

Photo- and Radiation-induced Chemical Generation and Reactions of Styrene Radical Cations in Polar and Non-polar Solvents

Ortwin Brede,^{*,a} Frank David^a and Steen Steenken^{*,b}

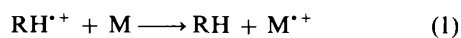
^a Max-Planck-Gesellschaft, Arbeitsgruppe Zeitaufgelöste Spektroskopie an der Universität Leipzig, Permoserstr. 15, D-04303 Leipzig, Germany

^b Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim, Germany

Radical cations of the substituted styrenes (M) 1–10 have been produced by pulse radiolysis of solutions of M in cyclohexane. The monomer radical cations, M^{•+}, are formed by fast electron transfer from the solute, M, to the solvent radical cation produced by the ionizing radiation. The decay of M^{•+} proceeds by an ion–molecule reaction with the parent styrene (dimerization; $k = 0.6\text{--}1.0 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) resulting in head-to-head connected distonic dimer radical cations which show properties of carbenium ions. At high styrene concentrations a trimerization which represents the start of the free cationic polymerization takes place with a rate constant of *ca.* $10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In aqueous or alcoholic solutions, radical cations were generated by direct two-photon ionization (indicated by the presence of the solvated electron) of the styrenes or by reactions with strong oxidants, such as SO₄^{•-} and Ti²⁺, generated by laser UV photolysis as well as by pulse radiolysis. Only for 4-methoxystyrene **6** and *trans*-anethole **7** could the (monomeric) radical cations be directly observed in the nanosecond to millisecond range. In the other cases, the radical cations decay within the sub-nanosecond timescale by reaction with H₂O forming β-hydroxybenzyl type radicals.

In preparative studies of radiation-induced alkene polymerization it has been found that under the condition of extreme dryness the polymerization process proceeds with a chain growth rate larger by four orders of magnitude than that of the 'classical' radical process. In the cases of styrene and 1-methylstyrene Okamura and his school,¹ Potter *et al.*² and Huang and Westlake³ characterized this rapid polymerization as driven by free (in contrast to ion paired) cations.

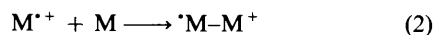
The formation of styrene radical cations, their ion–molecule reactions with styrene leading to dimer formation and the subsequent reactions have previously been studied by means of the pulse radiolysis technique.^{4,5} The ionizing radiation produces radical cations of the solvent which, in the case of solvents such as alkanes and chloroalkanes, have lifetimes in the nanosecond range and can thus be scavenged by solutes of concentrations of the order $10^{-3} \text{ mol dm}^{-3}$. In the case of styrene-containing solutions this reaction involves electron transfer from styrene to the solvent radical cation^{5,6} [reaction (1)], with typical rate constants of 10^{10} to $10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$



M = monomeric styrene
 $k_1 = 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ^{5b}

which are understandable on the basis of the fact that the mobility of the radiation-induced chemically formed primary solvent radical cation in cyclohexane is higher than that of relaxed molecular ions.^{6,7}

The styrene radical cation (M^{•+}) reacts with styrene with a diffusion-controlled rate^{5b} [reaction (2)]. On the basis of low-



temperature pulse radiolysis data, the structure of the product radical cation has been proposed to be that of a physically bonded and sandwich-like charge transfer adduct.⁴ However, since the reactivity with the styrene monomer is similar to that of the growing cationic chain,¹ it is more probable that the dimer has the structure of a chemically bonded ion.^{4e}

In the last few years methods have also been developed for the generation of organic radical cations in polar systems.⁸

With these methods, radical cations can be produced by reaction of the organic solute with a strong transient oxidant, such as SO₄^{•-} and Ti²⁺, produced by (pulse) radiolysis.^{9,10} These oxidants can also be generated by (laser) photolysis techniques.^{10,11} An additional way of producing radical cations is by photoionization with UV light in a polar environment in which the ionization products, radical cation and electron, are stabilized by solvation. The ionization process may be monophotonic¹² or biphotonic,¹³ depending on substrate and/or excitation wavelength.¹⁴

Based on this information, we have now performed time-resolved studies on the generation of radical cations of aromatic alkenes of the styrene type and characterized them by their spectral and kinetic properties. The study was performed, using the techniques of pulse radiolysis and laser photolysis, in solvents differing with respect to polarity. The following points were of special interest: reactivity of styrene radical cations as a function of their structure, *i.e.* the influence of substituents, influence of the solvent polarity, characterization of the radical cation reactions with nucleophiles, particularly the solvent and the parent styrenes (ion–molecule reactions), the latter relating to the primary steps of cationic polymerization.

Experimental

The aromatic alkenes, styrene **1**, 4-methylstyrene **2**, α-methylstyrene **3**, β-methylstyrene **4**, 4-methoxystyrene **6**, β-methoxystyrene **8**, *trans*-anethole **7**, 4-chlorostyrene **9** and 4-chloro-α-methylstyrene **10** were commercially available (Aldrich). 4-Methyl-α-methylstyrene **5** was synthesized *via* the Grignard reaction and subsequent dehydration of the resulting tertiary alcohol. Cyclohexane was treated three times with oleum, washed with water and dried by chromatography on molecular sieves A4 and X13. It was then distilled over a 1 m Vigreux column. Water was purified using a Millipore Milli-Q Plus system. All other chemicals were used as supplied.

For pulse radiolysis, samples were irradiated with 2 to 20 ns pulses of 1 MeV electrons from an Elit type accelerator. The dose per pulse was between 100 and 200 Gy, which corresponds to initial concentrations of radicals of 0.01 mmol dm⁻³. Detection of transients was performed by optical spectroscopy

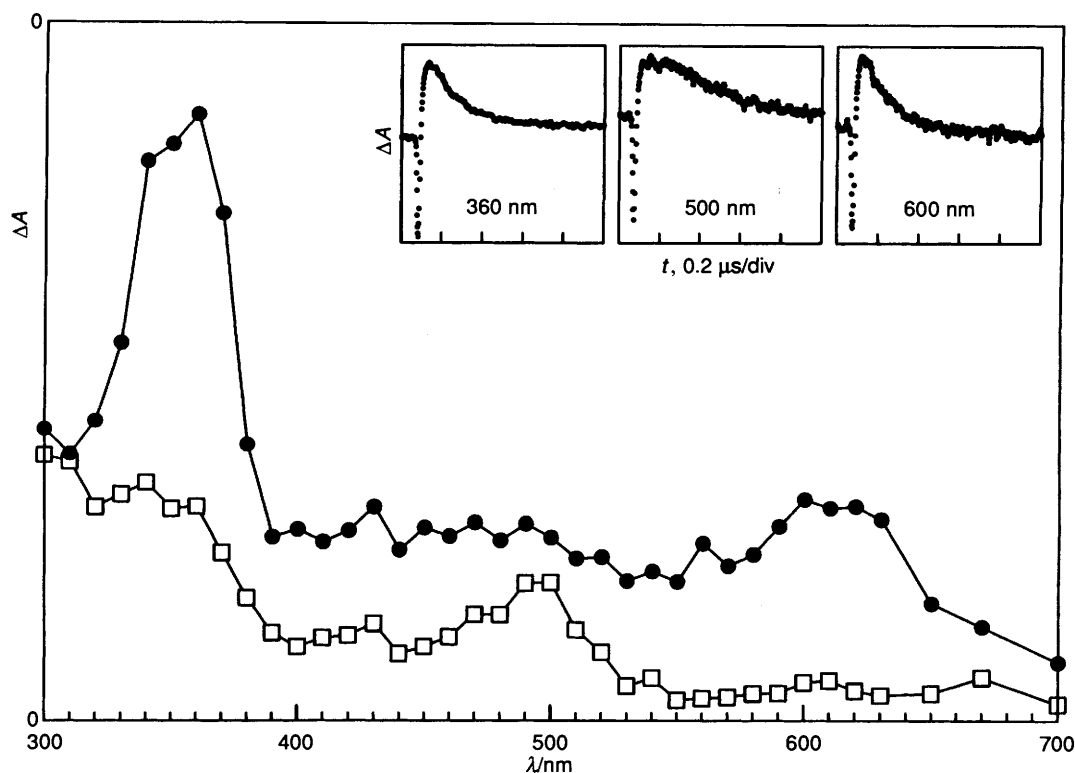


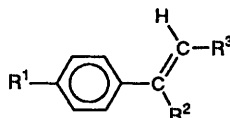
Fig. 1 Absorption spectra of transients recorded at 40 ns (●) and 500 ns (□) after the pulse on radiolysis of a 0.5 mmol dm⁻³ solution of 4-methoxystyrene **6** in cyclohexane containing 0.1 mol dm⁻³ CCl₄. The insets show time profiles at the absorption maxima.

using a boosted Xenon lamp, a grating monochromator and a 1P28 (RCA) photomultiplier. The signals were digitized by a Tektronix TDS 640 transient recorder and interfaced with a 486 PC which also process-controlled the apparatus and on-line preanalysed the data.

The flash photolysis experiments were performed with 248 nm light (20 ns, 5–100 mJ pulse⁻¹) of a Lambda-Physik excimer laser (Mülheim) or with 266 nm (3 ns, 1 mJ) of a Spectra-Physics GCR 11 Neodym Yag laser (Leipzig). Detection and data handling were carried out with equipment similar to that used in pulse radiolysis. In some cases AC and DC conductivity measurements were performed (Mülheim). All experiments were carried out at room temperature.

Results and Discussion

Styrene Radical Cations in Non-polar Solution.—A convenient method for generating styrene radical cations consists of one-electron oxidation of the solute by radiation-induced chemically produced solvent radical cations [eqn. (1)]. Appropriate solvents for such studies are alkanes, in particular cyclohexane, and alkyl chlorides.^{5,6} The driving force for this

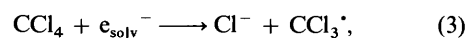


- 1 R¹ = H, R² = H, R³ = H
- 2 R¹ = CH₃, R² = H, R³ = H
- 3 R¹ = H, R² = CH₃, R³ = H
- 4 R¹ = H, R² = H, R³ = CH₃
- 5 R¹ = CH₃, R² = CH₃, R³ = H
- 6 R¹ = OCH₃, R² = H, R³ = H
- 7 R¹ = OCH₃, R² = H, R³ = CH₃
- 8 R¹ = H, R² = H, R³ = OCH₃
- 9 R¹ = Cl, R² = H, R³ = H
- 10 R¹ = Cl, R² = CH₃, R³ = H

Structure of the styrenes studied

electron transfer from solute to solvent radical cation is, to a first approximation, proportional to the ionization potential difference of the reactants. In the case of the solvent cyclohexane as used in our studies and the different styrenes this ionization potential difference is *ca.* 1 eV which enables the transfer to be very rapid (rate constants k_1 10¹⁰ to 10¹¹ dm³ mol⁻¹ s⁻¹).

In order to prevent any anion formation of the aromatic alkenes,⁵ 0.1 mol dm⁻³ tetrachloromethane was added as electron scavenger to the cyclohexane solvent [eqn. (3)]. A



$$k_3 = 10^{12} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

positive side effect is an increase of the radical cation yield caused by the fact that less electron-radical cation recombination takes place (the chloride anion has a much lower mobility than the solvated electron e_{solv}^- and is much less reactive).

Fig. 1 shows spectra of the transients recorded after pulsing a 0.5 mmol dm⁻³ solution of 4-methoxystyrene **6** in cyclohexane. Three absorption maxima can be distinguished at $\lambda = 360$, 500 and 610 nm. Addition of 10 mmol dm⁻³ ethanol removed completely these absorption bands which indicates that the species responsible is, or originates from, a cationic precursor. The maxima at $\lambda = 360$ and 610 nm are assigned to a monomeric radical cation of **6**, whereas that at $\lambda = 500$ nm is identified as a subsequent product, proposed in analogy to styrene^{5a} **1** to be the dimer radical cation of **6**. In agreement with this idea is the fact that the kinetics of monomer radical cation decay and dimer radical cation formation [eqn. (2)] fit well a pseudo-first order time law with respect to the styrene concentration. The kinetic simulation with a modified version of the Acuchem program¹⁵ using a reaction mechanism which takes into account the dimerization reaction [eqn. (2)], as well as neutralization reactions of all ions, results in the rate constant $k_2 = 1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In the case of 4-chlorostyrene **9** the absorption maxima of the monomer radical cation are at ≈ 375 and ≈ 650 nm (see Fig. 2),

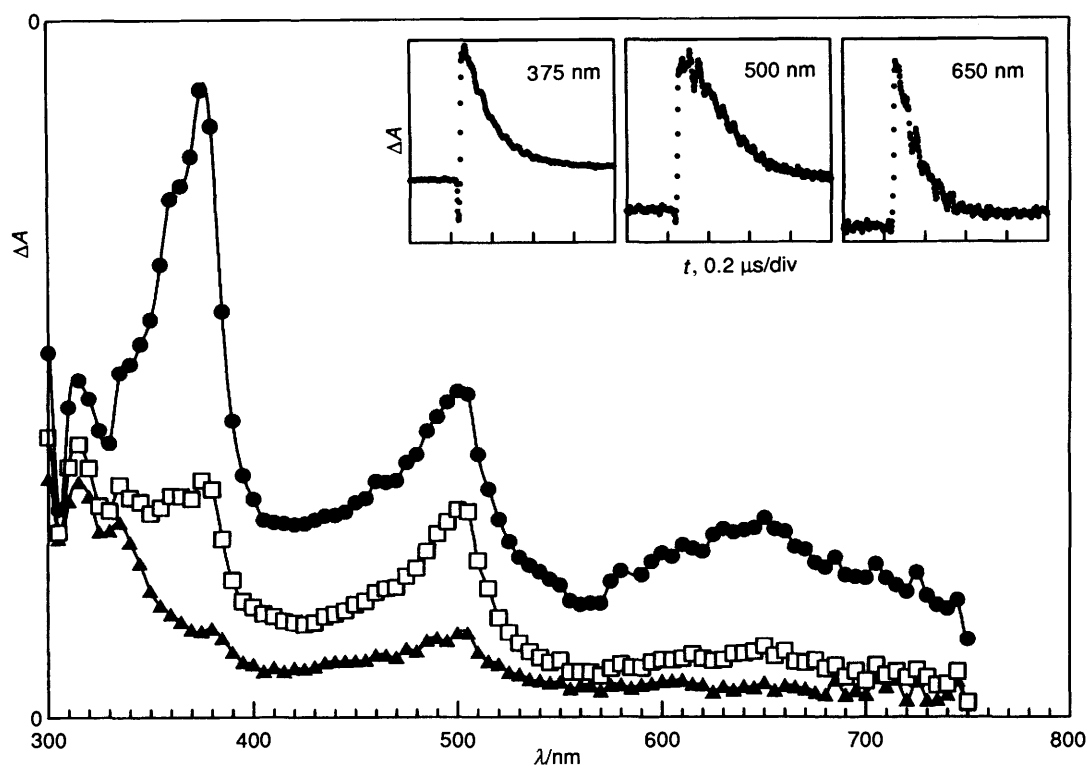


Fig. 2 Absorption spectra of transients measured at 100 (●), 250 (□) and 650 ns (▲) after the pulse on radiolysis of a 0.5 mmol dm⁻³ solution of 4-chlorostyrene **9** in cyclohexane containing 0.1 mol dm⁻³ CCl₄. The insets show time profiles taken at the absorption maxima.

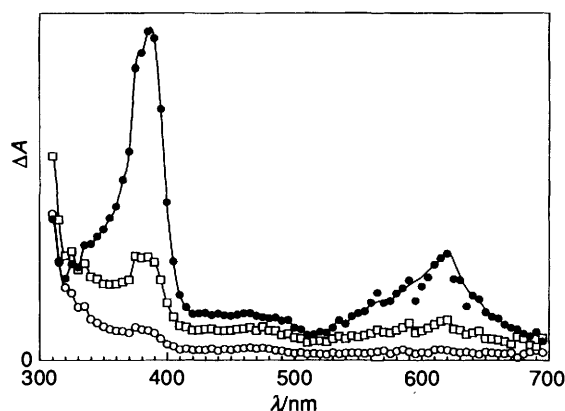


Fig. 3 Absorption spectra of transients recorded at different times after pulse radiolysis of a 0.5 mmol dm⁻³ solution of *trans*-anethole **7**, in cyclohexane containing 0.1 mol dm⁻³ CCl₄ measured at 220 ns (●), 2 μs (□) and 6 μs (○)

and that of the dimer radical cation is at $\lambda = 500$ nm, as in the case of **7**. In addition to these short-lived cationic species, there is a longer-lived species which absorbs at ≈ 315 nm. This species is assigned to a benzyl type radical. In contrast to the cationic species, benzyl radicals react rapidly with oxygen (see later, polar systems). In the case of the other styrenes, except *trans*- β -methylstyrene **4** and *trans*-anethole **7** (see below), observations similar to those reported for **6** and **9** were made.

In the case of β -substituted styrene derivatives only the typical monomer bands at ≈ 360 and ≈ 610 nm appeared upon pulse irradiation, but not the signal at 500 nm, as seen for *trans*-anethole **7** in Fig. 3. The lifetime of the monomer radical cation 7^+ (1–2 μ s) is not influenced by the concentration of **7** up to 10 mmol dm⁻³. This means that the rate constant for reaction of 7^+ with **7** is $\leq 6 \times 10^7$ dm³ mol⁻¹ s⁻¹, compared with (0.6–1) $\times 10^{10}$ dm³ mol⁻¹ s⁻¹ for the styrenes not carrying a substituent in the β -position. The low reactivity of the β -

substituted systems is explained in terms of steric hindrance caused by the β -substituent (plus the radical cation stabilization by the electron-donating substituent) by which charge transfer complex formation as known for unsubstituted aromatics¹⁶ followed by formation of a σ -bond is prevented.

Concerning the structure of the dimer radical cation observed for the styrenes except the β -substituted ones, it is assigned to a chemically bonded form (in contrast to a CT complex), produced by head-to-head addition of the monomer radical cation to the parent styrene (see also the Discussion section) as formulated below in structure **11**. This species is a distonic¹⁷



radical cation in which the radical and the cation centre are separated by two methylene groups. Thus charge and spin are contained in non-interacting π -systems insulated by the methylene groups. Therefore, a chemical reactivity different from that of 'normal' radical cations (where charge and spin are located in the same π -system) is expected. In particular, the distonic radical cation is expected to possess properties characteristic of carbenium ions, *i.e.* a high reactivity with nucleophiles. In the case of styrene **1** and 4-methylstyrene **2** we observed earlier¹⁸ a high reactivity of the dimer radical cation ($M-M^+$) with nucleophiles whereas the reactivity with the parent styrene ['trimerization', ion-molecule reaction, eqn. (4)] was relatively low. This reaction represents the first step of



the chain growth in free cationic polymerization and, therefore, is of interest also from a synthetic point of view.

Reaction (4) can be observed only at styrene concentrations > 0.1 mol dm⁻³. For example, in Fig. 4(a) are shown time profiles for the decay of the dimer radical cation, measured at 500 nm, for 4-chlorostyrene **9** in the concentration range 0.03–

Table 1 Absorption maxima of styrene radical cations and k values of dimerization [eqn. (2)] and trimerization [eqn. (4)] determined by pulse radiolysis in cyclohexane containing $0.1 \text{ mol dm}^{-3} \text{ CCl}_4$

Styrene	$\lambda_{\text{max}}/\text{nm}$	$k_2/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$k_4/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
1	350, 620 (m), 450 (d) ^a	8×10^9 ^a	2×10^6 ^a
2	360, 600 (m), 470 (d)	1×10^{10}	2.5×10^6
3	350, 620 (m), 470 (d) ^a	1×10^{10} ^a	5×10^6 ^a
4	370, 590 (m)	$< 6 \times 10^7$	<i>b</i>
6	360, 610 (m), 500 (d)	1×10^{10}	8.4×10^6
7	385, 620 (m)	$< 6 \times 10^7$	<i>b</i>
9	375, 650 (m), 500 (d)	6×10^9	1.0×10^7

(m) Monomer radical cation, (d) dimer radical cation. ^a From ref. 5(b). ^b Dimer radical cation not detected.

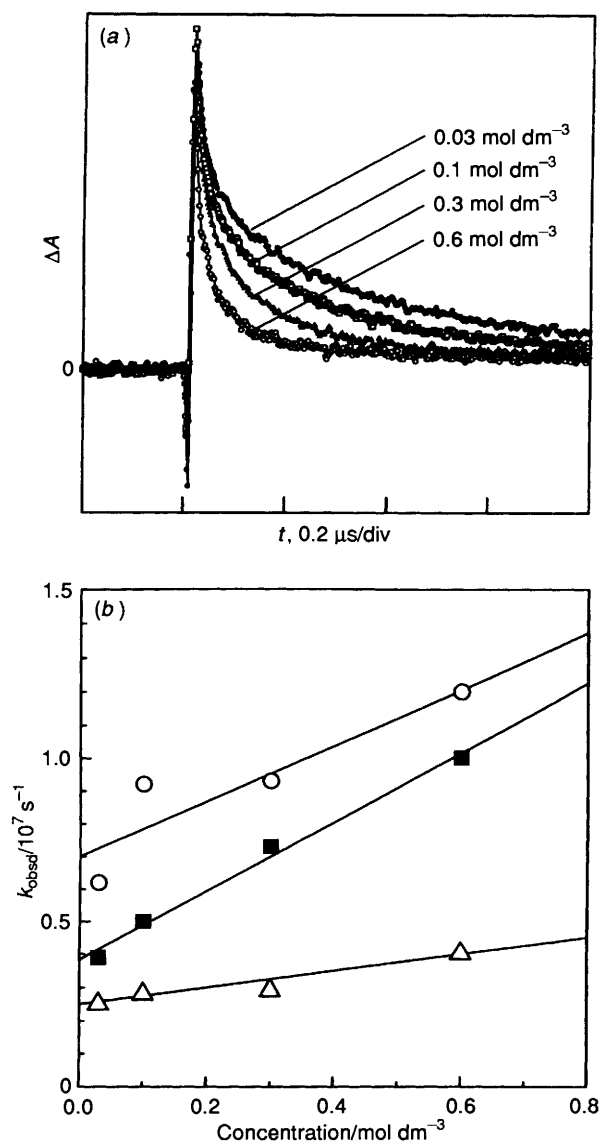
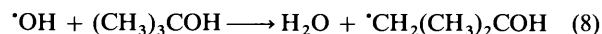
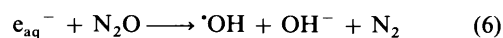
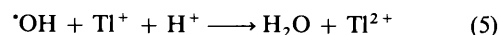


Fig. 4 Ion-molecule reactions [eqn. (4)]: (a) Decay of the dimer radical cation, monitored at 500 nm, after pulse radiolysis of 4-chlorostyrene **9** in the concentration range $0\text{--}0.6 \text{ mol dm}^{-3}$. (b) Plot of k_{observed} as a function of styrene concentration for several styrenes: (○) 4-methoxystyrene; (■) 4-chlorostyrene; (△) 4-methylstyrene.

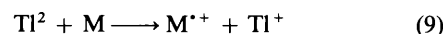
0.6 mol dm^{-3} . It is possible to analyse these concentration-dependent time profiles on the basis of model calculations, which take into account an 'inhomogeneous' (rapid, $< 20 \text{ ns}$) part due to scavenging of radicals in the radiation spurs as reported in ref. 5b, and a 'homogeneous' (slow, $> 20 \text{ ns}$) part. Concerning the latter, the decay rates were found to be proportional to the styrene concentration, as shown in Fig.

4(b), and from these dependences the rate constants for the trimerization reaction (4) were determined. For **9**, k_4 results as $1.0 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In the case of the other styrenes the rates of reaction (4) were found to be lower. These data are summarized in Table 1.

Pulse Radiolytic Generation of Styrene Radical Cations in Polar Media.—The OH radical, the primary oxidative species produced on irradiation of aqueous solutions, reacts preferentially with unsaturated systems, e.g. styrene, by addition and not by electron transfer.¹⁹ However, the OH radical can be transformed into a selective oxidant as shown, e.g., in reaction (5). The other primary species can be converted [eqn. (6) or (7)] or eliminated [eqn. (8)] using appropriate scavengers. As an

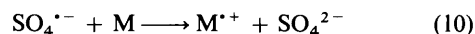


example, in Fig. 5 is shown the spectrum of the radical cation of 4-methoxystyrene **6** produced in N_2O saturated aqueous solution of Ti_2SO_4 containing the styrene. The radical cation is formed according to reaction (9) with the rate constant $k_9 =$



$8.5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In contrast to the situation concerning $\text{6}^{\cdot+}$ in cyclohexane (cf. Fig. 1), the spectrum of $\text{6}^{\cdot+}$ in water exhibits only the two bands of the monomer radical cation (cf. Fig. 5). Apparently, the dimer radical cation is not formed or it is too short-lived. This problem and the related subsequent reactions of the radical cation will be addressed in the laser photolysis section.

As an example of a sterically hindered styrene derivative, *trans*-anethole **7** radical cations were studied which were produced *via* oxidation with $\text{SO}_4^{\cdot-}$ [reaction (10)]. Fig. 6



shows absorption spectra of the transient(s) recorded in a 1 mmol dm^{-3} aqueous solution of potassium peroxydisulfate containing $0.1 \text{ mol dm}^{-3} \text{ Bu}^{\cdot}\text{OH}$ and 0.1 mmol dm^{-3} of **7**. After the decay of the solvated electron due to reaction (7), the two bands of the monomer radical cation of **7** are observed as described for the experiments in cyclohexane (cf. Fig. 3). Since a dimerization [reaction (2)] under non-polar conditions was not observed, the decay of the monomer radical cation in aqueous solution is assigned to the reaction with water [eqn. (11)] (see



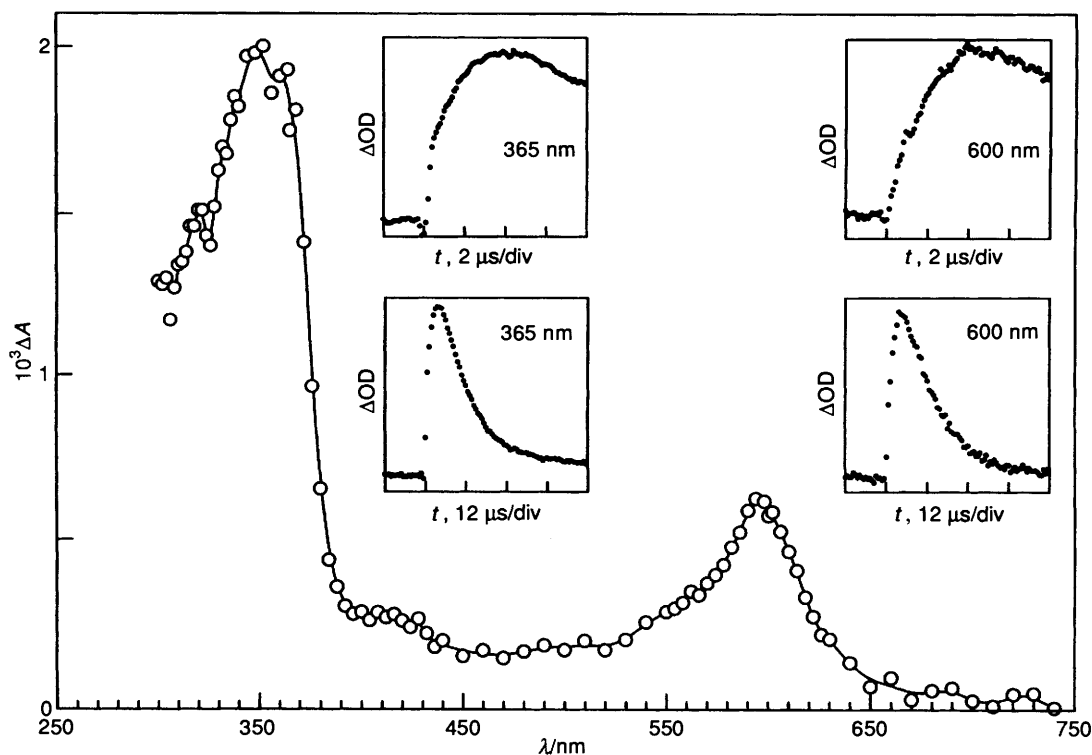


Fig. 5 Absorption spectra of transients measured at 4 μ s after the pulse on the radiolysis of an N_2O -saturated 0.2 $mmol\ dm^{-3}$ solution of 4-methoxystyrene **6** in water containing 1 $mmol\ dm^{-3}$ Tl_2SO_4 at pH = 4. In the insets are shown time profiles.

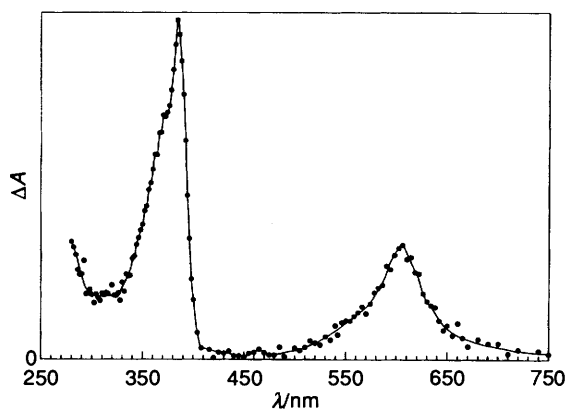
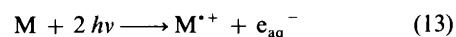
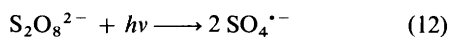


Fig. 6 Absorption spectra of transients observed at 4 μ s after the pulse on radiolysis of a saturated solution of *trans*-anethole **7** in water, deoxygenated by bubbling with Ar and containing 1 $mmol\ dm^{-3}$ $K_2S_2O_8$ and 0.1 $mol\ dm^{-3}$ *tert*-butyl alcohol

laser photolysis section). This conclusion is supported by the results of conductance studies which show the formation of H_3O^+ (see next section). Radical products of the benzyl type²⁰ can be seen in the spectrum at 270–320 nm. An analogous pulse radiolysis experiment with β -methoxystyrene **8**, using $SO_4^{\cdot-}$ as oxidant, resulted in the formation of only benzyl type radicals indicating a rapid reaction of the intermediate radical cation with the nucleophile [reaction (11)] as also observed in other cases.²¹

Laser Photolysis Studies in Aqueous Systems.—For the laser photolysis studies, two different paths of radical cation generation were used: (a) oxidation of the styrenes [see reaction (10)] with photolytically generated $SO_4^{\cdot-}$ [from peroxydisulfate, *cf.* reaction (12)] and (b) direct photoionization [reaction (13)].



Reaction of $SO_4^{\cdot-}$ with 4-methoxystyrene **6** and *trans*-anethole **7** [reactions (12) and (10)] led to the same transients as on pulse radiolysis of the compounds in cyclohexane *cf.* Figs. 5 and 6) or in aqueous solution using Tl^{2+} .

In the case of the experiments aimed at effecting direct photoionization, *ca.* 0.1 to 1 $mmol\ dm^{-3}$ aqueous solutions of the styrenes were irradiated with 248 or 266 nm laser light. In each case positive absorbance changes indicating the formation of (transient) products were apparent in the wavelength region >270 nm, and depletion of the styrene was observed at $\lambda < 250$ nm. An example for this, involving a deoxygenated aqueous solution of 4-methoxystyrene **6** in water, is shown in Fig. 7. At 100 ns after the 248 nm pulse, there is a strong depletion of optical density between 230 and 280 nm, where the parent alkene absorbs, a pronounced positive band peaking at 365 nm and a weaker (narrow) one at 600 nm which sits on top of a broad band extending up to 700 nm. The species responsible for the broad band has a high reactivity with typical electron scavengers such as O_2 and halogenated alkanes such as 2-chloroethanol. The rate constants measured for these reactions are in agreement with the literature values²² for reaction of e_{aq}^- . It is therefore concluded that the species giving rise to the broad band is the hydrated electron.

In Fig. 7(b) is shown the spectrum observed in the presence of 0.3 $mmol\ dm^{-3}$ 2-chloroethanol to scavenge e_{aq}^- . It is evident that the 376 and 600 nm bands are unaffected. These bands are also uninfluenced by O_2 , which means that they are not due to a triplet or neutral radical. The bands, which decay with the same rate giving rise (with the same rate) to a species absorbing at 280 nm (see insets), are the same as those measured on pulse radiolysis of **6** (see Fig. 5) and identified in terms of the monomer radical cation, $6^{\cdot+}$.

The solvated electron and the formation of a radical cation indicate ionization of the styrene derivatives. It was found that ionization of **6** and the other styrenes as indicated by the yield

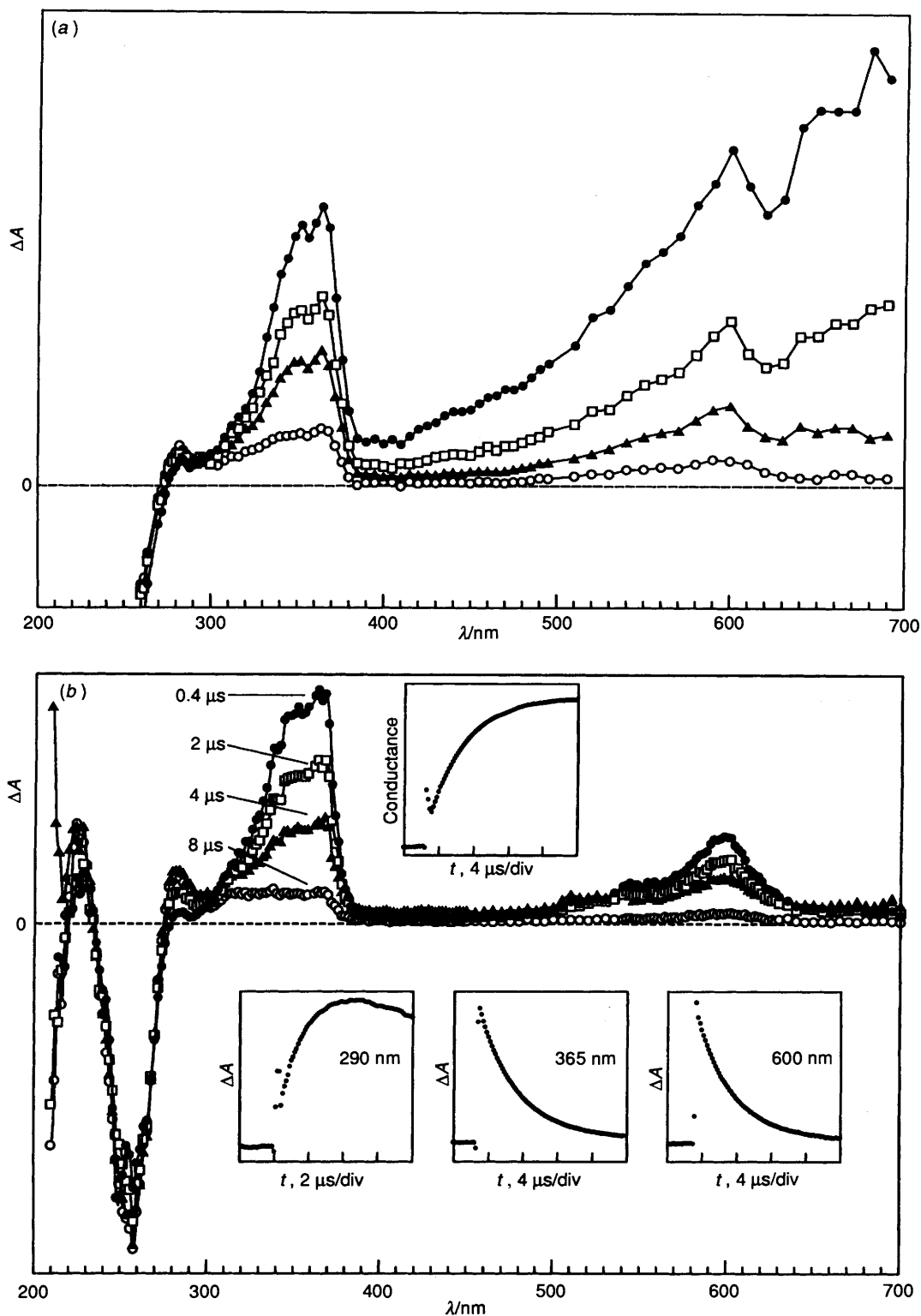


Fig. 7 Absorption spectra of transients measured after laser photolysis (248 and 266 nm) of solutions of 4-methoxystyrene 6: (a) $0.05 \text{ mmol dm}^{-3}$ in a mixture of water-isopropyl alcohol 4:1, (b) 0.1 mmol dm^{-3} in water containing 1% 2-chloroethanol (insets: time profiles at the absorption maxima, change in conductivity in the same time range)

of the solvated electron is proportional to the square root of the laser power (see Fig. 8). This means that the process leading to ionization requires two photons (is biphotonic). A similar observation has recently been made concerning styrenes in other solvents.²³

The 4-methoxystyrene radical cation, $6^{*\cdot}$, decays exponentially in a reaction whose rate depends on the parent styrene concentration. If the observed rate constant k_{obs} (measured at

the 365 or the 600 nm band) is plotted *vs.* the styrene concentration, a straight line is obtained whose slope (see Fig. 9) corresponds to a rate constant of $k_2 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the reaction which obviously takes place between the radical cation and its parent. It is very likely that this reaction is identical with the dimerization (2) which was observed in non-polar solution. The product of the dimerization, $\text{M}-\text{M}^{*\cdot}$, which in the non-polar phase absorbs around 500 nm, is not visible in

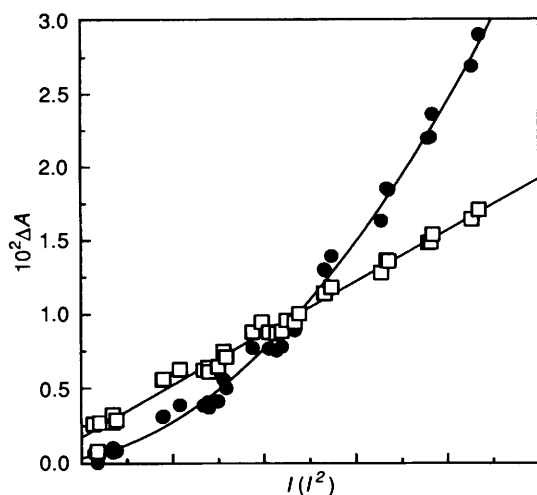


Fig. 8 Dependence of the absorbance at 580 nm due to e^-_{aq} (measured at 20 ns after the laser pulse) on (a) the laser intensity (in arbitrary units: ●), and (b) on the square of the laser intensity (□). The solution contained $0.18 \text{ mmol dm}^{-3}$ **9** in deoxygenated water:isopropyl alcohol 4:1 and was irradiated with 266 nm light.

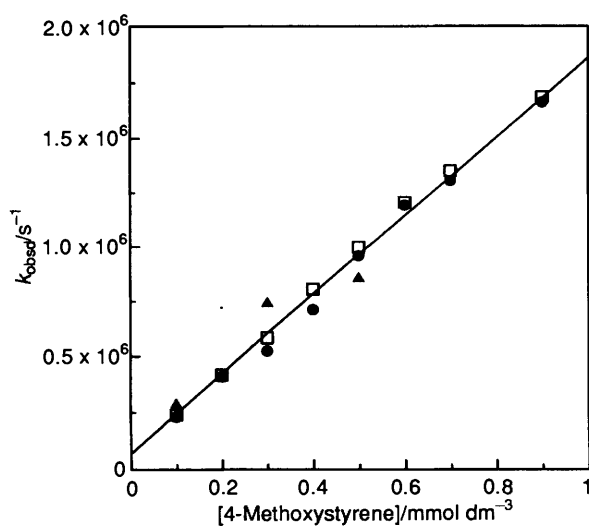


Fig. 9 Dependence of k_{obs} for the decay of 6^+ on the initial concentration of **6** in deoxygenated aqueous solution (pH 4) containing 1% 2-chloroethanol as electron scavenger (▲) conductance, optical signal at 365 nm (●) and 600 nm (□)

aqueous solution. The explanation is in terms of the rapid subsequent reaction (14) of the dimer radical cation with the



nucleophile H_2O . This reaction is understandable on the basis of the distonic radical cation structure **11**. A distonic radical cation is expected to have the properties of a carbenium ion, in this case a phenethyl-type cation, which are known to be very reactive electrophiles.^{23,24}

In reaction (14) the positive charge associated with the dimer radical cation shows up as the proton, which in aqueous solution has a much larger mobility than any other cation. Reaction (14) should therefore result in a conductance increase in acidic solution and a decrease in basic solution, due to neutralization of the proton by the excess OH^- ions. This was in fact observed. In Fig. 7, upper inset, is presented the conductance rise induced by the laser pulse in a solution of **6** at $pH \approx 5$ containing the same concentration of **6** as used for optical detection. It is evident that the rate of conductance

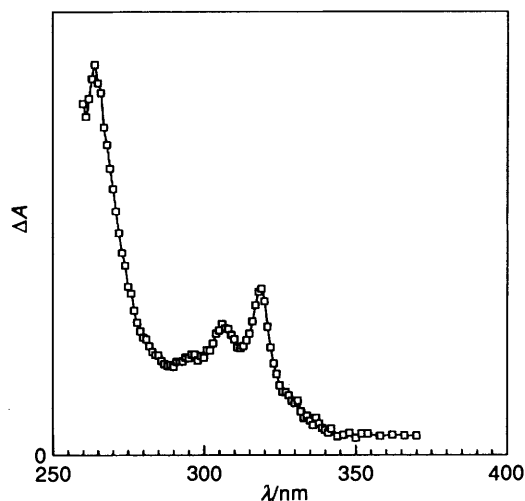


Fig. 10 Spectrum of the radical $\text{PhCH}^+\text{CH}_2\text{OH}$ obtained on pulse radiolysis ($5 \mu\text{s}$ after the pulse) of a solution containing 0.1 mmol dm^{-3} 2-phenylethanol and 0.5 mol dm^{-3} KOH

increase is the same as that of the decay of the radical cation as measured at 365 or 600 nm (lower central and right insets), or that of the build-up of the phenethyl-type radical, as monitored at 290 nm (lower left inset). The rate of conductance rise increased with increasing concentration of **6** in the same manner as the rate of decay of 6^+ and from this linear dependence (see Fig. 9) the rate constant for reaction (2) was obtained, in confirmation of the values obtained from the optical data.

Simultaneous with the decay of the radical cation and the conductance increase, a species absorbing at $\approx 285 \text{ nm}$ is formed (Fig. 7, main figure and inset 290 nm). This is identified as 4-MeOC₆H₄CH(OH)CH₂CH₂CH⁺C₆H₄OMe-4, the phenethyl-type radical product of the reaction of the (distonic) dimer radical cation with water.

In the case of *trans*-anethole **7**, after photoionization again the same long-lived monomeric radical cation was observed as in the pulse radiolysis experiments (*cf.* Figs. 3 and 6). The decay of 7^+ did not occur by a clean first-order reaction as expected for reaction (14), showing that this reaction is quite slow in the case of 7^+ . From the lifetime of 7^+ (at concentrations of **7** of 0.9 mmol dm^{-3}) in the millisecond-time range, k_{14} can be estimated to be $\leq 7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The radical cation of **7** is also unreactive with respect to other nucleophiles such as Cl^- and Br^- and also with O_2 .

As 7^+ decays, H^+ is produced as shown by conductance measurements. The kinetics of H^+ production indicate this to be a first-order process ($k \approx 5.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) which can be explained in terms of reaction of the radical cation with H_2O , reaction (11).

On photolysis in aqueous solution of the styrenes other than **6** and **7**, in addition to the solvated electron, only species absorbing between 270 and 320 nm were observed. An example for this is given in Fig. 11 which relates to 4-chlorostyrene **9**. These signals could be scavenged by oxygen [$k(O_2 + \text{benzyl radical}) = (1.6 \pm 0.2) \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$] as expected for neutral, carbon-centred radicals and in contrast to radical cations (as observed in the case of **6** and **7**), which typically have a low reactivity with O_2 . The 260 to 320 nm species are identified in terms of benzyl-type radicals formed by reaction of the radical cation with water [reaction (11)]. These radicals are substituted in the β -position by the OH-group. Benzyl type radicals show a well-structured spectrum in the region 250–330 nm with peaks at 270–275 (main peak), 310 and 320 nm.²⁵ In order to support this assignment, the spectrum of a β -hydroxy substituted model benzyl-type radical was measured by pulse radiolysis of 2-phenylethanol in alkaline solution (Fig. 10).

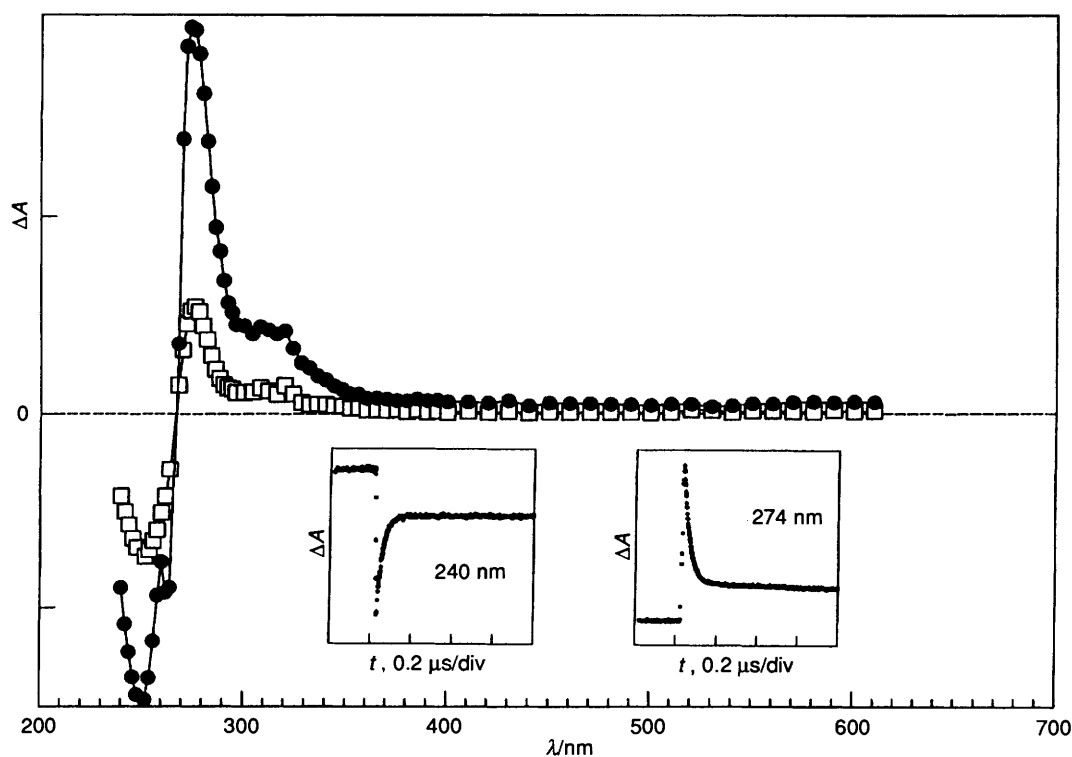


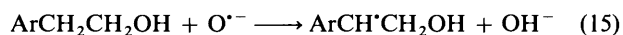
Fig. 11 Absorption spectra of transients after laser photolysis (266 nm) of 4-chlorostyrene **9**, 0.2 mmol dm^{-3} , in water–isopropyl alcohol 4:1 with 1% 2-chloroethanol added to scavenge e^-

Table 2 Absorption maxima of styrene radical cations and benzyl type radicals, k values of the reaction of monomer and dimer radical cations with the solute as nucleophile in polar medium (water containing 20–25% isopropyl alcohol)

Styrene	$\lambda_{\text{max}}/\text{nm}$	$k_{11}[\text{H}_2\text{O}]/\text{s}^{-1}$	$k_{14}[\text{H}_2\text{O}]/\text{s}^{-1}$
1	274 (r)	$> 3 \times 10^8$	1.4×10^9 ^d
2	274 (r)	$> 3 \times 10^8$	
3	274 (r)	$> 3 \times 10^8$	1.4×10^9 ^d
5	350 (r?) ^a		
6	365, 600 (m) ^b	7.5×10^4	$> 3 \times 10^8$
7	385, 610 (m) ^c	5.6×10^4	$> 3 \times 10^8$
8	300 (r)		
9	274 (r)	$> 3 \times 10^8$	
10	274 (r)	$> 3 \times 10^8$	

Abbreviations: (m) monomer radical cation, (r) benzyl type radical. ^a Purity 90%. ^b $k_2 = 2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ^c No dimerization observed. ^d Ref. 3a–c: γ -radiolysis of M in bulk.

Under these conditions the anionic form of the OH radical, $\text{O}^{\cdot-}$, is formed and reacts by H-abstraction from the side chain²⁶ producing benzyl-type radicals as described by reaction (15). As is evident from Fig. 10, the spectrum is very similar



to that of the benzyl-type radicals produced by reaction with water of the styrene radical cations. The benzyl radical formation is explained by two-photon ionization of the styrenes (13) followed by a rapid ($< 3 \text{ ns}$) reaction of the resulting radical cation with the nucleophile H_2O [reaction (11)]. This is supported by the observation of an immediate, step-like increase in the conductance after the laser pulse, caused by the production of H_3O^+ , as indicated in reaction (11).

In all cases the kinetics of the decay of the absorption at 270–290 nm were found to be two-component, the fast part having a half-life of about 20 ns and the slow one of several microseconds. Concomitant with the fast 20 ns decay there is an apparent

reformation of the photolytically consumed styrene. This can be seen by comparison of the time profiles taken at the benzyl radical maximum and at lower wavelength, *i.e.* at the absorption band of the styrene (*cf.* insets in Fig. 11 for the case of **9**). The short-lived transient is assigned to the triplet state of the styrene. This is concluded from the observation that the 270–290 nm transient could be produced by reaction ($k \approx 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) with triplet benzophenone produced by 355 nm photolysis of a solution in cyclohexane containing 5 mmol dm^{-3} benzophenone (triplet energy 287 kJ mol^{-1}) and 0.1 mol dm^{-3} 4-chlorostyrene (triplet energy 219 kJ mol^{-1}). The triplet nature of this transient is also evident from the fact that it can be quenched by cyclohexa-1,3-diene (triplet energy 219 kJ mol^{-1}). The 270–290 nm transient has previously been seen in cyclohexane and identified in terms of the triplet.²⁷ Concerning the slow part of the decay, this is due to the phenethyl-type radical produced according to reaction (14).

Table 2 contains a collection of spectroscopic and kinetic data of the styrene derivatives studied using photolysis.

Discussion

In this paper the generation of radical cations of substituted styrenes in non-polar as well as polar media is described. Concerning the pulse radiolysis experiments in alkane solution (styrenes **1–9**), in each case the electron transfer from the styrene to the solvent radical cation [reaction (1)] resulted in a monomeric styrene radical cation with the characteristic absorption spectrum with peaks around 360 and 620 nm (*cf.* Table 1).

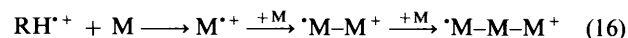
The radical cations from styrenes not substituted in the β -position react in a diffusion-controlled ion–molecule reaction with the parent styrene. For the case of unsubstituted aromatics, a sandwich-like charge transfer complex between radical cation and parent has been proposed for dimers.¹⁶ This concept explains the optical absorption spectra observed.²⁸ It is reasonable to assume that also in the case of the styrenes charge

transfer complexes are initially formed. Evidence for this interpretation is low-temperature pulse radiolysis data.⁴ However, the chemical reactivity of the styrene cationic transients at room temperature suggests that the species are distonic radical cations **11**. This means that a σ -bond between the β -carbons of styrene radical cation and styrene parent has been formed. In this case the absorption spectrum of the radical cation should be a superposition of that of a phenethyl-type radical ($\lambda_{\max} \approx 260$ nm)²⁵ with that²¹ of the corresponding carbenium ion ($\lambda_{\max} \approx 340$ nm). On this basis it is difficult to explain the existence of the experimentally observed ≈ 500 nm band. However, if it is assumed that the dimer molecule is folded such that the two π -systems separated by the methylene groups interact with each other, the 500 nm absorption of the system can be qualitatively understood. The transformation of the initially produced π -complex into the distonic radical cation by C–C bond formation has a rate constant $k \geq 5 \times 10^7$ s⁻¹. This is concluded from the fact that the absorption at 500 nm was observed to be produced without delay after the 20 ns pulse.

In the case of the styrene derivatives carrying a methyl group in the β -position, dimerization was not observed up to 1 ms, which is probably due to steric hindrance of this reaction by the β -substituent. The electronic effect of the methyl group (electron-donating) operates in the same direction. Since these radical cations $M^{\bullet+}$ are unreactive towards M, they decay predominantly by neutralization. On the basis of the presently available data, it cannot be distinguished whether the β -substituent inhibits the reaction between $M^{\bullet+}$ and M already at the stage of π -complex formation or at the 'M–M⁺' production level. In general, it appears as if the reactivity of the styrene monomer radical cations is dominated by the C _{α} –C _{β} double bond. The reason for this is that spin and charge are mainly localized at this site.²⁹

The dimers **11** react in a way typical for carbenium ions,³⁰ e.g. in alkane solution, where there is no nucleophile available other than the parent, reaction takes place with the parent styrene [cf. reaction (4)]. The rate constant for this reaction was determined by using 0.03 to 0.1 mol dm⁻³ styrene as scavenger for the radiation-induced solvent radical cations to make the electron transfer (1) fast. Under these conditions a superposition of non-homogeneous kinetics, caused by spur scavenging reactions,^{5b} and the homogeneous kinetics typical for scavenger concentrations below 2 mmol dm⁻³ was observed. The rate of this trimerization was determined (from the kinetic analysis of the dimer radical cation decay characteristics) to be in the range 2×10^6 to 2×10^7 dm³ mol⁻¹ s⁻¹, similar to those found for the average chain propagation rate^{1–3} of the radiation-induced polymerization *via* free, i.e. non-ion paired, radical cations. An influence of the 4-substituent of the aromatic ring exists but appears to be small. More data are probably necessary to discern structure–reactivity relations.

The studies using pulse radiolysis of styrenes in alkane solution yielded information about the first steps of the free cationic polymerization. The reaction sequence (16) summarizes the observations.

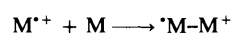


From the experiments involving the styrene radical cation kinetics in polar media, information about reactivity of 'strongly solvated' styrene radical cations and on their behaviour with respect to nucleophiles is expected. In aqueous or alcoholic solutions the radical cations were generated by pulse radiolysis as well as by laser photolysis, as described above [reactions (9), (10) and (13)]. Ionization of the styrenes by consecutive two-photon absorption turned out to be a particularly simple and efficient way of radical cation formation. In the case of the styrenes **1** to **10**, ionization took place in ≤ 3 ns as indicated by

the appearance of the solvated electron. Only with the 4-methoxy derivatives **6** and **7** the radical cations could be observed. In the cases **1–5** and **8–10** where there is no methoxy substituent, only β -hydroxy-substituted benzyl type radicals were detected (e.g. cf. Fig. 11). These radicals are formed within the subnanosecond time range by the reaction of the primarily produced radical cations with the nucleophile H₂O according to reaction (11). This means that the lifetime of the radical cation is ≤ 3 ns. Thus, $k_{14}[\text{H}_2\text{O}] > 3 \times 10^8$ s⁻¹ or $k_{14} > 6 \times 10^6$ dm³ mol⁻¹ s⁻¹ (see Table 1). In less electrophilic solvents such as acetonitrile and fluorinated alcohols, the styrene radical cations are expected to be longer-lived. Indeed, radical cations have been produced²³ by electron transfer from styrenes to the excited chloranil triplet in aprotic media, with absorption spectra similar to those observed in our pulse radiolysis experiments in cyclohexane.

In contrast to this, radical cations well-observable on the nanosecond timescale could be generated from the methoxy-substituted styrenes **6** and **7**. The radical cations decay in water with a rate constant $k = 3.3 \times 10^6$ s⁻¹, similar for both substances. The radical cation of *trans*-anethole **7** shows no dimerization tendency, a behaviour similar to that in cyclohexane solution. The 4-methoxystyrene **6** radical cation, however, reacts with its parent with $k = 2 \times 10^9$ dm³ mol⁻¹ s⁻¹, which is five times lower than in cyclohexane solution. A factor contributing to this difference in reaction rate may be a larger degree of solvation of the radical cation in water. The dimerization product, radical cation **11**, cannot be observed in aqueous solution, which is the consequence of its very high electrophilic reactivity, due to its carbenium ion character. The distonic radical cation of **6** decays rapidly according to reaction (14). Products of this reaction should be dimerized radicals, also β -hydroxy-substituted radicals as found for the products of reaction (11).

In aqueous solution, reactions of the styrene radical cation with nucleophiles other than the solvent, such as, e.g. Br⁻, Cl⁻, were not observed. This is the result of the unfavourable competition situation for these nucleophiles. Scheme 1 summarizes the reactions observed in aqueous solution.



Scheme 1

In summary, the experiments on the mechanism and kinetics of styrene radical cations in polar as well as non-polar media enabled a deeper insight into the primary processes of radiation-induced free cationic polymerization and yielded information on structure and reactivity of radical cations including distonic radical cations. The latter have a reactivity more comparable with carbenium ions than with radical cations.

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