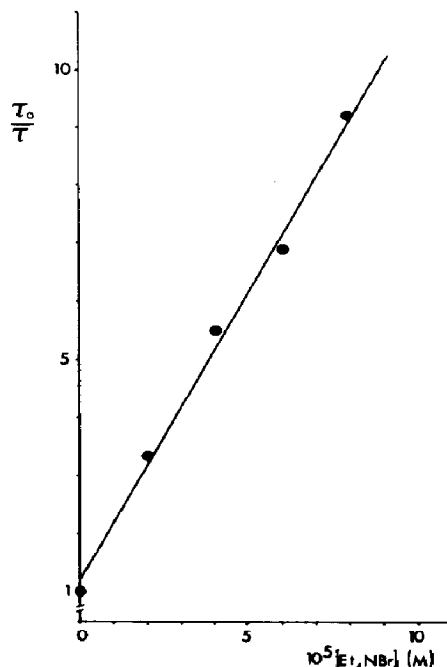


Fig. 7. The relative lifetime of the transient Y_1 in the electrical conductivity of the solution upon flash photolysis of 1 in acetonitrile as a function of the concentration of Et_4NBr .

350 nm. The maximum transient optical density of X_2 , normalized to excitation dose, is one third that of X_1 in acetonitrile. Species X_2 decays according to a first-order process with a decay time of 70 ns.

Neither the presence of piperylene (10^{-1} M) nor that of oxygen alters the lifetime of X_2 . Adding Et_4NBr (even up to a concentration as high as 1.0 M) also fails to produce a change in the lifetime of X_2 .

Electronic excitation of 1 (0.4×10^{-4} M) in acetic acid does not lead to any detectable transient in the electrical conductivity of the solution.

When sodium acetate, pyridine, Et_4NOAc , water or sulphuric acid is added to a solution of 1 in acetic acid, excitation yields an optically detectable species X_3 with a lifetime between 1 and 7 μs depending on the additive. X_3 is formed parallel to X_2 and is spectroscopically indistinguishable from it. Figure 8 shows the decay curves of the transients ($X_2 + X_3$) which are observed in acetic acid at various concentrations of water.

As can be seen from the increasing optical density at the tail section of the curves, the amount of X_3 increases with the concentration of water, while the optical density directly after excitation remains constant. The nature of the additive also plays an important role: the transient X_3 is only detectable when more than 1 vol.% water has been added, whereas the threshold concentration for detection of X_3 in the case of pyridine is only

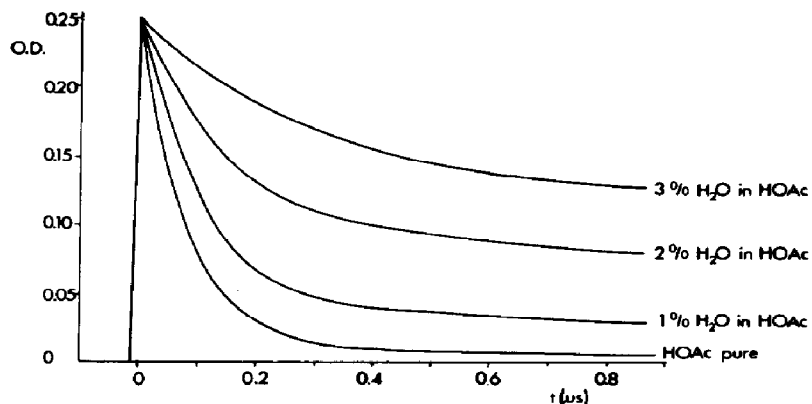


Fig. 8. The decay curves of the optically detected species in the flash photolysis of 1 in acetic acid as a function of the concentration of water.

4.5×10^{-4} M (see Tables 2 and 3). Addition of Et_4NBr (up to 1.0 M) to a solution of 1 in acetic acid leads neither to the appearance of X_3 nor to a decrease in the concentration of X_2 .

X_3 decays via a first-order process. The variation of the lifetime with the type of additive is shown in Table 4. The decay time of the short-lived species X_2 is insensitive to the presence of these compounds. At high concentrations of water the fast decay of X_2 is no longer seen and only X_3 is observed.

TABLE 2

Relative amounts^a of the transient X_3 in the flash photolysis of 1 in acetic acid at various concentrations of pyridine and sodium acetate

[Additive] ($\times 10^{-4}$ M)	X_3 (%)
<i>Pyridine</i>	
4.5	12
27	25
45	36
180	64
352	80
870	100
<i>Sodium acetate</i>	
50	12
100	18
190	24
370	38

^aDefined as a percentage:

$$\text{Relative amount} = \frac{100\text{OD}_{\max}[\text{X}_3]}{\{\text{OD}_{\max}[\text{X}_3] + \text{OD}_{\max}[\text{X}_2]\}}$$

TABLE 3

Threshold concentration for the detection of the transient X_3 in the flash photolysis of 1 in acetic acid as a function of the type of additive

<i>Additive</i>	<i>Threshold concentration (M)</i>
Water	5×10^{-1}
Pyridine	5×10^{-4}
Sodium acetate	5×10^{-3}

TABLE 4

Lifetimes of the transients X_3 in the flash photolysis of 1 in acetic acid as a function of the type of additive

<i>Additive</i>	<i>Concentration (M)</i>	<i>Lifetime of X_3 (μs)</i>
Sodium acetate	86×10^{-3}	1.0
Pyridine	52×10^{-3}	1.1
Et ₄ NOAc	13×10^{-3}	1.3
Water	1.67 ^a	2.7
Sulphuric acid	92×10^{-3}	7.0

^a3 vol. %.

An increase in the concentration of a single additive increases the amount of X_3 , but does not lead to a detectable shortening of the lifetime of X_2 . This shows that X_3 is not formed from X_2 , but in parallel with it. Since the amount of X_3 increases at the expense of X_2 , X_2 and X_3 are probably formed from a common precursor. Moreover, in the case of water addition it turns out to be possible, as shown in Fig. 9, to construct the actually observed decay curve as a sum of the individually measured decay curves of X_2 and X_3 .

Furthermore, as can be seen in Fig. 8, the slope of the tangent of the curve at $t = 0$ increases with increasing concentration of the additive (*i.e.* water). Again this indicates that X_3 is formed in parallel with X_2 (see Section 4).

Et₄NBr quenches the transient X_3 in acetic acid solutions of sodium acetate, water, pyridine or Et₄NOAc. This is illustrated for an acetic acid-3vol.%water mixture in Fig. 10. The rate constants for quenching in the various mixtures are given in Table 5. A shortening of the lifetime of species X_3 in acetic acid-3vol.%water is also brought about by sodium acetate, but here the plot of the relative lifetime of X_3 as a function of the concentration of sodium acetate does not show a linear dependence on the quencher concentration (Fig. 11). From the slope of the tangent of the curve at low

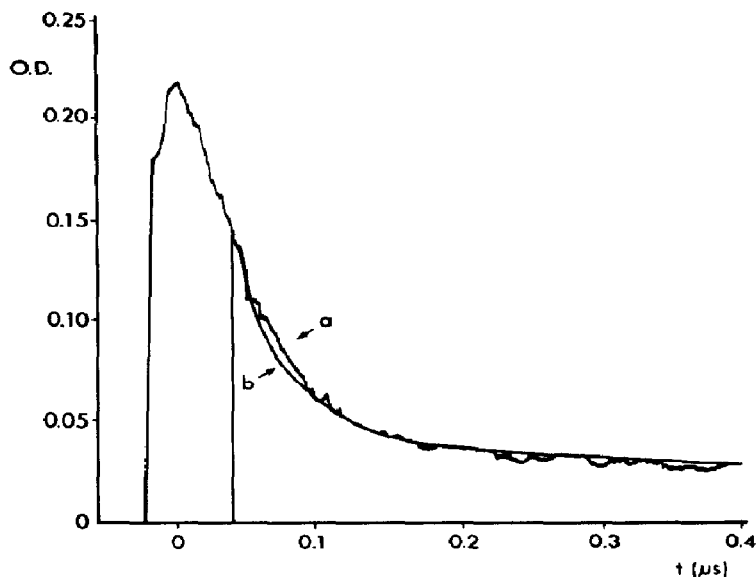


Fig. 9. (a) Decay curve of the transients X_2 and X_3 in the flash photolysis of 1 in acetic acid-1vol.%water. (b) Calculated decay curve: $OD = A(X_2) \exp\{-t/\tau(X_2)\} + A(X_3) \exp\{-t/\tau(X_3)\}$ with $A(X_2) = 1.1$, $A(X_3) = 0.4$, $\tau(X_2) = 70$ ns and $\tau(X_3) = 2.5$ μ s.

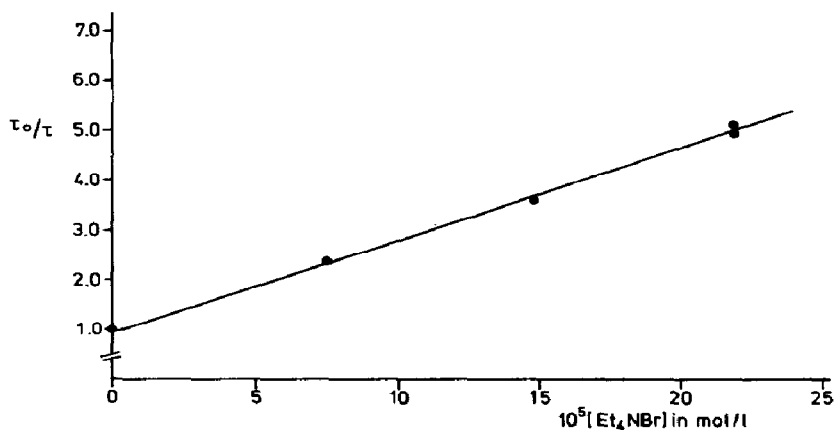


Fig. 10. The relative lifetime of the transient X_3 in the flash photolysis of 1 in acetic acid-3vol.%water as a function of the concentration of Et_4NBr .

concentrations of sodium acetate a quenching rate constant of the order of $(1 - 2) \times 10^7 M^{-1} s^{-1}$ is obtained.

In contrast with the situation in pure acetic acid, electronic excitation of 1 in acetic acid-1vol.%water produces a transient (Y_3) in the electrical conductivity of the solution. The magnitude of the signal Y_3 in acetic acid-3vol.%water is about 3% that of Y_1 in CH_3CN . It increases by a factor of 5 in going from 1 vol.% to 4 vol.% water in acetic acid. The decay of this signal (Fig. 12) is described very well by first-order kinetics. The lifetime of the transient photocurrent is 3.8 μ s. Again a residual constant conductivity is seen at longer observation times. Studying the possible quenching by

TABLE 5

Rate constants for quenching of the transient X_3 by Et_4NBr in the flash photolysis of 1 in acetic acid as a function of the type of additive

Additive in acetic acid	Additive concentration ($\times 10^{-3}$ M)	k_q ($\text{M}^{-1} \text{s}^{-1}$)
NaOAc	72	5×10^8
Pyridine	52	3×10^8
H_2O	1670	6×10^9
Et_4NOAc	25	5×10^8

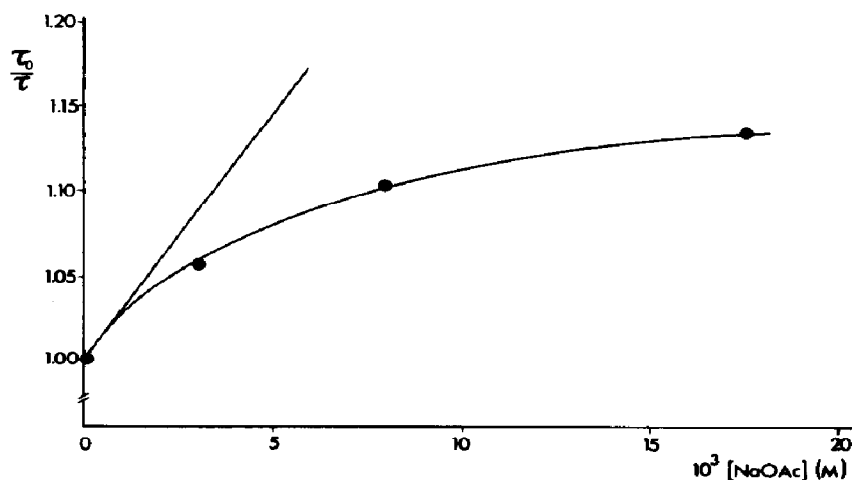


Fig. 11. The relative lifetime of the transient X_3 in the flash photolysis of 1 in acetic acid-3vol.%water as a function of the concentration of sodium acetate.

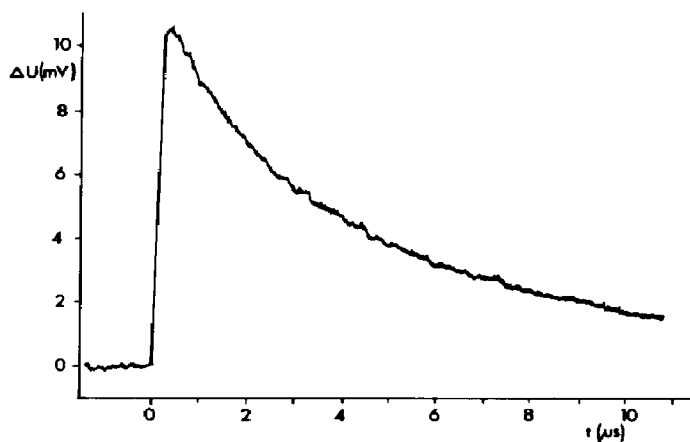


Fig. 12. The decay curve of the transient Y_3 in the electrical conductivity of the solution upon flash photolysis of 1 in acetic acid-4vol.%water.

Et_4NBr of the very small transient photocurrent signal is virtually impossible because of the large amount of permanent electrical conductivity caused by the introduction of salts such as Et_4NBr .

4. Discussion

The results of the laser flash photolysis experiments with the vinyl bromide 1 in acetonitrile and acetic acid are summarized in Table 6.

TABLE 6

Summary of the results of laser flash photolysis experiments with the vinyl bromide 1 in acetonitrile and acetic acid

<i>Solvent</i>	<i>Experiment</i>	<i>Transient</i>	<i>Lifetime</i>	<i>Remarks</i>	<i>Quenching experiments^a</i>
<i>Acetonitrile</i>	Optical detection	X_1	12 μs	Absorption spectrum with maximum at 350 nm	Piperylene (—) Oxygen (—) Water, methanol (+) Et_4NBr , Et_4NOAc (+)
	Electrical conductivity	Y_1	20 μs	Free ions formed	Et_4NBr (+) Water (+)
<i>Acetic acid</i>	Optical detection	X_2	70 ns	Absorption spectrum with maximum at 350 nm ($\text{OD}_{\text{max}} = \frac{1}{3} \text{OD}_{\text{max}}$ in acetonitrile)	Piperylene (—) Oxygen (—) Et_4NBr (—)
	Electrical conductivity	\bar{b}	—	No free ions formed	
<i>Acetic acid plus water, sodium acetate, Et_4NOAc, sulphuric acid and pyridine</i>	Optical detection	X_3	0.9 - 7 μs	Absorption spectrum with maximum at 350 nm	Et_4NBr (+) Sodium acetate (+)
	Electrical conductivity	Y_3	3.8 μs^c	Free ions observed when $[\text{H}_2\text{O}] > 1 \text{ vol.}\%$	—

^a+, quenching detected; —, quenching not detected.

^bNo transient observed.

^cIn acetic acid—4vol.%water.

4.1. Experiments in acetonitrile

In acetonitrile the transient X_1 is quenched neither by oxygen nor by dienes such as piperylene, which indicates that X_1 is neither a radical nor a triplet state.

A crude calculation shows that the lifetime of X_1 should decrease by at least a factor of 50 in going from a nitrogen to an oxygen atmosphere if X_1 were a radical and k_q would have a value of $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [15]. Similarly the lifetime of X_1 should decrease by a factor of 1000 in the presence of 0.1 M piperylene ($k_q = 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [16]) if X_1 were a triplet with a triplet energy higher than 60 kcal mol^{-1} [17].

X_1 is quenched by nucleophiles such as water, methanol, Et_4NBr and Et_4NOAc , which indicates that X_1 may very well be a cation. At the quencher concentrations used Et_4NBr and Et_4NOAc are more than 99% dissociated into ions. This can be estimated on the basis that the known value of K_{diss} for Me_4NBr in acetonitrile is 4×10^{-2} [18]. For the dissociated quenchers Et_4NBr and Et_4NOAc the rate constant of quenching is much larger than that of the non-charged nucleophiles water and methanol. The relative magnitudes of the rates of quenching by water and methanol are those expected on the basis of the nucleophilicity of these reagents: the solvent nucleophilicity parameter N [19] of methanol (0.01) is larger than that of water (-0.26) [20]; the same is true for the solvent nucleophilicity parameter B : $B(\text{methanol}) = 114$ and $B(\text{water}) = 90$ [21].

X_1 is formed instantaneously in the experimental set-up used. This means that species formed prior to X_1 (e.g. singlet or triplet states of 1) have lifetimes shorter than 5 ns. It has been proposed that the photochemical formation of vinyl cations from vinyl halides occurs via homolytic cleavage of the carbon-halogen bond followed by electron transfer [2, 3]. The results show that if this is the route followed it has to be very fast.

The observation of transient electrical conductivity Y_1 shows that ions are formed in the photoreaction of 1 in acetonitrile. Again Y_1 is formed instantaneously. Upon addition of Et_4NBr the lifetime of the transient photocurrent decreases. The rate constant for quenching of Y_1 by Et_4NBr is $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is in agreement with the rate constant of quenching of X_1 by Et_4NBr , i.e. $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (Table 1). This indicates that the transient species detected optically is responsible for the occurrence of the transient photoconductivity. The cationic species X_1 is assumed to be a vinyl cation. Vinyl cations are thought to be reactive intermediates in the formation of vinyl acetates from vinyl bromides. Moreover the UV absorption of X_1 with a maximum optical density at 350 nm is in accordance with the absorption maximum of cations such as the benzyl cation (λ_{max} in dichloromethane is 363 nm) [22]. Both the decay of X_1 and of the transient photocurrent follow first-order kinetics, which is confirmed by the observation that their lifetimes are independent of the intensity of the laser pulse. This means that the recombination reaction of Br^- with the vinyl cation X_1 could be held responsible for the observed decay but only if the recombination involves geminate ions. Recombination of free ions would not result in first-order decay. The observation that the lifetime of X_1 is increased on decreasing the initial concentration of 1 in acetonitrile (Fig. 4) leads to the assumption that some kind of interaction (complexation or reaction?) occurs between X_1 and ground state 1 molecules. The formation of such a

“complex” between X_1 and 1 could account for the observed decay of X_1 because the large excess of 1 over X_1 would give pseudo-first-order kinetics. This assumes that the X_1-1 complex does not significantly contribute to the absorption at 350 nm. The calculation of the rate constant of complexation of X_1 with 1 molecules gives a value of $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which indicates a nearly diffusion-controlled reaction. Reaction of X_1 with the solvent can also account for the observed first-order decay.

The magnitude of the transient photocurrent in electrical conductivity experiments is determined by the magnitudes of the concentrations and mobilities of the charged species formed as shown in eqn. (1).

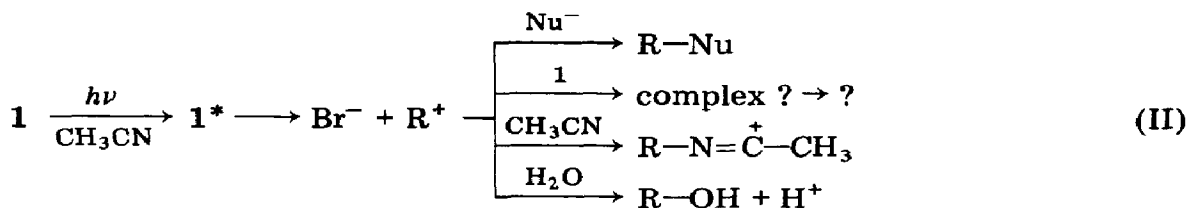
$$j = F(c^+\mu^+ + c^-\mu^-)E \quad (1)$$

j is the current density, F is the Faraday constant, E is the strength of the electric field, c is the concentration of the (positive or negative) charged species and μ is its mobility. Based on the ratio of μ^+ and μ^- the following cases may be discerned.

(a) $\mu^+ \gg \mu^-$. In this case the magnitude of the transient current density is largely determined by the positively charged species, *e.g.* the vinyl cation (X_1). When the vinyl cation reacts with ground state 1 molecules or with solvent molecules, charged complexes are formed which are of much lower mobility than X_1 . This explains the first-order decay of the conductivity Y_1 . The lifetime of Y_1 is 20 μs . This value is equal (within experimental error) to the lifetime of X_1 (21 μs) which is observed in laser flash experiments using a solution of the same concentration of 1 as in the transient photocurrent studies (see Fig. 4).

(b) $\mu^+ \approx \mu^-$ or $\mu^+ \ll \mu^-$. In these cases the negatively charged species, *e.g.* the Br^- ions, are at least as responsible for the transient electrical conductivity as the positively charged species (CH_3CN : $\mu(\text{Br}^-) = 1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [23]). The observed first-order decay of Y_1 may be interpreted as the result of a complexation of Br^- ions with ground state 1 molecules. The equality of the lifetimes of the vinyl cation X_1 and the conductivity Y_1 implies that the rate constant of the disappearance of X_1 (*e.g.* by reaction with ground state 1 molecules or with solvent molecules) has to be identical with the rate constant of disappearance of Br^- ions (*e.g.* by complexation with 1 molecules). As shown above, the rate constant of the interaction of X_1 with 1 molecules is (nearly) diffusion controlled.

Rather stable ions are formed at the same time as the vinyl cation X_1 , causing a conductivity that is permanent, at least within the 500 μs time scale of the experiments. Excitation of a solution of 1 in acetonitrile containing water leads to a transient photocurrent with a smaller lifetime but with a larger amount of “permanent” conductivity. The long-lived conductivity may be associated with a reaction of the vinyl cation with water molecules. This produces protons next to the already present Br^- ions (reaction II; Nu \equiv nucleophile).



In Table 1 the rate constants of the quenching of X_1 by Et_4NBr and Et_4NOAc are given. The rate constants of the quenching of X_1 by Et_4NBr ($2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) and Et_4NOAc ($3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) indicate that in acetonitrile the selectivity of the vinyl cation X_1 with respect to bromide *versus* acetate ions is low (about 1). This is in agreement with the preliminary results of the steady state photochemical experiments for 1 in acetonitrile. In this solvent we found a selectivity constant $\alpha \approx 2$ [24].

4.2. Experiments in acetic acid

A transient X_2 with a relatively short lifetime of 70 ns is optically observed in the laser flash photolysis in pure acetic acid. Its decay follows first-order kinetics. X_2 is formed instantaneously and shows a UV absorption similar to that of X_1 in CH_3CN . However, in the electrical conductivity no transient photocurrent is observed in acetic acid. Apparently X_2 is not a free charged species. This is confirmed by the fact that addition of Et_4NBr does not shorten the lifetime of X_2 . Pure acetic acid is not a suitable medium for free ions. Its dielectric constant is low (6.2) and the dissociation constant for salts is small ($K_{\text{diss}} \leq 10^{-6}$) [25]. This means that less than 10% of the salts are dissociated into free ions at a salt concentration of 10^{-4} M . X_2 is quenched neither by dienes nor by oxygen, which indicates that it is probably neither a triplet state of 1 nor a radical.

In the flash photolysis of 1 in acetic acid in the presence of additives such as water, sodium acetate, Et_4NOAc , pyridine and sulphuric acid, the species X_2 and another transient species X_3 are detected optically, the latter with a lifetime between 1 and 7 μs . In acetic acid-water a transient photoconduction Y_3 is also observed. Apparently the presence of an additive is necessary for the formation of ionic intermediates. X_3 has an absorption spectrum similar to that of X_1 . X_3 , like X_1 , is quenched by Et_4NBr and sodium acetate. Therefore, X_3 may be considered to be a vinyl cation analogous to that in acetonitrile. The lifetimes of X_3 and Y_3 are approximately equal. This indicates that the optically detected transient species is responsible for the observed transient photoconductivity.

The following observations indicate that species X_2 and X_3 are formed in parallel reactions.

(a) The amount of X_3 increases with the concentration of the additive, but the lifetime of X_2 is not shortened.

(b) It is possible to construct the actually observed decay curve as a superposition of the individual decay curves of X_2 and X_3 .

(c) When X_2 and X_3 are formed simultaneously (reaction (III)) the slopes of the tangents of the decay curves of $(X_2 + X_3)$ are defined by eqn. (2).



$$s = \frac{dOD}{dt} = -\epsilon_2[X_2]_0 k_2 \exp(-k_2 t) - \epsilon_3[X_3]_0 k_3 \exp(-k_3 t) \quad (2)$$

In eqn. (2) k_2 and k_3 are the decay rate constants, ϵ_2 and ϵ_3 are the absorption coefficients at the detection wavelength and $[X_2]_0$ and $[X_3]_0$ are the concentrations at $t = 0$ of X_2 and X_3 respectively. At the maximum of the curve (*i.e.* at $t = 0$) s is given by

$$s = -\epsilon_2 k_2 [X_2]_0 - \epsilon_3 k_3 [X_3]_0 \quad (t = 0) \quad (3)$$

On a short time scale the decay of X_3 is negligible compared with the decay of X_2 , so eqn. (3) may be approximated by

$$s = -\epsilon_2 k_2 [X_2]_0 = -f[X_2]_0 \quad (t = 0) \quad (4)$$

An increase in the concentration of the additive increases $[X_3]_0$, decreases $[X_2]_0$ and thus increases s . This effect is in agreement with the experimental observations (Fig. 8).

If X_3 is formed from X_2 (reaction (IV)) the slope s is defined by eqn. (5), assuming again that k_3 is negligible.



$$s = \frac{dOD}{dt} = (k_2 \epsilon_3 - k_1 \epsilon_2 - k_2 \epsilon_2) [X_2]_0 \exp(-tk_1 - tk_2) \quad (5)$$

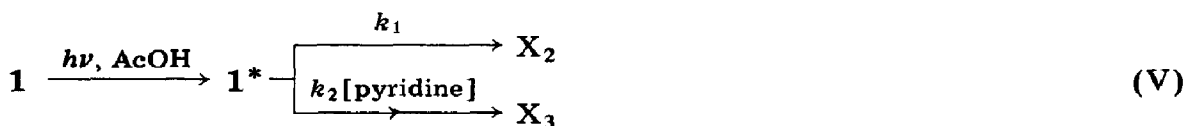
In eqn. (5) k_1 is the rate constant of the decay of X_2 in the absence of the additive, k_2 is the rate constant of the formation of X_3 from X_2 , ϵ_2 and ϵ_3 are the absorption coefficients at the detection wavelength of X_2 and X_3 respectively and $[X_2]_0$ is the concentration of the initially formed X_2 . $[X_2]_0$ is independent of the additive (see reaction (IV)). The rate constant k_2 is a function of the concentration of the additive. At $t = 0$ the magnitude of the slope s is given by

$$s = (k_2 \epsilon_3 - k_1 \epsilon_2 - k_2 \epsilon_2) [X_2]_0 \quad (t = 0) \quad (6)$$

With the approximation that the value of ϵ_3 is not significantly different from that of ϵ_2 , $s = -k_1 \epsilon_2 [X_2]_0 = \text{constant}$. This means that the slope s is independent of the concentration of the additive. This is not in agreement with the experimental results (Fig. 8).

The identity of X_2 is not clear. An attractive assignment for X_2 is a radical pair, but this would require its absorption spectrum to be similar to that of X_3 (the vinyl cation). Benzyl radicals have a near-UV absorption band around 320 nm [26]. X_2 might also be a solvent-separated ion pair, but if X_2 and X_3 are indeed formed separately it is not easily understood why a free ion is not formed from the solvent-separated ion pair. X_2 could be a tight ion pair. The UV spectrum of such an ion pair is not likely to be very different from that of the free ion X_3 .

The influence of the additives water, pyridine and sodium acetate is qualitatively similar but quantitatively different. In the case of addition of water, at least 1 vol.% water is necessary to produce a detectable amount of the transients X_3 and Y_3 . The necessity of a relatively high concentration of additive leads to the conclusion that a change in the polarity of the medium may be the cause of the existence of X_3 . However, excitation of 1 in acetic acid with a pyridine concentration as low as 4.5×10^{-4} M already shows an X_3 intensity that is 12% of the maximum (see Table 2). Therefore the influence of pyridine does not arise from the macroscopic properties of the medium. The following kinetic analysis shows that a bimolecular reaction of pyridine with excited 1 (reaction (V)) does not lead to X_3 either.

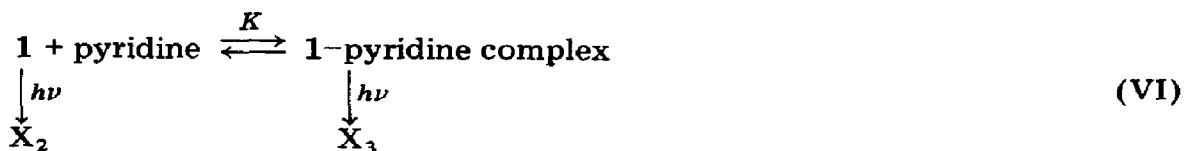


$$\frac{[X_3]}{[X_2]_0 - [X_3]} = \frac{k_2[\text{pyridine}]}{k_1} \quad (7)$$

Plotting the data in Table 2 according to eqn. (7) gives a straight line with a slope $(k_2/k_1) \approx 100$.

As the rise time of X_2 is less than 5 ns, $k_1 \geq 2 \times 10^8 \text{ s}^{-1}$. Therefore $k_2 \geq 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. This is an unlikely value for a reaction rate constant in such a medium (the viscosity of acetic acid at 23 °C is 1.18 cP [25]). (Based on the ratio of the viscosity of acetic acid and that of acetonitrile, a maximum value for the rate constant k_2 is estimated to be approximately $10^9 \text{ M}^{-1} \text{ s}^{-1}$.)

Complexation of pyridine and ground state 1 prior to the photochemical reaction is a more probable cause for the influence of pyridine. This can be visualized as



$$K[\text{pyridine}] = \frac{[X_3]}{100 - [X_3]} \quad (8)$$

where $[X_3]$ is expressed as a percentage. Equation (8) is valid when the absorption coefficients ϵ at the wavelength of excitation of 1 and of the 1-pyridine complex are equal, and when the quantum yields for the production of X_2 from 1 and X_3 from the 1-pyridine complex are equal.

A graphical representation of the results listed in Table 2 according to eqn. (8) gives a straight line of slope $K = 93 \text{ M}^{-1}$.

The effect of sodium acetate may be caused by a bimolecular reaction with excited 1. In this case a value of $k_2 \geq 3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ is calculated. In contrast with the value for the reaction rate constant in acetic acid-pyridine this value of k_2 is not impossible, although it is relatively high in such a viscous medium (see above). Consequently a bimolecular pathway cannot be ruled out.

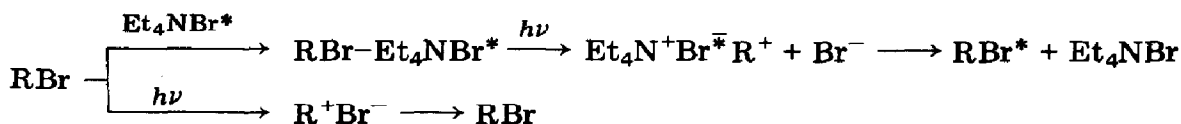
A graphical presentation of the results given in Table 3, for the case of addition of sodium acetate to the solution, according to eqn. (8) gives a straight line of slope $K = 15 \text{ M}^{-1}$.

On the basis of these results complexation of sodium acetate and ground state 1 prior to the photochemical reaction also seems possible. Complexation of 1 with sodium acetate is less efficient than with pyridine.

Both X_2 and X_3 are formed very rapidly. The rate constants of formation have to be larger than $2 \times 10^8 \text{ s}^{-1}$. In principle, the precursor of X_2 and X_3 could be an excited state of 1 (reaction (V)) or X_2 could be formed via excitation of 1 and X_3 via excitation of a complex of 1 with an additive (reaction (VI)). At least for the two cases mentioned above, *i.e.* with pyridine or sodium acetate as the additive, it has been concluded that the ratio of the concentrations of X_2 and X_3 is determined in reaction step preceding the initial excitation of 1. This means that reaction (VI) is valid.

If Et_4NBr is present in a solution of 1 in acetic acid a long-lived transient such as X_3 is not observed upon excitation. Quenching of X_2 by Et_4NBr is not observed either. Et_4NBr quenches the transient species X_3 in acetic acid-sodium acetate, acetic acid- Et_4NOAc , acetic acid-water (Fig. 10) or acetic acid-pyridine (see Table 5). An obvious conclusion would be that X_3 is not formed when a solution of 1 in acetic acid- Et_4NBr is excited. However, if X_3 is indeed a vinyl cation it should be present in the reaction mixture, because bromide exchange is observed in the photochemistry of 1 in acetic acid- Et_4NBr [4]. The fact is that bromide exchange is believed to occur via a vinyl cation as a reactive intermediate.

An explanation for this apparent contradiction would be that Et_4NBr induces the formation of X_3 in acetic acid, but destroys the same transient faster than it is formed. Quenching of X_3 by Et_4NBr shows a linear Stern-Volmer plot. Diffusion-controlled values are found for the quenching rate constants of Et_4NBr in acetic acid plus additives. However, if this is true the optical density of X_2 should be greatly diminished. This is not in accordance with the experimental observations. A possible explanation is given by the following reaction sequence:



Excitation of the vinyl bromide RBr (1) in pure acetic acid results in the formation of the tight ion pair R^+Br^- , *i.e.* X_2 . Upon excitation in the presence of Et_4NBr , complexation of this compound with ground state RBr leads to the formation of R^+Br^* , *i.e.* a tight ion pair which has exchanged its counterion Br^- for a radioactive bromide ion. The original Br^- can be expelled into the solution. The reaction pattern shown accounts for the experimental observations described: the occurrence of bromide exchange, no detection of a free vinyl cation (X_3) and no quenching of X_2 by Et_4NBr . R^+Br^- and R^+Br^* have identical optical properties and lifetimes.

Stern-Volmer analysis of the kinetics of the quenching by sodium acetate in acetic acid containing 3 vol.% water shows a non-linear relationship (Fig. 11). This non-linearity could be interpreted as the net result of two counteracting forces: addition of sodium acetate to acetic acid-water not only quenches X_3 but at the same time produces X_3 . Obviously induction of the formation of X_3 by sodium acetate is more pronounced than quenching of the same transient.

It is very difficult to abstract the correct values of the quenching rate constants from the non-linear quenching plots. From the slope of the line in Fig. 10 and the tangent of the curve in Fig. 11, at low concentrations of sodium acetate the following rate constants can be obtained for quenching of X_3 : $k_q(\text{Et}_4\text{NBr}) = 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_q(\text{NaOAc}) = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. Exact determination of the selectivity of X_3 with respect to bromide *versus* acetate ions is therefore made difficult as a consequence of the equivocal values of the quenching rate constants. The data listed above suggest a selectivity constant $\alpha \gg 1$ in acetic acid. The results are, at least qualitatively, in accordance with the conclusion obtained from the experiments with continuous irradiation of 1 in acetic acid-sodium acetate- Et_4NBr . In this system we found the selectivity constant $\alpha = 23$ [4].

5. Concluding remarks

The nanosecond time-resolved spectroscopy studies described in this paper of the events that occur upon laser flash excitation of 1-anisyl-2,2-diphenylvinyl bromide (1) in acetonitrile and in acetic acid media have revealed a rather straightforward mechanistic picture for the reaction in acetonitrile and a complicated picture for the reaction in acetic acid.

In acetonitrile the laser flash photolysis studies show the intermediacy of vinyl cations. The optically detected species and the transient photoconductivity are formed instantaneously and decay according to first-order kinetics with identical lifetimes. The precursor of the vinyl cation might

be an excited state of **1** with a very short lifetime. The decay of the vinyl cation may be caused by reaction with solvent molecules or with ground state **1**.

Rather stable ions are formed at the same time as the vinyl cations. These ions may be protons produced by a reaction of the vinyl cations with water molecules.

The quenching data show that in acetonitrile there is little if any selectivity with respect to bromide *versus* acetate ions in accordance with the results of the steady state photochemical experiments. The quenching by Et₄NBr and Et₄NOAc is diffusion controlled.

In pure acetic acid no free ions are formed upon laser flash excitation. The presence of polar additives is necessary for vinyl cations to appear. The minimum concentration of additive necessary to produce a detectable quantity of vinyl cations depends on the nature of the additive. A relatively high concentration of additive, as in the case of water, is probably associated with a medium effect and relatively low concentrations of additives, as in the case of pyridine and sodium acetate, are probably associated with a complexation of the additive and ground state **1** prior to the photochemical reaction. In the latter cases formation of the vinyl cation occurs via excitation of a complex of **1** and additive.

The vinyl cation is formed in parallel with a short-lived species, the identity of which is not clear, though it is tentatively considered to be a radical pair or a tight ion pair. The formation of the short-lived species occurs via excitation of unassociated **1**.

As an accurate value for the rate constant of quenching by sodium acetate could not be obtained, exact determination of the selectivity of the vinyl cation with respect to bromide *versus* acetate ions is not possible. The experimental data suggest a selectivity constant $\alpha \gg 1$, in qualitative accord with the results of the steady-state irradiations.

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