LASER SPECTROSCOPIC STUDY OF THE NUCLEOPHILIC PHOTOSUBSTITUTION OF 4-CHLOROANISOLE AND 4-FLUOROANISOLE IN AQUEOUS SOLUTIONS

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Summary

The nucleophilic photosubstitution reactions, photocyanation and photohydrolysis, of 4-chloroanisole (ACl) and 4-fluoroanisole (AF) have been studied by time resolved spectroscopy and by measurements of transient photoconductivity in anhydrous and aqueous acetonitrile and *tert*-butyl alcohol solutions. The mechanism involves in its initial step the formation of a triplet state transient complex composed of an excited and a ground state aromatic molecule. This complex dissociates into radical ions only in the presence of water and this step determines the quantum yield of the product. The formation of a solvated electron is ruled out as a step in the substitution mechanism.

Attack of the nucleophile on the radical cation yields a neutral radical from which the reaction product is formed in a single step. The transient species which have been observed spectroscopically are $^3ACl^*$, $^3AF^*$, $[ACl^{\delta-}\cdots^{\delta+}ACl]$, ACl^{+}, AF^{+}, $AClOH^{\cdot}$, $AClCN^{\cdot}$, $AFOH^{\cdot}$ and $AFCN^{\cdot}$.
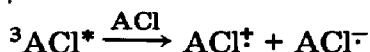
1. Introduction

The mechanism of the nucleophilic photosubstitution of aryl halides has been studied intensively since it was first reported [1] and is still a topic of discussion. Several proposals, which can be classified according to their mechanistic criteria [2] as $S_N2(Ar^*)$-, $S_{R^+N}1(Ar^*)$- and $S_{R-N}1(Ar^*)$-type reactions, have been put forward.

In the $S_N2(Ar^*)$-type reaction a Meisenheimer complex is formed [1] in the interaction between the excited substrate and nucleophile which is then followed by the departure of a substituent from the complex. In the

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$S_{R^+N}1(Ar^*)$-type reaction, which is adopted mainly for the nucleophilic substitutions of excited aromatic molecules activated by electron-donating groups, the first chemical step is the ionization of the excited aromatic compound [3] followed by the attack of a nucleophile on the resulting radical cation. In the $S_{R-N}1(Ar^*)$ reaction the excited aryl compound abstracts an electron from an electron donor to give a radical anion [4], which yields the reaction product after ejection of a negative ion.

Recently Siegman and Houser [5] proposed an $S_{R-N}1(Ar^*)$ reaction for the methoxylation of 4-chloroanisole (ACl) in methanol, which has the formation of a radical anion of the substrate and a radical cation of the solvent molecule as the first chemical step, which is followed by the combination of these radicals and then the formation of the final product 1,4-dimethoxybenzene. A variation of the $S_{R^+N}1(Ar^*)$-type reaction has been suggested by Soumillion and De Wolf [6], in which the formation of radical cations of chlorobenzene and chloroanisole proceeds via an electron transfer to a ground state molecule in methanol solution:

$$ACl \longrightarrow {}^1ACl^* \longrightarrow {}^3ACl^*$$

$$^3ACl^* \xrightarrow{ACl} ACl^{\ddagger} + ACl^{\bar{}}$$

$$ACl^{\ddagger} \xrightarrow{N^-} \text{substitution product}$$

$$ACl^{\bar{}} \longrightarrow \text{reduction product}$$

Similar reaction mechanisms have also been proposed by Bunce *et al.* [7] and Lemmetyinen and coworkers [8, 9] for the formation of radical cations of unsubstituted aromatic hydrocarbons in aqueous and non-aqueous acetonitrile solutions.

Steady-state studies of the mechanism of the photosubstitution of aryl halides have been reported from our laboratory previously [3, 10]. In these reports it is suggested that an absorption of a single photon causes an electron to be ejected from the excited triplet state of the aromatic molecule, resulting in a radical cation and a solvated electron. The overall mechanism proposed for the photocyanation (and photohydrolysis) of halogenated anisoles can be presented as follows:

$$AX \xrightarrow{h\nu} {}^1AX^* \xrightarrow{k_1} {}^3AX^* \tag{1}$$

$$^3AX \xrightarrow{k_i} AX^{\ddagger} + e_{aq} \tag{2}$$

$$AX^{\ddagger} + e_{aq} \xrightarrow{k_2} AX \tag{3}$$

$$AX^{\ddagger} + N^- \xrightarrow{k_N} AXN^{\cdot} \tag{4}$$

$$AXN^{\cdot} \xrightarrow{k_3} AN^{\ddagger} + X^- \tag{5}$$

$$AN^{+} + e_{aq} \xrightarrow{k_4} AN \tag{6}$$

This mechanism is based on the electron-donating nature of the methoxy group, the observed formation of radical cations and solvated electrons, the long lifetime of the triplet state which could favour the ionization, semiempirical quantum chemical calculations of the charge distribution in the radical cation and the similarity of the yields of different products in the photochemical and the electrochemical substitution [3]. Recently, all these arguments, particularly the monophotonic formation of the radical cation, have been criticized and the $S_N2(Ar^*)$-type reaction has been offered as an alternative [11].

A kinetic spectroscopic study of the mechanism of the $S_{R^+N}1(Ar^*)$-type photosubstitution reaction has so far not been reported. We have performed kinetic spectroscopic and transient electrical conductivity measurements to arrive at a mechanism of the nucleophilic hydrolysis and cyanation of 4-chloroanisole and 4-fluoroanisole (AF) and to identify the transient species appearing during the reaction in non-aqueous and aqueous solutions.

2. Experimental details

The quantum yields of photohydrolysis in water–acetonitrile solutions were measured using the method of Calvert and Pitts [12] with a potassium ferrioxalate actinometer. As a light source we used a 1000 W Hg–Xe lamp from Oriel Spectroirradiation Set, model 8600. The excitation wavelength was 275 ± 6 nm. The yield of the product, 4-hydroxyanisole, was determined as its phenolate ion which was formed on the addition of two drops of concentrated KOH solution to the reaction cuvette after irradiation, and its absorbance was measured at 305 nm. The time of irradiation was selected to yield about 2% product from the starting material. The presence of air had less than 2% effect on the values of the quantum yields. For this reason the quantum yield measurements were performed in non-degassed solutions.

The transient optical absorption experiments were performed [13] using primary excitation at 248 nm (Lambda Physik Excimer laser, model EMG 100: pulse energy, 15 mJ; pulsewidth, 10 ns). The analysing light from a pulsed xenon lamp (Osram XBO-450) passed through a monochromator, the sample (optical path of 2.0 cm, perpendicular to the laser beam) and a second monochromator prior to detection by an RCA 4840 photomultiplier. The analysing light pulse had a constant peak intensity over a period of 100 μs during which the primary excitation was deposited in the sample. The transient photomultiplier signals were fed into a Tektronix R 7912 transient digitizer and stored in a PDP 11/10 computer. The transient optical densities were calculated using the peak intensities of the analysing light and were normalized with respect to the total primary excitation energy. In order to monitor the variation in the pulse energy from shot to shot a beam splitter in front of the sample cell was adjusted to reflect a certain amount

(less than 10%) of the photolysing laser pulse onto a vacuum photodiode. The variation in the pulse energy is taken into account in calculating the final transient absorbances. The intensities of the excitation pulses were varied using neutral grey filters or filter solutions and the relative flash intensities were measured using the beam splitter between the filter and the sample.

Photoinduced transient electrical conductivity of the solutions was studied [14] by exciting the sample with an attenuated light pulse of wavelength 248 nm, using the Lambda Physik Excimer laser, model EMG 100. The conductivity cell consists of two quartz plates 30 mm apart with two mutually parallel glassy carbon electrodes placed 5 mm apart. The excitation beam was shaped by a convex cylindrical quartz lens to obtain a constant cross section of 10 mm × 1 mm throughout the cell. The absorbance of the sample at 248 nm over the 30 mm path length was about 0.9 in all cases. The technique for observing the transient signals was essentially the same as that used for the transient optical absorption observations.

Fluorescence decay was studied using a single-pulse excitation from a mode-locked Nd^{3+}–YAG laser (λ = 265 nm) and real-time detection by a photodiode and 500 MHz transient digitizer Tektronix R 7912. The lifetime was obtained after a proper simulation of the decaying signal taking into account single exponential decay, the temporal profile of the excitation pulse, and the response of the detection system. Absorbances of the samples were 0.9 at 265 nm.

Perfluorohexane (Ventron GMBH) was distilled before use. Acetonitrile (Janssen Chimica, spectrophotometric grade, Gold Label) and *tert*-butyl alcohol (J. T. Baker Chemicals B.V., "Baker Analyzed" Reagent) were used without further purification. In all experiments distilled ion-free water of pH 7.0 was used. The anisole derivatives (Fluka AG, purissimum) were distilled or recrystallized. Dicyanoethylene (DCE) (Janssen Chimica) was recrystallized several times before use.

The samples for the transient absorption measurements were prepared in a 6.0 cm^3 quartz cuvette, with optical paths of 2.0 cm (the analysing light) and 1.0 cm (the excitation light) from known stock solutions to obtain the ground state absorbance of 0.9 at 248 nm. This absorbance was used in all experiments except for those where the dependence on concentration was studied. Air was removed from the sample cuvettes by refluxing samples for several minutes in a flow of nitrogen gas. The transient conductivity measurements were performed in the presence of air. In all flash photolysis experiments samples were changed after every two shots to avoid the effect of product formation on the experimental results.

3. Results and discussion

3.1. Quantum yields of photohydrolysis in aqueous acetonitrile

In the photosubstitution reaction of anisole derivatives in aqueous solutions, reactions of the aromatic compounds with the nucleophile and

with the water molecule are competing processes. In solution in a *tert*-butyl alcohol–water mixture and in the absence of added nucleophile only products of the photohydrolysis are formed [10].

In various water–acetonitrile mixtures the quantum yield of photohydrolysis increases with increasing amounts of water for both 4-chloroanisole (Fig. 1) and 4-fluoroanisole (Fig. 2). The dependence of the quantum efficiency ϕ of nucleophilic photohydrolysis of anisole derivatives on the water concentration in acetonitrile is very similar to that of nucleophilic photocyanation on the water concentration in *tert*-butyl alcohol [3, 10]. The reactivities of 4-chloroanisole and 4-fluoroanisole differ from each other. A value of $\phi = 0.1$ is reached in the reaction of chloroanisole in 20 vol.% (40 mol.%) water in acetonitrile, while fluoroanisole displays the same reactivity only at 55 vol.% water in acetonitrile (80 mol.%). We have not observed photohydrolysis of anisole in water–acetonitrile solutions in either the absence or in the presence of oxygen.
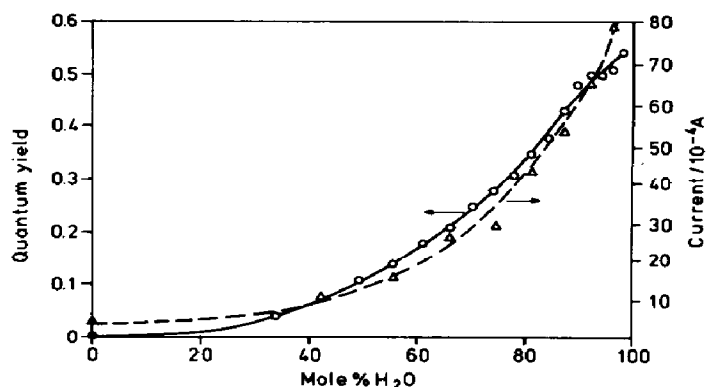
Fig. 1. Dependence of the quantum yield of photohydrolysis and the transient conductivity ($I = \kappa U$) of ACl on water concentration in acetonitrile.
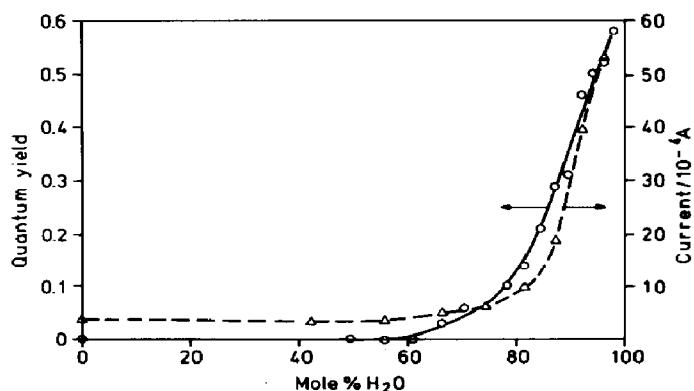

Fig. 2. Dependence of the quantum yield of photohydrolysis and the transient conductivity ($I = \kappa U$) of AF on water concentration in acetonitrile.

3.2. Photoinduced transient electrical conductivity

The electrical conductivity induced by laser pulse excitation of the solutions in acetonitrile–water increases with the water concentration. The maxima in the conductivities are reached rapidly with measured rate constants of 1.2×10^7 s^{-1} and 2.2×10^7 s^{-1} for the formation of ionic species of 4-chloroanisole and 4-fluoroanisole at concentrations of 2.9×10^{-3} mol dm^{-3} and 2.2×10^{-3} mol dm^{-3} respectively. The rates of formation are almost independent of the amount of water in the solution. The short average fluorescence lifetimes of 0.5 ns and 3.1 ns for chloroanisole and fluoroanisole, respectively (Table 1), in water–acetonitrile solutions indicate that the fluorescent state does not yield ionic species directly.

TABLE 1

Dependence of fluorescence lifetimes of anisole (A), 4-fluoroanisole (AF) and 4-chloroanisole (ACl) on water concentration in acetonitrile

[H$_2$O] (mol.%)	τ(A) (ns)	τ(AF) (ns)	τ(ACl) (ns)
0	6.8	3.5	0.5
66.1	7.4	3.3	0.6
92.1	6.0	2.9	0.4
98.1	5.2	2.8	0.4

The transient conductivity decays in two stages. In the first stage there is a sharp drop in the conductivity in less than 1 μs and in the second stage the decay is much slower. At high concentrations of water there is almost no decay in the second stage and a constant conductivity is obtained. This indicates that, simultaneously with the decay of the primary ionic species, new ionic species are formed which are long lived transients and/or final products of the reaction. The decay of the transient conductivity follows second-order kinetics for anisole at all water concentrations, but only at low water concentrations for chloroanisole and fluoroanisole.

The photoinduced current measured in the solution immediately after excitation is shown as a function of water concentration in the solvent for the reactions of 4-chloroanisole and 4-fluoroanisole in Fig. 1 and Fig. 2, respectively. The photoinduced conductivities of the solutions of anisole, 4-bromoanisole and 4-iodoanisole are low at all water concentrations.

The change in current density Δj is the sum of two terms related to the positive and the negative species

$$\Delta j = F(\Delta c_+ \mu_+ + \Delta c_- \mu_-)$$

where F is the Faraday constant, the Δc are ion concentrations and the μ are their mobilities. We may assume that initially only one type of cation and one type of anion are formed in the excitation. Then Δj is directly proportional to the concentration of either type of ion since $\Delta c_+ = \Delta c_-$. Because

the mobilities of aromatic ions are approximately equal in magnitude, a low conductivity is thus due to a low ion concentration. The conductivity–water concentration and quantum yield–water concentration curves for chloroanisole (Fig. 1) and for fluoroanisole (Fig. 2) are almost identical. The slopes of the curves for fluoroanisole differ from those for chloroanisole. This strongly suggests that the ionization process is the quantum yield determining step in the nucleophilic photosubstitution of the anisole derivatives. Because the quantum yield–concentration curves are similar for photohydrolysis and photocyanation [3, 10], we may conclude that the ionization process is not brought about by the nucleophile, but by the amount of water in the solvent, which changes the dielectric constant of the solvent mixture.

3.3. Photoinduced transient optical absorptions

3.3.1. Solvated electron

In *tert*-butyl alcohol–water solutions of chloroanisole and fluoroanisole a broad absorption is observed between 500 and 800 nm. The absorption has a maximum at 700 nm and its decay follows first-order kinetics. Irradiation of ferrocyanide ($K_4Fe(CN)_6$) in the same solvent leads to an identical absorption which has been shown to be due to the solvated electron [15]. In water–acetonitrile a transient absorption is not observed in the range 500 - 800 nm for either ferrocyanide or the chloroanisole or fluoroanisole. This is due to scavenging of electrons by acetonitrile molecules [16]. We have measured a value of 4.0×10^7 M^{-1} s^{-1} for the rate constant of the reaction of acetonitrile with a solvated electron, formed after excitation of 4-fluoroanisole in 40vol.%water–*tert*-butyl alcohol.

The absorption due to solvated electrons formed from ferrocyanide ion is a linear function of the integrated laser pulse energy I_{ex}. The lifetime of the solvated electron decreases with increasing water concentration (Table 2). The absorbance of the solvated electrons formed in the excitation of fluoroanisole is almost independent of the water concentration in *tert*-butyl alcohol (Table 2). In this case the quantum yields of the formation of the solvated electron ϕ_e may be estimated by using a quantum yield of 1.0 for

TABLE 2

Absorbances OD and lifetimes τ of solvated electrons in excitation of ferrocyanide (Fe(II)) and 4-fluoroanisole (AF) in water–*tert*-butyl alcohol solutions and the estimated quantum yields ϕ_e for the formation of solvated electron from 4-fluoroanisole compared with the quantum yields ϕ_{OH} of the hydrolysis reaction of 4-fluoroanisole

[H_2O] (mol.%)	OD(Fe(II))	τ(Fe(II)) (μs)	OD(AF)	τ(AF) (μs)	ϕ_e	ϕ_{OH}
66.1	0.315	8.5	0.081	1.1	0.25	0.05
81.4	0.364	5.4	0.085	0.9	0.27	0.15
92.1	0.402	5.9	0.075	0.4	0.20	0.50
100	0.412	3.1				

the formation of solvated electrons from ferrocyanide [17]. The quantum yields of the solvated electron in the case of fluoroanisole are independent of water concentration and differ from the quantum yields of the photoproduct ϕ_{OH} in the hydrolysis reaction (Table 2). The same phenomenon is also observed in the case of 4-chloroanisole.

The absorption of the solvated electron is a linear function of I_{ex}^2 for fluoroanisole (Fig. 3) and chloroanisole. Addition of a nucleophile (OH⁻ or CN⁻) to the reaction mixture increases slightly (less than 10%) the lifetime and the absorbance of the solvated electrons and the proportionality to I_{ex}^2 is retained. It seems obvious that the solvated electron reacts with a species, which itself can react with the nucleophile.

The formation of the solvated electron plays an important role in the mechanism presented earlier [3, 10], in which the first chemical step in the nucleophilic photosubstitution is the monophotonic ionization (reaction (2)) of the aromatic compound. However, according to our latest experimental evidence the absorbance of the solvated electron is a linear function of the square of flash intensity (I_{ex}^2) (the photohydrolysis and photocyanation reactions are one-photon processes), is independent of the concentration of water in the solvent, and the quantum yields of the formation of the solvated electron do not correlate with those of the substitution reactions. The solvated electrons have very short lifetimes (less than 1 μs) in water–tert-butyl alcohol solutions compared with the lifetimes of the transient species participating in the nucleophilic substitution reaction (see later). This rules out the possibility that the solvated electron plays any role in the later stages of the substitution mechanism (reaction (6)).

A possible explanation for the formation of the solvated electron is a sequential two-photon process involving either an excited singlet or triplet state as an intermediate state:

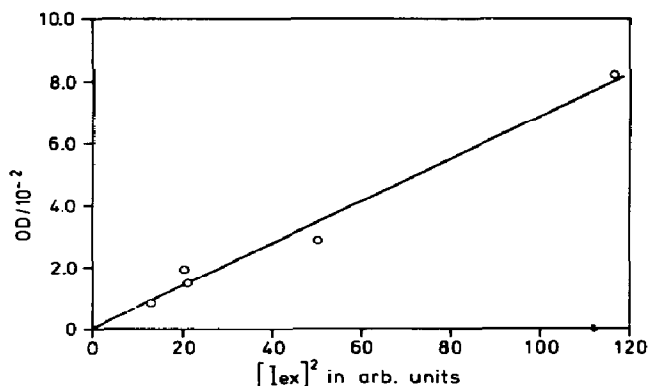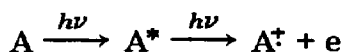$$A \xrightarrow{h\nu} A^* \xrightarrow{h\nu} A^{\dagger} + e$$

Fig. 3. Absorbance of the solvated electron formed in the excitation of 4-fluoroanisole as a function of the square of flash intensity at 650 nm in 80vol.%water–tert-butyl alcohol.

The measured fluorescence lifetimes of the anisole compounds (Table 1) indicate that the first excited singlet state may be the intermediate state. Fluoroanisole has a fluorescence lifetime which is six to seven times longer than that of chloroanisole. The absorbance of solvated electrons formed from fluoroanisole is three times higher than that of chloroanisole. The short fluorescence lifetimes of bromoanisole and iodoanisole may be reponsible for the absence of solvated electrons in their solutions in water–*tert*-butyl alcohol.

3.3.2. Transient absorption spectra of 4-chloroanisole

In the non-polar solvent perfluorohexane an absorption between 300 and 370 nm is observed (T in Fig. 4). In the deoxygenated solution its lifetime is 0.9 μs, but saturation of the solution with air causes a decrease in the lifetime to 0.1 μs. The observed transient decays by first-order kinetics. Somewhat to the red of 370 nm a species with a lifetime of about 7 - 8 μs is observed. In the polar solvents acetonitrile and *tert*-butyl alcohol the absorption at 330 nm is absent, but another absorption between 400 and 500 nm (A in Fig. 4) with a lifetime of 7.0 μs is seen. The presence of oxygen has no effect on its lifetime, but decreases its intensity.
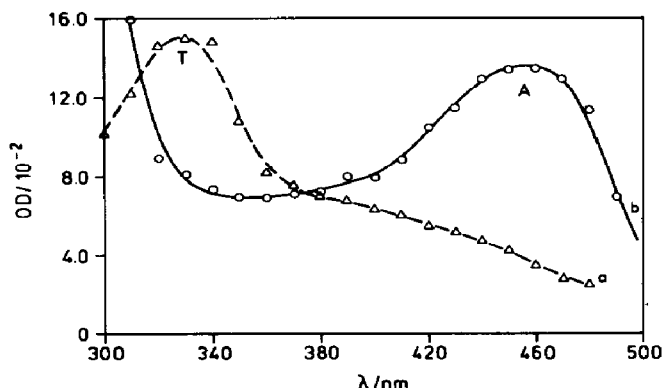
Fig. 4. Transient absorption spectra of 4-chloroanisole observed in anhydrous perfluorohexane (a) and acetonitrile (b).

The properties of the transient species T in perfluorohexane indicate that it could be 4-chloroanisole in its lowest triplet state T_0. The transient species A in acetonitrile could be a transient species formed from T_0, but is not the ionic species participating in the substitution reaction, since the transient conductivity in anhydrous acetonitrile is very low (Fig. 1).

In the presence of water the behaviour of the absorption in the region 430 - 500 nm (A in Fig. 5) changes. The intensity of the absorption is independent of the amount of water in the solvent (acetonitrile or *tert*-butyl alcohol), but water shortens its lifetime while the transient is transformed into another species (B in Fig. 5). This species is quenched by water. The rate constant for the decay of B can be written as

$$k(H_2O) = k_0 + k_{H_2O}[H_2O]$$

This linear dependence of $k(H_2O)$ on $[H_2O]$ is illustrated in Fig. 6. The values $k_0 = 1.44 \times 10^5\,s^{-1}$ and $k_{H_2O} = 5.8 \times 10^3\,M^{-1}\,s^{-1}$ can be calculated.

Increasing the amount of water in the solvent increases the values of both the quantum yields for the hydrolysis and the transient conductivities of the reaction system. The reactive species B is formed under the influence of water and is quenched by the nucleophile H_2O. B may therefore be identified as a transient ionic species formed from the species A in the ionization process.

In trying to identify transient species B we have measured the spectrum appearing when chloroanisole is excited in the presence of the good electron acceptor DCE. This spectrum is shown in Fig. 7 and is almost identical with that appearing in the absence of DCE (B in Fig. 5). In both cases the absorption can be quenched by nucleophiles (OH^- or CN^-). Transient B may thus be identified as the radical cation of 4-chloroanisole, ACl^{+}.
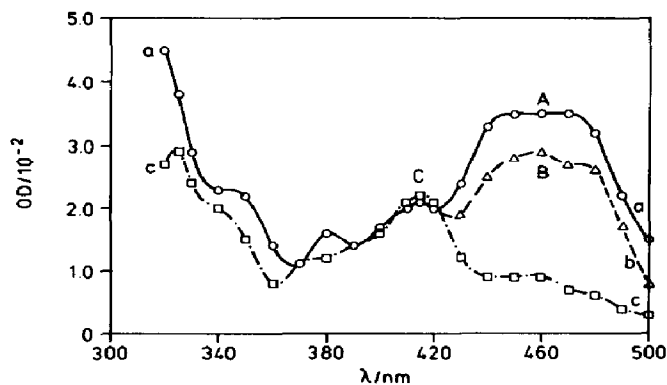
Fig. 5. Transient absorption spectra of 4-fluoroanisole observed 0.1 (a), 2.0 (b) and 18 μs (c) after laser excitation in 70vol.%water–*tert*-butyl alcohol.
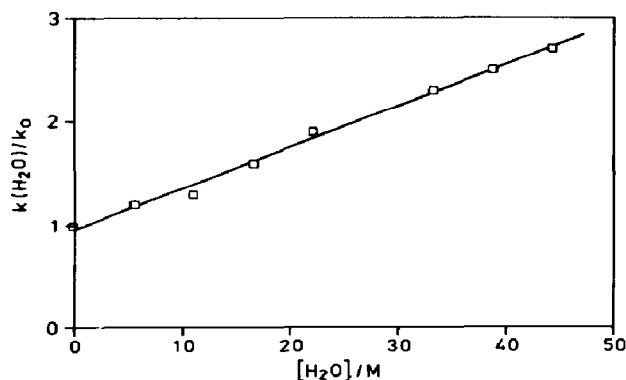
Fig. 6. Stern–Volmer plot for the quenching of transient species B (ACl^{+}) of 4-chloroanisole by water at 450 nm in acetonitrile.
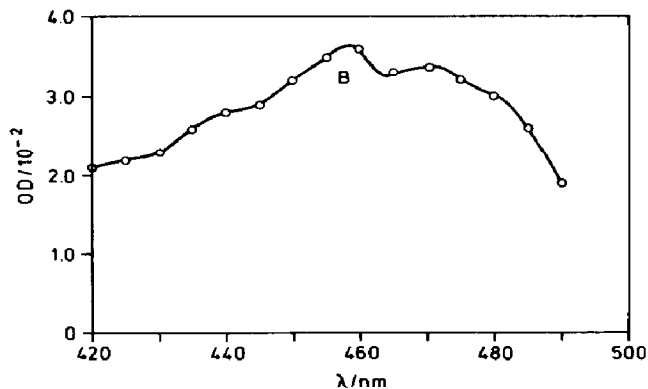
Fig. 7. Absorption spectrum of radical cation of 4-chloroanisole formed in the presence of dicyanoethylene (1.9×10^{-3} M) in 50vol.%water−*tert*-butyl alcohol.
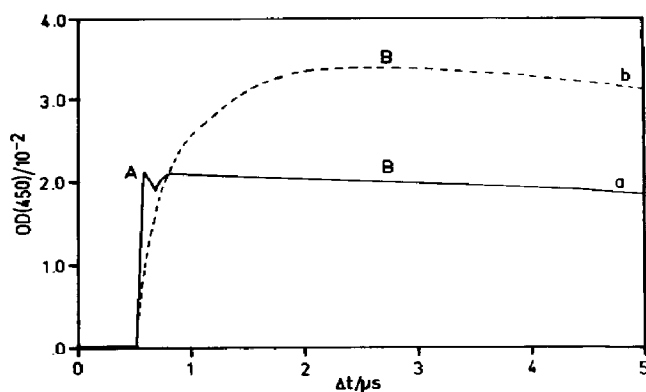

Fig. 8. Formation of transient species A and B of 4-chloroanisole in the absence (a) and presence (b) of dicyanoethylene (0.75×10^{-3} M) at 450 nm in 50vol.%water−*tert*-butyl alcohol.

In the presence of DCE the kinetics of the formation of ACl^+ differs from that observed in its absence (Fig. 8). In the latter case the maximum of the absorbance of transient A is reached rapidly. Its decay and the simultaneous formation of the absorption of ACl^+ can be seen. In the presence of DCE a higher absorbance of ACl^+ is observed and the plateau is reached within 2 - 3 μs. The slow formation indicates that, in the presence of DCE, the radical cation ACl^+ is not formed from the singlet or triplet state of chloroanisole, because their decay rates are fast relative to the formation rate of ACl^+. The ion ACl^+ is formed from A in both the presence and the absence of DCE. This conclusion is also supported by the observation that addition of a small amount of DCE reduces the height of the absorption of A immediately after termination of the laser pulse. At a DCE concentration of 0.75×10^{-3} M (Fig. 8) transient species A transforms to the radical cation ACl^+ probably simultaneously through direct transformation and through involvement of DCE. The lifetime of the radical cation of chloroanisole in

the presence of DCE, 30 μs in 50vol.%water–*tert*-butyl alcohol, is considerably longer than in the absence of DCE (4 μs). This is probably due to the slow back electron transfer from $DCE^{\cdot}$ to $ACl^{\cdot}$.

Figure 5 presents the transient absorption spectra of chloroanisole immediately (t = 0.1 μs), 2 μs and 18 μs after the laser pulse excitation in water–*tert*-butyl alcohol. In the course of time a new transient C at 415 nm is formed; the intensity of its absorption increases with the water concentration. The measured rate constants k_c for the formation of C are presented as a function of water concentration in Table 3. The second-order rate constant k_{H_2O} for the formation of C may be calculated as $k_{H_2O} = k_c/[H_2O]$. The values obtained for k_{H_2O} in this manner (Table 3) are close to that determined from the quenching of $ACl^{\cdot}$ by water (5.8×10^3 M^{-1} s^{-1}) (Fig. 6). It is evident that transient C is formed in a reaction of $ACl^{\cdot}$ with water. To identify C we measured the transient spectrum of 4-chloroanisole in the presence of 0.02 M OH^- in 70vol.%water–*tert*-butyl alcohol. Within 1 μs a transient absorption at 415 nm is formed and the transient absorption at 450 nm (arising from B) has decayed. The transient species formed is obviously due to the same transient species C formed in the absence of OH^-. On this basis C can be identified as the neutral $AClOH^{\cdot}$ radical.

TABLE 3

First-order k_c and second-order k_{H_2O} rate constants for formation of the $AClOH^{\cdot}$ radical at different water concentrations in acetonitrile

[H2O] (M)	k_c ($\times 10^5$ s^{-1})	$k_{H_2O} = k_c/[H_2O]$ ($\times 10^3$ M^{-1} s^{-1})
28	1.43	5.1
39	1.67	4.3
44	2.00	4.5

Identical absorptions are observed at t = 0.1 μs in the presence (Fig. 9, $[CN^-]$ = 2.4×10^{-3} M) and in the absence (Fig. 5) of cyanide anion. Thus the cyanide anion does not affect the formation of transient A. The nucleophile reacts fast with the radical cation resulting in a new transient species (D in Fig. 9) which absorbs at 390 nm. This absorption is obviously due to a neutral $AClCN^{\cdot}$ radical. The $AClOH^{\cdot}$ radical is not observed in the presence of a cyanide anion concentration of 2.4×10^{-3} M.

The quenching of $ACl^{\cdot}$ by the cyanide anion is studied in 40vol.%- and 80vol.%water–acetonitrile solutions. The decay of the radical cation follows the relation

$$k(CN) = k_0 + k_N[CN^-]$$

from which the following values for the rate constants are obtained: k_0 = 2.7×10^5 s^{-1} and k_N = 1.35×10^9 M^{-1} s^{-1} in 40vol.%water–acetonitrile and
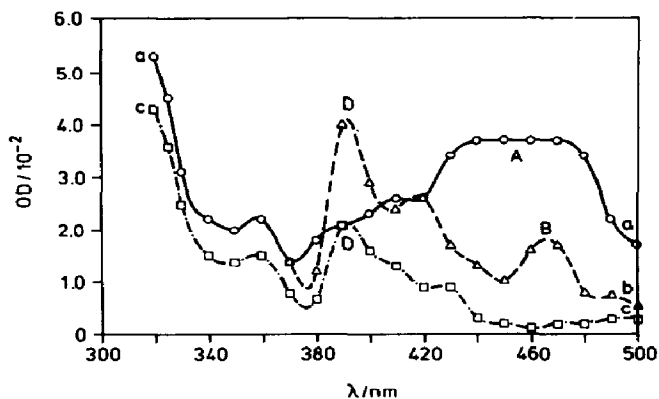
Fig. 9. Transient absorption spectra of 4-chloroanisole in the presence of cyanide anion $(2.4 \times 10^{-3}$ M) observed 0.1 (a), 2.0 (b) and 18 μs (c) after laser excitation in 70vol.%-water–*tert*-butyl alcohol.
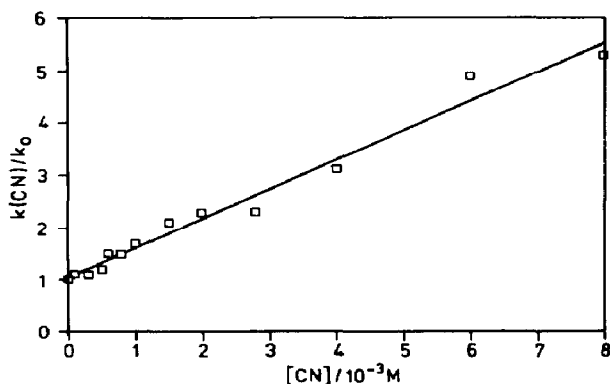

Fig. 10. Stern–Volmer plot for quenching of the radical cation of 4-chloroanisole by the cyanide anion at 450 nm in 80vol.%water–acetonitrile.

$k_0 = 3.8 \times 10^5$ s^{-1} and $k_N = 2.13 \times 10^8$ M^{-1} s^{-1} in 80vol.%water–acetonitrile (Fig. 10).

The relation between the quantum yield of photocyanation and cyanide anion concentration has been studied by den Heijer [10] and the following expression has been given:

$$\frac{1}{\phi} = 1.89 + 0.012 \, \frac{1}{[CN^-]}$$

which applies to the case of a 1:3 *tert*-butyl alcohol:water mixture (75-vol.%water–*tert*-butyl alcohol) as solvent. From the simple reaction scheme (reactions (1) - (4), independent of the mechanism of reaction (2)) the ratio

$$\frac{k_N}{k_2} = \frac{1.89}{0.012} = 157.5$$

is obtained from the above relation. Using the lifetime of the radical cation from our work, $\tau = 1/k_2 = 2.6 \times 10^{-6}$ s (in 75vol.%water–acetonitrile), a value $k_N = 6.1 \times 10^7$ M^{-1} s^{-1} close to that measured directly by us, is obtained. A value $k_N/k_{H_2O} = 6300$ has been reported for a *tert*-butyl alcohol–water (1:3) mixture as the solvent [10]. This corresponds to a value of $k_{H_2O} = 9.6 \times 10^3$ M^{-1} s^{-1} when we use the value of k_N obtained from den Heijer's relation. This value for k_{H_2O} is about twice as high as that (5.8 × 10^3 M^{-1} s^{-1}) obtained in our work by direct measurements of quenching of ACl$^+$ by water in acetonitrile.

The absorbance at 450 nm is a linear function of the flash intensity I_{ex}. The increase in the ground state concentration of 4-chloroanisole leads to an increase of the absorbance at 450 nm which is non-linear in the amount of light absorbed. The lifetime of radical cation decreases with increasing ground state concentration in water–*tert*-butyl alcohol or water–acetonitrile solutions. The influence of the ground state molecule on the decay of ACl$^+$ may be explained by a known reaction of radical cations [18]:

$$A^+ + A \longrightarrow [A]_2^+$$

Consider the case that a single ground state molecule is involved in the formation of a radical cation:

$$ACl \xrightarrow{I_a\phi} ACl^* \xrightarrow{k_i} ACl^+ + e$$
$$\downarrow{k_1}$$
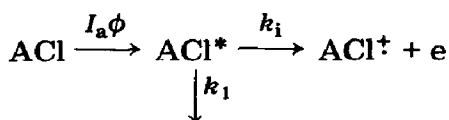
Then the following relation holds:

$$OD(450) = \alpha(1 - 10^{-D})$$

where I_a is the amount of light absorbed, OD(450) is the absorbance of the radical cation, D is the absorbance of the ground state compound and α is a constant which depends on I_a and ϕ. OD(450) should thus be a linear function of $1 - 10^{-D}$, but as may be seen from Fig. 11 this is not the case.
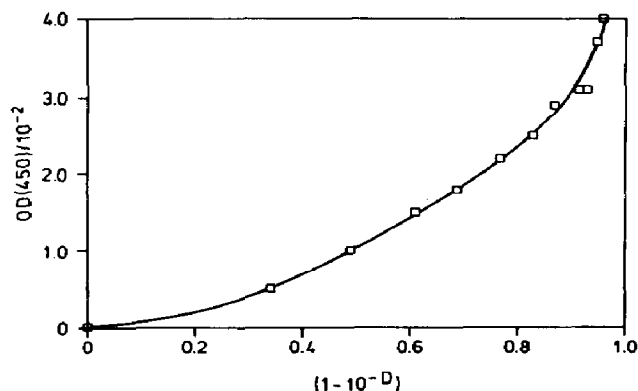

Fig. 11. Dependence of the absorbance of radical cation of 4-chloroanisole on the amount of absorbed light at 450 nm in 50vol.%water–acetonitrile.

Because the ground state concentration has an effect on the formation of $ACl^{\ddagger}$, we propose the following scheme:

$$ACl \xrightarrow{\ I_a\phi\ } ACl^* \xrightarrow{\ k_i[ACl]\ } ACl^{\ddagger} \qquad\qquad (7)$$
$$\downarrow k_1$$

The relation between the ground state concentration and the transient absorbance can now be written as

$$\frac{(1 - 10^{-D})}{OD(450)} = \frac{1}{\beta}\left(k_i + \frac{k_1}{[ACl]}\right)$$

where β is a constant which depends on I_a and ϕ. Using the same experimental values as in Fig. 11 a straight line (Fig. 12) is obtained when $(1 - 10^{-D})/OD(450)$ is plotted as a function of $1/[ACl]$.

It is obvious, that the radical cation of 4-chloroanisole is formed in a bimolecular reaction of the excited triplet state with the ground state molecule. The singlet state is too short lived (fluorescence lifetimes, 0.4 - 0.6 ns (Table 1) depending on water concentration) to react with the ground state molecule at the concentrations used in our experiments.

From the ratio of the intercept and the slope of the straight line in Fig. 12 a value of $k_i/k_1 = 250$ mol^{-1} dm^3 in 50vol.%water–acetonitrile solution is calculated. In the case of 80vol.%water–acetonitrile a value of 170 mol^{-1} dm^3 is obtained.

The bimolecular rate constant k_i for the formation of ionic species can be calculated from the first-order rate constant of 1.2×10^7 s^{-1} at a chloroanisole concentration of 2.9×10^{-3} mol dm^{-3} derived earlier from the transient photoconductivity measurements. Thus

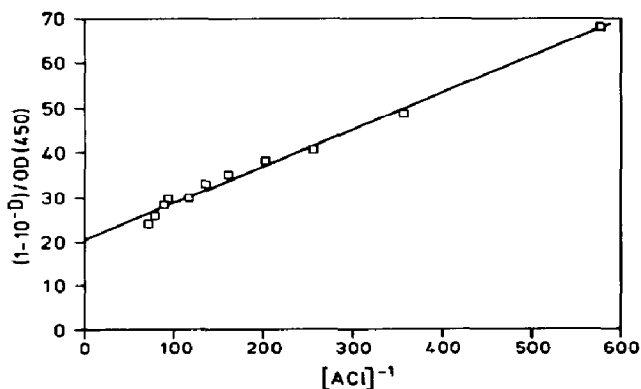$$k_i = \frac{1.2 \times 10^7}{2.9 \times 10^{-3}}\ M^{-1}\,s^{-1} = 4.1 \times 10^9\ M^{-1}\,s^{-1}$$

Fig. 12. Dependence of $(1 - 10^{-D})/OD$ on the inverse of the ground state concentration of 4-chloroanisole at 450 nm in 50vol.%water–acetonitrile.

This result allows the calculation of k_1. The values of k_1 are $1.6 \times 10^7 \text{ s}^{-1}$ in 50vol.%water–acetonitrile and $2.4 \times 10^7 \text{ s}^{-1}$ in 80vol.%water–acetonitrile solutions, respectively. The triplet state lifetimes τ may now be calculated from $k_1 = 1/\tau$. We find that τ is reduced from the value of 0.9 μs, measured in perfluorohexane, to 0.061 μs in 50vol.%water–acetonitrile and 0.042 μs in 80vol.%water–acetonitrile solution.

The dependence of the quantum yield of photocyanation of chloroanisole on the ground state concentration has also been observed in the earlier studies [3, 10]. This is in accordance with the mechanism which we propose (reactions (7)). The measured value of 1.21 for the quantum yield at high concentration ($D = 1.9$ at the excitation wavelength), which could be attributed to a chain reaction following the reaction (5), is, however, not in accordance with our transient spectroscopic experiments, which do not support reaction step (5) (see later).

In anhydrous *tert*-butyl alcohol (and acetonitrile) a broad absorption band is observed at 450 nm arising from species A (Fig. 4). This species, not observed in non-polar solvents, transforms to a radical cation B in the presence of water. The presence of nucleophiles has no effect on the absorption maximum at 450 nm (Fig. 9) and the absorption does not disappear even at very high concentration of the cyanide anion, although the lifetime of the radical cation is shortened. On this basis we propose that transient species A, which is a precursor of $\text{ACl}^{\ddagger}$, is an ion pair formed from two chloroanisole molecules, one in its triplet state T_0 and the other in its ground state. The ion pair dissociates to the radical cation and anion of 4-chloroanisole in the presence of water in the solution. In the presence of water the radical anion has not been observed.

3.3.3. Transient absorption spectra of 4-fluoroanisole

In perfluorohexane an absorption is observed with a maximum at 390 nm and a lifetime of 0.5 μs. In anhydrous acetonitrile the absorption is between 320 and 460 nm with maximum at 400 nm (Fig. 13). In a de-
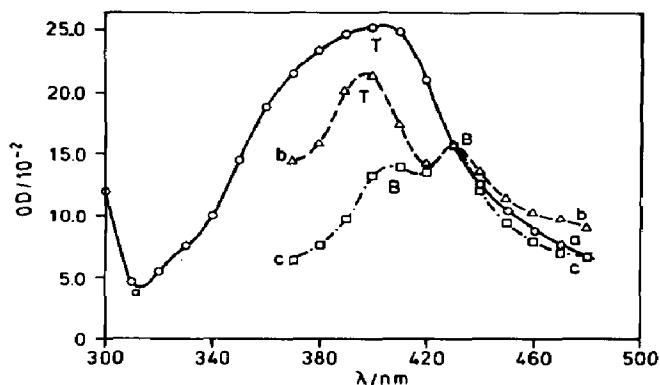

Fig. 13. Transient absorption spectra of 4-fluoroanisole observed 0.1 μs after laser excitation in anhydrous acetonitrile (a), 40vol.%water–acetonitrile (b) and 80vol.%water–acetonitrile (c).

TABLE 4

Dependence of transient absorbance of radical cation of 4-fluoroanisole on water concentration in acetonitrile at 430 nm

[H_2O] (mol.%)	OD($\Delta t = 1.0$ μs)
0	0.030
81.4	0.040
87.2	0.054
92.1	0.090
96.3	0.105

oxygenated solution its lifetime is 0.4 μs, but in the presence of oxygen (partial pressure of O_2 in the gas phase 31 mmHg) it is reduced to 50 ns, which corresponds to a quenching rate constant $k_q = 7 \times 10^9$ M^{-1} s^{-1}.

Transient spectra of 4-fluoroanisole observed 0.1 μs after laser excitation in 40vol.%- and 80vol.%water–acetonitrile are presented in Fig. 13. The maximum at 400 nm is no longer observed in 80vol.%water–acetonitrile but instead two new maxima appear at 390 and 430 nm. It is worth noticing that the transient conductivity in the acetonitrile solution is still negligible at 40 vol.% water in the solvent, but is considerable at 80 vol.% water (Fig. 2). The height of the absorption at 430 nm depends strongly on the concentration of water in the solution (Table 4), and the lifetime depends on the concentrations of both the water and the ground state molecule. In the presence of the OH$^-$ ion the spectrum at $t = 0.1$ μs in 80vol.%water–acetonitrile is similar to that between 340 and 450 nm in anhydrous acetonitrile (Fig. 13). From this or from some other transient a new absorption is formed within 2 μs which has absorption maxima at 415 nm and 390 nm. This transient absorption spectrum changes in the course of time to another longer-lived (18 μs) one with maximum at about 380 nm. At $t = 2.0$ μs and in the presence of the OH$^-$ ions (0.015 M) the two maxima are no longer observed, but the long-lived (about 18 μs) maximum at about 380 nm appears. The first-order rate constant for the growth of this transient absorption is 5.7×10^5 s^{-1} at an OH$^-$ concentration of 0.015 M. Obviously, the transient species absorbing at 380 nm in the presence and in the absence of OH$^-$ ion are the same type of species (AFOH$^{\cdot}$) as species C in the case of chloroanisole and is also related to species C of fluoroanisole.

The decay of the transient absorption of 4-fluoroanisole at 430 nm in 80vol.%water–acetonitrile is shown in Fig. 14 for various conditions. In the absence of the OH$^-$ ion the absorption is formed during the laser pulse and the decay follows first-order kinetics with a lifetime of about 2 μs. In the presence of the OH$^-$ ion (0.015 M) the absorption is similarly formed very fast and followed by a fast decay (less than 0.5 μs) which is accompanied by a weak long-lived transient absorption of C. The same fast decay is also observed on addition of CN$^-$ ion to the reaction mixture. The

nucleophiles CN⁻ and OH⁻ have no effect on the intensity of the absorption and even large amounts of the nucleophile in the solution do not reduce the lifetime of the short-lived transient. The transient species with a lifetime less than 0.5 μs is probably the triplet state T_0 and the transient with a lifetime of 2 μs is a radical cation B of 4-fluoroanisole.

To prove that the radical cation AF^+ of 4-fluoroanisole is formed we have studied the system with DCE in the solution in the range 340 - 450 nm. The transient absorption is formed almost during the laser pulse, and the form of the spectrum with two maxima is about the same as in the absence of DCE. In the presence of CN⁻ ions (0.015 M) the absorption is quenched with the exception of the fast decaying component, similar to that shown in Fig. 14. At low DCE concentration two transients are observed at 430 nm, the first T_0 with a lifetime of less than 0.5 μs and the second B with a lifetime of about 12 μs. With increasing DCE concentration the height of the short-lived transient absorption decreases (Table 5), which implies that either the triplet state T_0 or its precursor, *i.e.* the excited singlet state of fluoro-
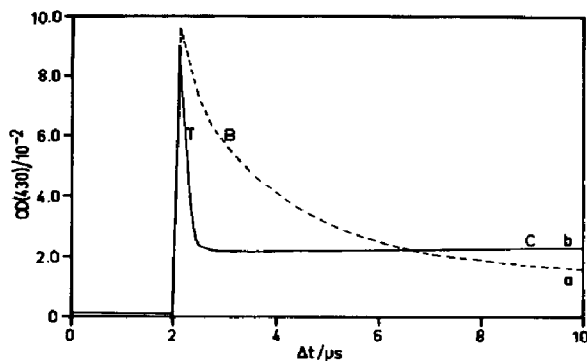

Fig. 14. Decay of the transient species T (the triplet state) and B (AF^+) of 4-fluoroanisole at 430 nm in the absence (a) and presence (b) of an added nucleophile ([OH⁻] = 1.5 × 10^{-2} M) in 80vol.%water–acetonitrile.

TABLE 5

Absorbances OD_T and OD_B of the triplet state and radical cation respectively of 4-fluoroanisole as function of dicyanoethylene at 430 nm in 50vol.%water–*tert*-butyl alcohol

[DCE] (mM)	$OD_T(\Delta t = 0.1 \mu s)$	$OD_B(\Delta t = 1.0 \mu s)$
0.5	0.063	0.026
1.0	0.049	0.024
1.5	0.043	0.024
2.0	0.034	0.024
2.5	0.025	0.023
3.0	0.024	0.023

anisole is quenched by DCE. The absorbance at $t = 1.0$ μs is, however, independent of the DCE concentration.

The absorbance at 430 nm is strongly dependent on the water concentration (Table 4) and depends non-linearly on the amount of light absorbed by 4-fluoroanisole in its ground state. If the ionization process starts from the excited singlet state, the ionization and the fluorescence would be competing processes. The weak dependence of the fluorescence lifetime on water concentration (Table 1) cannot explain the large dependence of the quantum yields of the cyanation and the hydrolysis reactions. However, if the crucial step in the ionization is an interaction of excited state and a ground state molecule and if water causes ionic dissociation of the resulting complex, then water does not have to quench the fluorescence or the triplet state.

The type of linear relation between $(1 - 10^{-D})/OD$ and the inverse of the ground state concentration obtained for chloroanisole also holds for fluoroanisole. The value 1800 mol^{-1} dm^3 for k_i/k_1 is obtained for fluoroanisole in 70vol.%water–acetonitrile solution. In the transient photoconductivity measurements the first-order rate constant for the formation of ionic species was 2.2×10^7 s^{-1} at fluoroanisole concentration of 2.2×10^{-3} mol dm^{-3}. Thus

$$k_i = \frac{2.2 \times 10^7}{2.2 \times 10^{-3}} \, \text{M}^{-1} \, \text{s}^{-1} = 1.0 \times 10^{10} \, \text{M}^{-1} \, \text{s}^{-1}$$

Furthermore, the rate constant $k_1 = 1/\tau$ now takes a value of 5.5×10^6 s^{-1}. The lifetime of the excited state is thus 0.18 μs, corresponding to the reduced lifetime of the triplet state and it is about the same as that of the fast transient in Fig. 14. This favours the reaction of a triplet state and a ground state molecule to obtain the radical cation.

According to the earlier quantum yield measurements of the cyanation reaction the quantum yields in the case of 4-fluoroanisole are independent of the ground state concentration [3, 10]. The experiments reported here show that the lifetime of the radical cation depends on the concentration of 4-fluoroanisole in the reaction mixture. This phenomenon might explain the difference between our present and the earlier results. We have determined a rate constant $k = 6.5 \times 10^7$ M^{-1} s^{-1} for the reaction

$$AF^{+\cdot} + AF \xrightarrow{k} [AF]_2^{+\cdot}$$
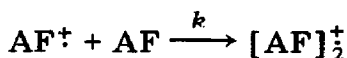
in both 50vol.%- and 80vol.%water–acetonitrile solutions. This value is about the same as is the value of k_N for the attack of cyanide anion on radical cation. These two reactions thus are competitive at high ground state concentrations of fluoroanisole, and this may reduce the yield of product from $AF^{+\cdot}$, provided that $[AF]_2^{+\cdot}$ does not lead to this product. At low enough concentration of CN^- the dependence of product quantum yield on the ground state concentration of anisole may disappear.
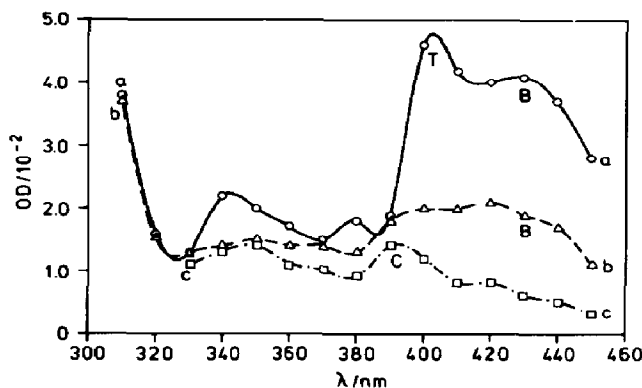
Fig. 15. Transient absorption spectra of 4-fluoroanisole observed 0.1 (a), 2.0 (b) and 18 μs (c) after laser excitation in 70vol.%water–*tert*-butyl alcohol.

Figure 15 presents changes in the transient spectrum of 4-fluoroanisole in 70vol.%water–*tert*-butyl alcohol in the course of time. In the absence of an added nucleophile the absorption at 400 nm is due to T_0 and that at 430 nm is due to the radical cation B. Within 2 μs of the excitation the broad absorption, observed between 390 and 450 nm, is due to the absorption by radical cations B and C radicals, *i.e.* radical AFOH˙. At $t = 18$ μs absorptions at 390 nm and 350 nm are both due to the radical AFOH˙ and have a lifetime of about 18 μs. In the presence of CN⁻ ions a long-lived transient species is formed which has an absorption band at 350 nm. This species is probably the radical AFCN˙. The radical AFOH˙ is not observed in the presence of cyanide anions at concentration of 2.4×10^{-3} mol dm⁻³.

3.4. Transient species after attack of a nucleophile on the radical cation

We have shown that the attack of the water molecule on the radical cation yields the neutral radical AXOH˙ (absorptions at 415 nm (AClOH˙) or between 380 - 390 nm (AFOH˙)), which indicates that the attacking water molecule releases a proton less than 10^{-7} s after encountering the radical cation.

In the presence of cyanide anion absorptions at 390 nm (AClCN˙) and 330 nm (AFCN˙) appear. If the next step in the substitution reaction were departure of a halogen ion (X⁻) from the radicals AClCN˙ or AFCN˙, as proposed [3, 10] earlier (reaction (5)) this would yield the radical cation ACN⁺ in the case of both 4-fluoroanisole and 4-chloroanisole. We have not observed the formation of ACN⁺ in the reactions of either 4-fluoroanisole or 4-chloroanisole with the CN⁻ ion. According to reaction (6) the new radical cation, ACN⁺ or AOH⁺, would combine with an electron to form the product molecule. However, it now appears that the solvated electron in the system has a lifetime which is too short for a reaction at this stage of the mechanism. On this basis we conclude that a halogen atom X˙ rather than a halogen ion is released from the neutral radical AXCN˙ or AXOH˙ to form a product molecule.

3.5. The role of water

It has been proved that the ionization process determines the quantum yield of the substitution reaction. The ionization, on the other hand, depends on the amount of water in the solution. The concentration of water probably does not determine the quantum yield, but the presence of water changes the dielectric constant of the solvent mixture thereby increasing the probability of ionization.

In anhydrous acetonitrile an absorption of a transient species arising from 4-chloroanisole is observed between 420 - 500 nm (Fig. 4). This absorption band cannot be attributed to the triplet state T_0 and the absorbance in the band increases with the ground state concentration of 4-chloroanisole. The transient conductivity of solutions in anhydrous acetonitrile is negligible, but increases at higher water concentrations (Fig. 1). At the same time the transient species begins to transform to another species which reacts with nucleophiles. The formation of the former transient species A is evidently not influenced by water. It might be a tight ion pair, which is formed from an excited and a ground state molecule of 4-chloroanisole, and which dissociates to free ions under the influence of water or the higher dielectric constant of the solvent.

Empirical relations between the ionic dissociation yield and the dielectric constant of solvent have been established. In Onsager's ion recombination model [19] it is assumed that the fraction α of the dissociative state in the encounter collision yield the ion pair state at distance r_0, and that the dissociation and recombination of the pair compete with each other. The probability of escape of oppositely charged ions with charge e is

$$W_{esc} = \alpha \exp\left(-\frac{r_c}{r_0}\right)$$

where

$$r_c = \frac{e^2}{4\pi k T \epsilon_0} \frac{1}{\epsilon_r} = \text{constant} \frac{1}{\epsilon_r}$$

and ϵ_r is the dielectric constant of the solvent.

If all radical ions become ion pairs with the same separation from the counter ion we may expect the quantum yield ϕ of the product formation to vary as a function of the dielectric constant of the solvent in the following manner:

$$\ln \frac{1}{\phi} = -\ln \alpha + \frac{\text{constant}}{r_0} \frac{1}{\epsilon_r}$$

Plotting $\ln(1/\phi)$ (values of ϕ from Figs. 1 and 2) as a function of $1/\epsilon_r$ [20] for acetonitrile–water solutions (Fig. 16) shows satisfactory linearity. This may be taken as evidence that the reactive radical cation is formed from an ion pair.
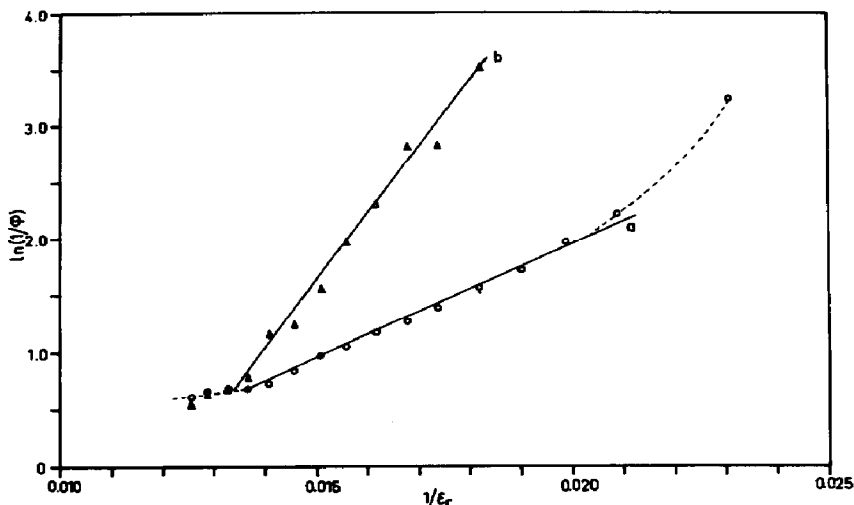
Fig. 16. The dependence of the quantum yield of the hydrolysis reaction on the dielectric constant of solvent according to Onsager's equation $\ln(1/\phi) = -\ln \alpha + \text{constant}/\epsilon_r$ for (a) 4-chloroanisole and (b) 4-fluoroanisole in water–acetonitrile. The linearity is satisfied with the exceptions of the highest values of ϕ at water concentrations of 85 - 95 mol.%.

3.6. The mechanism

The nucleophilic photosubstitution of 4-chloroanisole and 4-fluoroanisole can be described as a mechanism of five different steps. In the first step the lowest excited triplet state of the anisole derivative is formed.
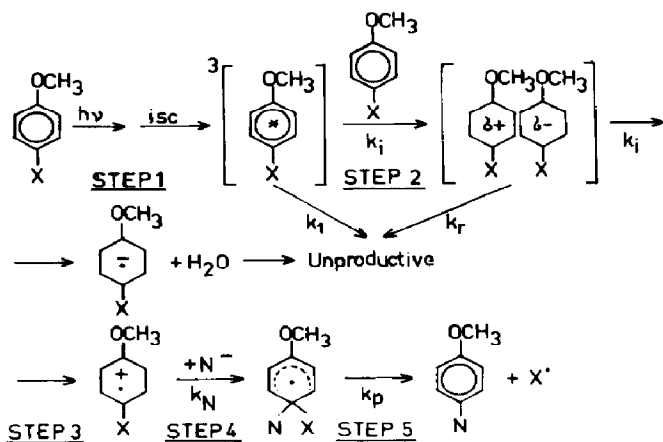
The main relaxation process of the triplet state in non-polar solvents is monomolecular decay (k_1). The triplet state lifetimes of chloroanisole and fluoroanisole are in perfluorohexane 0.9 μs and 0.5 μs respectively, but are reduced in acetonitrile owing to the solvent polarity and the interaction with the ground state molecule which yields an ion pair (Step 2).

The calculated lifetimes of the triplet state of 4-chloroanisole are 61 ns in 50vol.%water–acetonitrile and 42 ns in 80vol.%water–acetonitrile solutions, and that for 4-fluoroanisole is 180 ns in 70vol.%water–acetonitrile. In anhydrous acetonitrile the lifetime of the ion pair is 7.0 μs in the case of chloroanisole. The ion pair mainly decay by a recombination process (k_r).

With increasing dielectric constant of the solvent the probability of the dissociation increases and the radical ions are formed (Step 3).

The measured rate constants (k_i) for the formation of free ions (involving Steps 2 and 3) in water–acetonitrile are $k_i = 4.1 \times 10^9$ M^{-1} s^{-1} and $k_i = 1.0 \times 10^{10}$ M^{-1} s^{-1} for chloroanisole and fluoroanisole respectively. Reaction of radical anion with water is so rapid that the transient is not observed in aqueous solutions. The lifetimes of radical cation of chloroanisole and fluoroanisole are 7 μs and 9 μs (estimated at low water concentration), but are reduced by nucleophiles (Step 4).

The measured rate constants k_N for reaction of radical cation of 4-chloroanisole with nucleophiles are $k_N(H_2O) = 5.8 \times 10^3$ M^{-1} s^{-1}, $k_N(OH^-) = 5.2 \times 10^7$ M^{-1} s^{-1} in 80vol.%water–acetonitrile, $k_N(CN^-) = 1.35 \times 10^9$ M^{-1} s^{-1} in 40vol.%water–acetonitrile and $k_N(CN^-) = 0.21 \times 10^9$ M^{-1} s^{-1} in 80vol.%water–acetonitrile. The value $k_N(OH^-) = 3.8 \times 10^7$ M^{-1} s^{-1} in 80-vol.%water–acetonitrile was measured for fluoroanisole.

Neutral radical AXN$^\bullet$ formed in Step 4 yields the reaction product in a single step (Step 5). The first-order rate constants k_p for formation of product molecules in Step 5 are about $k_p(ACl) = 1.4 \times 10^5$ s^{-1} and $k_p(AF) = 0.6 \times 10^5$ s^{-1}. The released halogen atom $X^\bullet$ will probably combine with the negative species which is formed in reaction of radical anion with water and yields the halogen anion X^-.

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