Photolysis of Tris(4-*tert*-butoxycarbonyloxyphenyl) Sulphonium Salts. A Mechanistic Study

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Tris(4-*tert*-butoxycarbonyloxyphenyl)sulphonium salts of the structure $Ar_3S^+X^-$ (X^-: $CF_3SO_3^-$ or AsF_6^-) were irradiated with UV light in acetonitrile or dimethyl sulphoxide solution. Product analysis by ion pair chromatography (IPC), ^1H NMR measurements and IR spectroscopy revealed that simultaneously bis(4-*tert*-butoxycarbonyloxyphenyl) sulphide, Ar_2S, and a protonic acid (CF_3SO_3H or $HAsF_6$) were formed. The latter catalyses the decomposition of the *tert*-butylcarbonate groups in the absence of water at room temperature. In the presence of water the acids dissociate, and H_3O^+ ions, thus formed, only catalyse the decomposition significantly at elevated temperatures ($T > 70\,°C$). Therefore, photolysis products formed in the absence of water consist, apart from $(4\text{-}HO\text{-}C_6H_4)_2S$, essentially of a mixture of salts of the ions: $Ar_2(4\text{-}HO\text{-}C_6H_4)S^+$, $Ar(4\text{-}HO\text{-}C_6H_4)_2S^+$ and $(4\text{-}HO\text{-}C_6H_4)_3S^+$. In addition to these products, $(Bu^tOCO_2\text{-}C_6H_4)_2S$ and an as yet unidentified product were formed when the irradiation was performed in the presence of water. Quantum yields (in the absence of water) determined by IPC are: $\varphi[-\text{salt}] = 0.2$ and $\varphi[(4\text{-}HO\text{-}C_6H_4)_2S] = 0.1$.

Recently, various sulphonium salts, such as triarylsulphonium salts of the general formula **I**,

$$Ar_3S^+X^-$$

I

$$X = BF_4, AsF_6, PF_6 \text{ or } CF_3SO_3$$

have attracted great attention because of their efficiency in acting as photoinitiators.[1-5] The mode of action refers, in this case, to the generation of protons which are formed upon UV irradiation of triaryl sulphonium salts. Two mechanisms based on homolytic or heterolytic bond scission, respectively, have been proposed for proton generation,[6,7] as can be seen from Scheme 1.

Homolytic bond scission

$$Ar_3S^+X^- \xrightarrow{h\nu} [Ar_3S^+X^-]^* \longrightarrow Ar_2S^{\cdot +} + Ar^{\cdot} + X^- \quad (1)$$

$$Ar_2S^{\cdot +} + RH \longrightarrow Ar_2HS^+ + R^{\cdot} \quad (2)$$

$$Ar_2HS^+ \longrightarrow Ar_2S + H^+ \quad (3)$$

Heterolytic bond scission

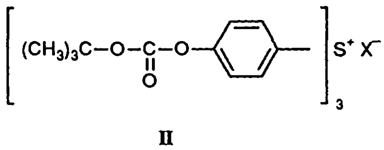
$$[Ar_3S^+X^-]^* \longrightarrow Ar_2S + Ar^+ + X^- \quad (4)$$

$$Ar^+ + RH \longrightarrow Ar - R + H^+ \quad (5)$$

Scheme 1 Proton generation by photolysis of sulphonium salts

Since the photolysis of compounds **I** leads to the formation of protons, they can be used to initiate the cationic polymerization of appropriate monomers or the crosslinking of polymers possessing appropriate functional groups. In fact, protons act as a catalyst in these processes and, therefore, only rather low proton concentrations and, consequently, only rather low absorbed doses are needed for the initiation. This implies 'chemical amplification' with respect to the action of the primary photochemical reaction. At present, photoinitiators giving rise to chemical amplification play a dominant role in the technical applications of photoresist formulations operating on the solubility inhibitor principle. Commonly, such formulations consist, apart from the photoinitiator, of a polymer whose solubility is prevented by the presence of a low molecular weight additive, denoted as a solubility inhibitor. The polymer becomes soluble upon decomposition of the latter by irradiation. Quite recently, sulphonium salts acting both as photoinitiator and solubility inhibitor have been synthesized in the laboratories of BASF AG.[8-10] They are quite appropriate for applications in photoresist formulations used for the generation of submicrometer line patterns. The structure of these sulphonium salts which have been introduced to the technical community as SUCCESS (sulphonium compounds containing expellable sophisticated side groups) corresponds to **I**, with Ar partially being the *tert*-butoxycarbonyloxyphenyl group.

This work concerns experiments performed with tris(*tert*-butoxycarbonyloxyphenyl)sulphonium salts (**II**) in acetonitrile and dimethyl sulphoxide (DMSO) solutions. Product analysis and flash photolysis studies were aimed at elucidating the mechanism of the photolysis of salts of type **II**. Special attention was given to the question of whether water influences the photolysis of **II**.



II

a $X = CF_3SO_3$
b $X = AsF_6$

Experimental

Synthesis of **II**.—Bis-4-hydroxyphenyl sulphide (5.46 g) was converted to the sulphonium salt by reaction with bis(4-

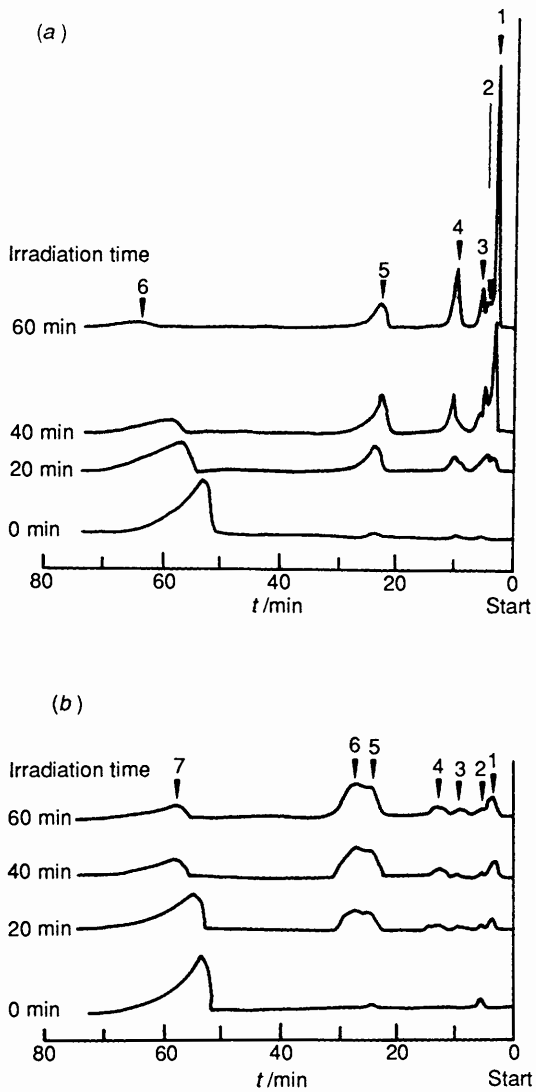


Fig. 1 Continuous irradiation of **IIa** (1×10^{-3} mol dm^{-3}) in Ar-saturated acetonitrile solution in the absence and presence of water. IP chromatograms of solutions of **IIa** recorded before and after continuous irradiation at $\lambda_{inc} = 254$ nm: (*a*) in the absence and (*b*) in the presence of water (1%, v/v)

hydroxyphenyl)iodonium salt (11.75 g), by analogy with the procedure described by Crivello and Lam for the synthesis of triphenylsulphonium salts.[5] The resulting tris(4-hydroxyphenyl)sulphonium salt (52%) was dissolved in dry tetrahydrofuran (THF) and treated first with potassium *tert*-butoxide and subsequently with di-*tert*-butyl dicarbonate. The salt was purified in the following manner. A dichloromethane solution was washed with aqueous Na_2CO_3 (1%, w/w), and the organic phase was separated and dried over Na_2SO_4. After evaporation of the solvent the salt was recrystallized from ethanol. In this study two salts were used: hexafluoroarsenate, $[(Bu^tOCO_2-C_6H_4)_3S^+AsF_6^-]$ and trifluoromethylsulphonate (triflate), $[(Bu^tOCO_2-C_6H_4)_3S^+CF_3SO_3^-]$ [Found (arsenate: C, 49.5; H, 5.0; S, 4.1; As, 8.7; F, 12.8. $C_{33}H_{39}SAsF_6O_9$ requires C, 49.5; H, 4.9; S, 4.0; As, 9.4; F, 14.2) (triflate: C, 54.0; H, 5.2; S, 9.0; F, 7.6. $C_{34}H_{39}S_2F_3O_{12}$ requires C, 53.7; H, 5.1; S, 8.4; F, 7.5)].

Solvents.—Acetonitrile (Merck) was distilled after boiling overnight with CaH_2. It was stored over molecular sieves. DMSO (Uvasol grade), and deuteriated solvents [$^2H_6$]DMSO and D_2O, both 99.9% pure, were obtained from Fluka and were used without further treatment.

Continuous Irradiations.—Salt solutions were irradiated in rectangular quartz cells either at $\lambda_{inc} = 254$ nm (light emitted by a low pressure mercury lamp) or at $\lambda_{inc} = 280$ nm (light emitted by a xenon lamp passing through a monochromator set in front of the quartz cell). In the case of NMR studies air-saturated solutions were irradiated in rectangular quartz cells (1×1 cm) with the light of a 200 W high pressure mercury lamp which passed a filter (Schott, UG 5; $\lambda_{max} = 325$ nm, FWHM 100 nm) immersed in water. The irradiated solutions were transferred to NMR tubes for measurement. Actinometry was performed with the aid of the potassium ferrioxalate actinometer.[11]

Flash Photolysis.—Direct excitation was performed by irradiating salt solutions in rectangular quartz cells with single flashes of 266 nm light (flash duration 20 ns) generated by a Nd-YAG laser system operated in conjunction with two frequency doublers. Transient photocurrents were measured by applying an AC technique similar to that described by Lilie and Fessenden.[12]

Product Analysis.—The ion-pair chromatography set-up consisted of a pump (Beckman 114 M), a column (Knauer, LiChroSorb RP 18, 5 µm) and a UV-detector (Knauer, Variable wavelength monitor) operated at $\lambda = 254$ nm. The eluent passing the column at 45 °C with a flow rate of 1 cm^3 min^{-1} was a mixture of 2 cm^3 K2 solution (Knauer, Berlin), 228 cm^3 water and 770 cm^3 acetonitrile (Merck). The injection volume was 20 mm^3.

A FT-NMR spectrometer (Bruker WP80) operating at 80.13 MHz was used to obtain ^1H NMR spectra, which were recorded at room temperature.

A Perkin-Elmer FTIR spectrometer, model 1760 X was used to record IR spectra. Spectra of acetonitrile solutions were recorded at room temperature in a gas-tight cell which was irradiated with the light of a 200 W high pressure mercury lamp using a Schott filter (UG 5). Spectra were taken every 10 s during a total irradiation time of 2 min.

Results

Continuous Irradiations: Product Analysis.—Ion-pair chromatography. Fig. 1 shows IP chromatograms recorded with samples irradiated in acetonitrile solutions both in the absence and presence of H_2O. The position of the peak of the parent ion $(Bu^tOCO_2-C_6H_4)_3S^+$, located at retention times $t_R > 47$ min, depends on the salt concentration. The peak is shifted to higher retention times with decreasing concentration. This was evidenced by recording a calibration curve with compound **IIa** which revealed that the peak area increased linearly with the salt concentration although the peak position was shifted. From Fig. 1 it can be seen that the $(Bu^tOCO_2-C_6H_4)_3S^+$ ion concentration decreases in both cases with increasing time of irradiation. Fig. 2 shows the conversion of the salt *vs.* the irradiation time. Obviously, water retards the conversion of **IIa**. From the initial slope of the curves the following quantum yields are obtained: $\varphi[-\text{salt}] = 0.2$ ('dry' CH_3CN) and $\varphi[-\text{salt}] = 0.1$ ('wet' CH_3CN). The same quantum yield resulted from irradiations of solutions containing either 1 or 10% (v/v) water. From Fig. 1 it can be seen that the chromatograms of the unirradiated samples exhibit, apart from the peak of the parent ions, small peaks which are assigned to the ions $(Bu^tOCO_2-C_6H_4)_2S^+(4\text{-HO-}C_6H_4)$, $(Bu^tOCO_2-C_6H_4)S^+(4\text{-HO-}C_6H_4)_2$ and $(4\text{-HO-}C_6H_4)_3S^+$ at $t_R \approx 20$, 7 and 3.5 min, respectively, resulting from partial or full conversion of the *tert*-butylcarbonate groups of the parent ions into hydroxy groups as described by eqn. (6).

This assignment was arrived at by recording IP chromato-

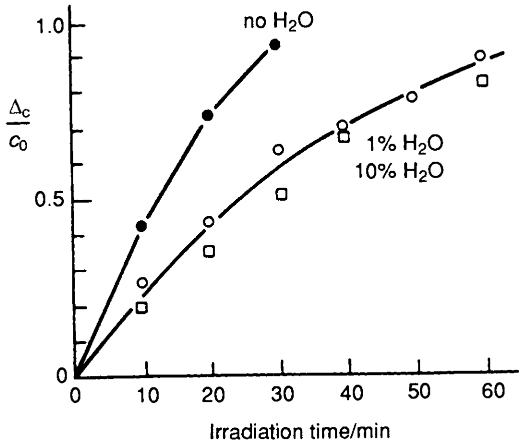
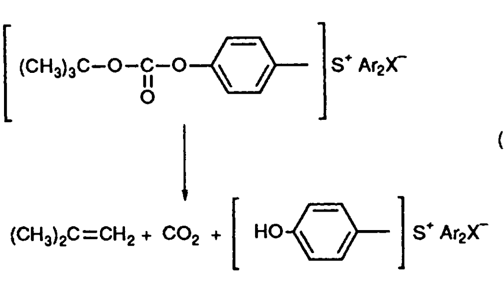


Fig. 2 Continuous irradiation of **IIa** (1×10^{-3} mol dm^{-3}) in Ar-saturated acetonitrile solution in the absence and presence of water (○ 1%, □ 10%). Conversion of the sulphonium salt as a function of irradiation time. $Dr_{abs} = 2.0 \times 10^{-4}$ Einstein dm^{-3} min^{-1}, $\lambda_{inc} =$ 254 nm



(6)

grams of acetonitrile solutions of **IIa** containing CF_3SO_3H. It can be seen from Fig. 3 how the conversion of the *tert*-butylcarbonate groups proceeded as a function of time after the addition of the acid. It is noteworthy that the conversion was drastically retarded by water. In fact, rates comparable to those observed in dry acetonitrile were measured only at elevated temperatures ($T > 70$ °C). This is explained by the fact that the protonic acid formed according to the mechanisms depicted in Scheme 1 dissociates in aqueous acetonitrile. Obviously, in contrast to CF_3SO_3H or $HAsF_6$, H_3O^+ is hardly capable of catalysing the conversion of the *tert*-butylcarbonate groups at room temperature.

By comparing the IP chromatograms shown in Fig. 1(*a*) and (*b*) it becomes obvious that water drastically affects the formation of photoproducts. In dry acetonitrile solution the ions $(Bu^tOCO_2-C_6H_4)_2S^+(4-HO-C_6H_4)$, $(Bu^tOCO_2-C_6H_4)S^+(4-HO-C_6H_4)_2$ and $(4-HO-C_6H_4)_3S^+$ are formed by irradiation as indicated by the growth of the peaks 3–5, respectively. Most interestingly, a large peak at $t_R \approx 1$ min (peak 1) grows as irradiation continues. By comparison with the chromatogram of the authentic sample this peak was assigned to di-4-hydroxyphenyl sulphide, $(4-HO-C_6H_4)_2S$, which seems to be formed very rapidly from primarily generated $(Bu^tOCO_2-C_6H_4)_2S$ by acid catalysed conversion of the *tert*-butyl carbonate groups into OH groups. The area of peak 1 increased linearly with irradiation time and with the aid of a calibration curve the quantum yield $\varphi[(4-HO-C_6H_4)_2S] = 0.1$ was obtained. Interestingly, $(Bu^tOCO_2-C_6H_4)_2S$, the unconverted disulphide, was not observed by IP chromatography. The IP chromatograms recorded in these experiments contain another peak (number 2, $t_R \approx 1.5$ min) that was tentatively assigned to isobutene, $(CH_3)_2C{=}CH_2$. In water-containing acetonitrile solution the ions $(Bu^tOCO_2-C_6H_4)_2S^+(4-HO-C_6H_4)$, $(Bu^tOCO-C_6H_4)S^+(4-HO-C_6H_4)_2$ and $(4-HO-C_6H_4)_3S^+$ are also formed, as can be seen from the chromatograms presented in Fig. 1(*b*) (peaks 2, 3 and 5). Notably, $(HO-Ph)_2S$ is also formed (peak 1), but to a much lower extent than in the absence of water. On the other hand, $(Bu^tOCO_2-C_6H_4)_2S$ is clearly detectable in this case (peak 4, $t_R \approx 10.5$ min). Moreover, another new peak (6) at $t_R \approx 24.5$ min grows in this case. It has not yet been identified and is ascribed to a product resulting from the reaction of water with $(Bu^tOCO_2-C_6H_4)_2S^{\cdot+}$, the primarily generated radical cation, eqn. (7).

$$(Bu^tOCO_2-C_6H_4)_2S^{\cdot+} + H_2O \longrightarrow (Bu^tOCO_2-C_6H_4)_2\dot{S}-OH + H^+ \quad (7)$$

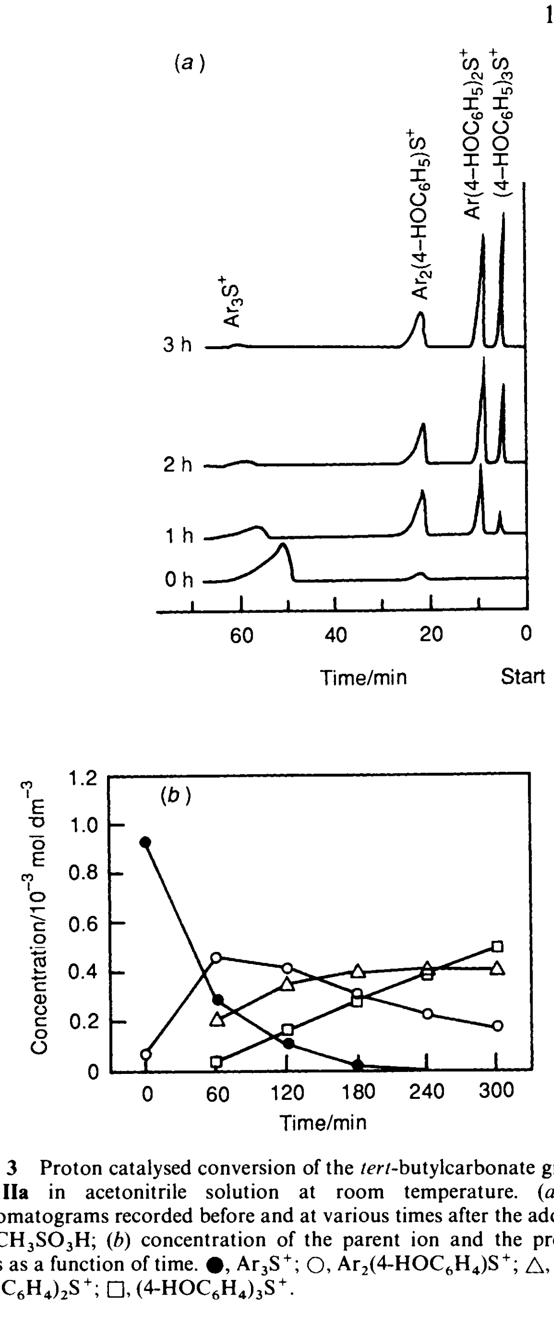


Fig. 3 Proton catalysed conversion of the *tert*-butylcarbonate groups of **IIa** in acetonitrile solution at room temperature. (*a*) IP chromatograms recorded before and at various times after the addition of CH_3SO_3H; (*b*) concentration of the parent ion and the product ions as a function of time. ●, Ar_3S^+; ○, $Ar_2(4-HOC_6H_4)S^+$; △, $Ar(4-HOC_6H_4)_2S^+$; □, $(4-HOC_6H_4)_3S^+$.

Concerning the quantum yield of the photolysis of **II** according to eqn. (1) or (4), an order of magnitude estimate on the basis of the yield of the formation of di-4-hydroxyphenyl sulphide in dry acetonitrile yields $\varphi \approx 0.1$. This value compares fairly well with $\varphi[(4-HO-C_6H_4)_2S^+] = 0.16$ determined by IP chromatography for the photolysis of $(4-HO-C_6H_4)_3S^+ CF_3SO_3^-$. In former work, $\varphi[(Ph)_2S] = 0.26$ was found in the case of the photolysis of $(Ph)_3S^+AsF_6^-$.[13,14]

^1H *NMR measurements.* The results obtained by IP chromatography were corroborated to some extent by ^1H

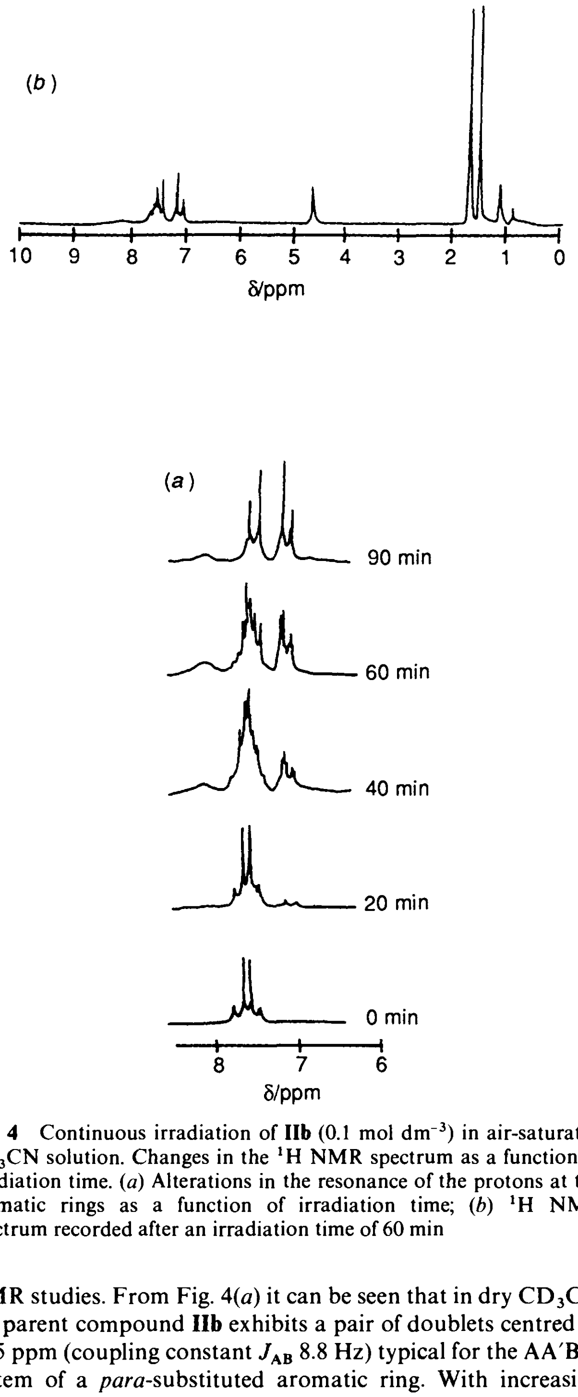


Fig. 4 Continuous irradiation of **IIb** (0.1 mol dm^{-3}) in air-saturated CD_3CN solution. Changes in the ^1H NMR spectrum as a function of irradiation time. (*a*) Alterations in the resonance of the protons at the aromatic rings as a function of irradiation time; (*b*) ^1H NMR spectrum recorded after an irradiation time of 60 min

NMR studies. From Fig. 4(*a*) it can be seen that in dry CD_3CN the parent compound **IIb** exhibits a pair of doublets centred at 7.65 ppm (coupling constant J_{AB} 8.8 Hz) typical for the AA′BB′ system of a *para*-substituted aromatic ring. With increasing irradiation time this signal pattern disappears and a new pair of doublets centred at *ca.* 7.26 ppm (J_{AB} 11.4 Hz) is formed together with a broad signal at 8.1 ppm indicating the presence of OH groups [see Fig. 4(*b*)]. Apart from the signals at 4.66 and 1.7 ppm the final spectrum obtained is almost equal to that of $(4\text{-HO–}C_6H_4)_3S^+$. The two additional lines are assigned to isobutene which is formed by the conversion of the *tert*-butylcarbonate groups. Notably, irradiation of **IIb** in the presence of water (solvent DMSO–D_2O) also resulted in the disappearance of the pair of doublets centred at 7.89 ppm (J_{AB} 8.8 Hz) and the simultaneous formation of a new pair of doublets centred around 7.37 ppm (J_{AB} 8.8 Hz). Concomittantly, the methyl group signal at 1.56 ppm disappeared and a new signal at 1.54 ppm was formed. These changes are due to the formation of $(Bu^tOCO_2–C_6H_4)_2S$ which was confirmed by comparing the spectrum obtained (see Fig. 5) with the ^1H NMR spectrum of authentic $(Bu^tOCO_2–C_6H_4)_2S$. The formation of the H_2O peak at *ca.* 3.4 ppm is mainly due to atmospheric moisture which is absorbed by the solution and presumably also in part due to a H–D proton exchange. The shift of this peak to lower field strength with increasing irradiation time reflects the increase in acidity due to the photolytic formation of protons.

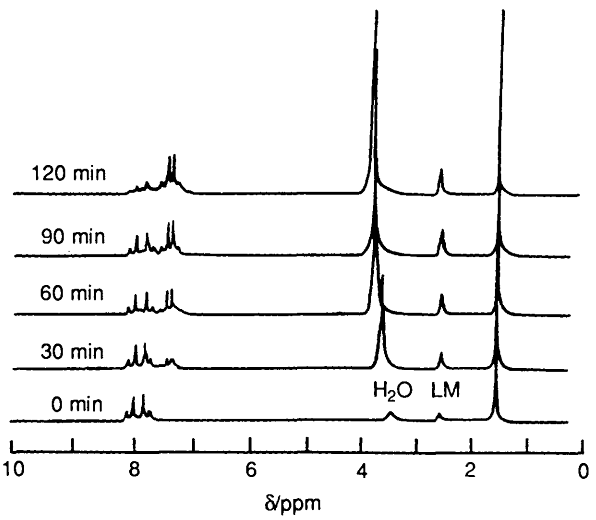


Fig. 5 Continuous irradiation of **IIb** (0.1 mol dm^{-3}) in air-saturated [$^2H_6$]DMSO–D_2O. Changes in the ^1H NMR spectrum as a function of irradiation time

IR Measurements.—Significant light-induced changes in the IR spectrum of **IIa** were observed at *ca.* 2343 cm^{-1} and *ca.* 1765 cm^{-1} as can be seen from Fig. 6. The band at 2343 cm^{-1} is assigned to CO_2 which is formed during the conversion of the *tert*-butylcarbonate groups according to eqn. (6). The band at 1765 cm^{-1} is the carbonyl stretching mode of **IIa**. In the case of the photoproduct $(Bu^tOCO_2–C_6H_4)_2S$ the carbonyl stretching mode is located at 1759 cm^{-1} as was concluded on the basis of the authentic IR spectrum of this sulphide. Obviously, significant amounts of CO_2 are formed only in the absence of H_2O [see Fig. 6(*a*) and (*b*)], which is in accordance with the fact (*vide ante*) that, in the absence of water, *tert*-butylcarbonate groups are strongly affected, but in its presence they are quite stable. Irradiation of **IIa** in 'wet' acetonitrile results in the formation of $(Bu^tOCO_2–C_6H_4)_2S$ which is reflected by the shift in the carbonyl stretching band from 1765 to 1759 cm^{-1} [Fig. 6(*d*)]. In water-free solution, on the other hand, the 1765 cm^{-1} band disappears much faster than in 'wet' acetonitrile and the formation of the band at 1759 cm^{-1} is much less pronounced [Fig. 6(*b*)]. Interestingly, both bands, at 1765 and 1759 cm^{-1}, decreased after irradiation at room temperature indicating the catalytic activity of the photolytically-generated undissociated acid with respect to the conversion of *tert*-butylcarbonate groups of both **IIa** and Ar_2S into phenol groups. The formation of the latter was also detected by the build-up of a broad band around 3350 cm^{-1}.

Flash Photolysis Studies.—Fig. 7 shows typical oscilloscope traces obtained upon irradiation of **IIb** in acetonitrile and acetonitrile–water mixtures. It can be seen that at first the signal voltage corresponding to the conductivity Λ increases very rapidly (actually during the flash) from Λ_0 to Λ' and later it decreases from Λ' to a constant value Λ''. In the absence of water Λ'' is lower than Λ_0, but at $[H_2O] = 40\%$ Λ'' is higher than Λ_0. These results are interpreted in terms of Ar_2S^+ ions being converted into ions of different mobility μ by taking into account the fact that the conductivity is proportional to $\mu(\Lambda \propto \mu)$. The initial increase in conductivity is due to the formation of $Ar_2S^{\cdot +}$ or Ar^+ (Scheme 1), *i.e.* of ions of larger

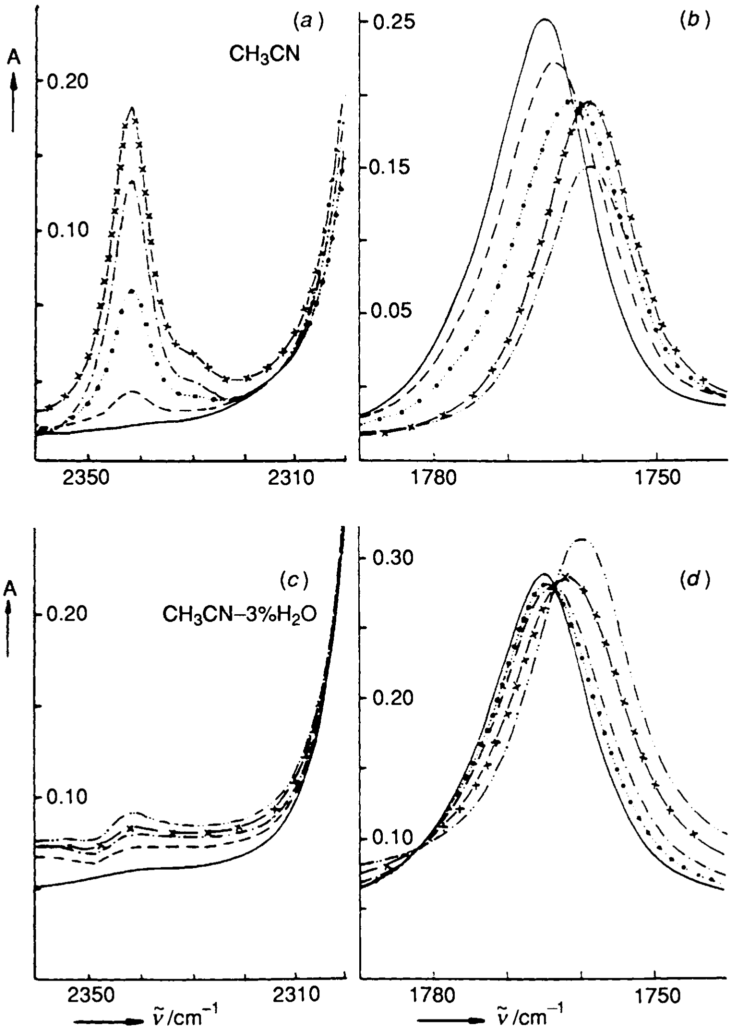


Fig. 6 Continuous irradiation of **IIa** (2.5×10^{-2} mol dm^{-3}) in air-saturated acetonitrile solution in the absence (*a*) and (*b*) and presence (*c*) and (*d*) of water (3%, v/v). Changes in the IR absorption spectrum as a function of irradiation time. —— (0 s); – – – (10 s); · · · (20 s); –·– (30 s); – × – (60 s); –··– (120 s).

mobility than that of Ar_3S^+. The subsequent decrease in conductivity reflects the formation of $HAsF_6$ which does not dissociate in water-free acetonitrile solution. Therefore, $\Lambda'' < \Lambda_0$ [Fig. 7(*a*)]. In the presence of water the acid dissociates according to eqn. (8), and therefore, $\Lambda'' > \Lambda_0$

$$HAsF_6 \xrightarrow{H_2O} H_3O^+ + AsF_6^- \qquad (8)$$

[Fig. 7(*b*)]. In fact, Λ'' increased gradually when the water concentration was increased. This can be seen from Fig. 7(*c*) where the signal voltage change ΔU corresponding to Λ'' is plotted *vs.* the water content of the solution.

Discussion

From the results obtained by continuous irradiation of **II** it is concluded that the primary photolytic reaction does not differ significantly from that observed with other non-substitued triaryl sulphonium salts. In other words, the mechanism described in Scheme 1 applies in this case also. This was clearly evidenced by the detection of $(4\text{-HO-}C_6H_4)_2S$ formed in the absence of water and of $(4\text{-HO-}C_6H_4)_2S$ and $(Bu^tOCO\text{-}C_6H_4)_2S$ formed in the presence of water. Regarding the quantum yield of the photolysis of **II** according to eqns. (1) and (4), $\varphi[(4\text{-HO-}C_6H_4)_2S)] \approx 0.1$ was found in dry acetonitrile. This value compares reasonably well with $\varphi[(4\text{-HO-}C_6H_4)_2S] = 0.16$ determined by IP chromatography for the photolysis of $(4\text{-HO-}C_6H_4)_3S^+CF_3SO_3^-$. In earlier work, $\varphi[(Ph)_2S)] = 0.26$ was found in the case of the photolysis of $(Ph)_3S^+AsF_6^-$.[11,12] It has been shown by Dektar and Hacker[15,16] that, in the photolysis of $(Ph)_3S^+AsF_6^-$, additional products [(phenylthio)biphenyl isomers] are formed at a total yield somewhat exceeding that of Ph_2S. Similar products were not looked for in this work. If they were also formed to a similar extent in the photolysis of **II** the total quantum yield would be $\varphi[-\mathbf{II}] \approx 0.2$ which compares well with $\varphi[-\mathbf{II}] = 0.2$ obtained by IPC. It should be pointed out that quantum yields for the decomposition of *tert*-butylcarbonate groups are much larger because of the catalytic effect of the protonic acid generated by the primary photolytic act on this process. Protonic acids such as CF_3SO_3H and $HAsF_6$ catalyse the decomposition of *tert*-butylcarbonate groups quite effectively even at room temperature and also after irradiation. This applies to water-free systems such as in this work, where fully and partially de-blocked triarylsulphonium ions were detected by IPC, NMR measurements and IR spectroscopy. In this case, the action of water applies mainly to the dissociation of the protonic acids and the formation of H_3O^+, which is a poor de-blocking catalyst at room temperature but becomes significantly effective as such at much higher temperatures (80–100 °C). Moreover, at relatively high concentrations water may react with the radical cation $(Bu^tOCO_2\text{-}C_6H_4)_2S^{\bullet+}$.

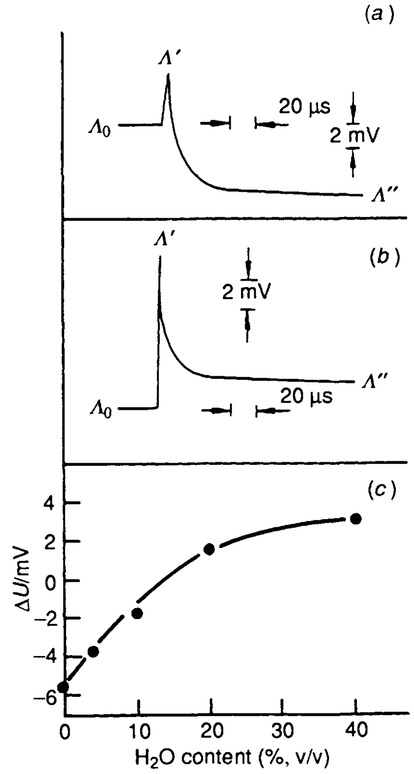


Fig. 7 Flash photolysis of **IIb** in Ar-saturated solutions: (*a*) acetonitrile and (*b*) acetonitrile–water (40%, v/v). Oscilloscope traces illustrating changes in the electrical conductivity during and after the 20 ns flash (λ_{inc} = 266 nm). [**IIb**] = 2×10^{-5} mol dm^{-3}. AC measurements, applied voltage: 40 V. (*c*) Dependence of Λ″ on the concentration of water in acetonitrile solution at constant absorbed dose.

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