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Excited state reactions of acridinedione dyes with onium salts: mechanistic details☆

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Abstract

Diaryliodonium and triarylsulphonium salts are thermally stable UV photoinitiators for cationic polymerization. Diaryliodonium salts (DPI-1–7) and triarylsulphonium (type-I, type-II and type-III) salts with different substituent have been prepared. Excited state reactions of these onium salts with decahydroacridinedione dyes (ADD-1–6) have been studied. ADD acts as an efficient sensitizer for the decomposition of these onium salts. Photosensitization occurs through electron transfer, which is confirmed by the observation of enol radical cation of ADD and diarylsulphinium radical cation in the laser flash photolysis. The mechanism of photosensitization and the mechanism of photoacid release have been discussed. Both singlet and triplet state of the ADD are involved in the photosensitization of diaryliodonium salts, whereas singlet state of ADD is alone involved in the photosensitization of triarylsulphonium salts. The quantum yield of photoacid generated in direct and the sensitized process is determined and this allows to gauge the practical efficiency of onium salts/ADD combinations as the photoinitiator for the cationic polymerization applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Acridinedione dyes; Diaryliodonium salts; Triphenylsulphonium salts; Photoacid generation; Photosensitization

1. Introduction

Cationic photoinitiators have found a wide range of uses in UV-curing technologies, microlithography, photodoping to make conducting polymers, holography and other optical applications [1]. The onium salt with non-nucleophilic counter anion on irradiation with UV light produces the corresponding Brönsted acid that can be used to rapidly polymerize the epoxides. The fundamental process involved in the photolysis of onium salt and the mechanism of the photoinitiation was studied by Crivello and Lam [2,3]. Since Brönsted acid is the initiating species, the nucleophilicity of anion has a decisive role to play in the rate and on the overall efficiency of the polymerization process. The efficiency of the initiator towards the polymerization process increases with the decreasing nucleophilicity ($BF_4^- < PF_6^- < AsF_6^- < SbF_6^-$) of the counter anion.

Among the onium salts, diaryliodonium and triarylsulphonium salts are most important cationic photoinitiators. The efficiency of onium salt as photoinitiator depends on the structure of the cationic and anionic moieties of the onium salts. The spectral sensitivity can be extended to near UV region by substituting electron withdrawing or donating groups in the phenyl ring. In this way, diaryliodonium salt with different substituents have been prepared to get compounds with improved absorption characteristics. Structural modification of sulphonium salts have been reported by Crivello [4] et al. and the photoinitiator activity of complex sulphonium salts have been reported to be greater than the corresponding triarylsulphonium salts.

The onium salts have their primary absorption band in the UV region (below 300 nm). So, it is necessary to extend the spectral sensitivity of the onium salts to improve the efficiency of polymerization process in the visible region. The spectral sensitivity can be extended to longer wavelength by introducing a long wavelength absorbing chromophore, into the onium salts, but their synthetic complexities prevent their application in industry. Alternatively, the spectral sensitization of onium salts can be achieved by photosensitization using several organic dyes as photosensitizer. Photosensitization of diaryliodonium salts and triarylsulphonium salts occur by energy transfer, electron transfer, and redox sensitization.

Sensitization of iodonium salts by ketocoumarin [5] and thioxanthone [6] occur through electron transfer involving

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☆ Dedicated to Professor V.T. Ramakrishnan on the occasion of his 60th birth anniversary.

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the triplet state, whereas in the case of anthracene and 9,10-diethoxyanthracene [7,8] electron transfer from singlet state was observed. Linden and Neckers [9] observed the quenching of excited singlet state of Rose Bengal disodium and monosodium salts by iodonium salts with a bimolecular quenching rate constant in methanol, though it seems clear that in this solvent these compounds exist as solvent separated ion pairs. Photosensitization of triarylsulphonium salts by anthracene, pyrene [10], ketocoumarins and heterocyclic amines [11] occur through electron transfer. Photosensitization of iodonium salts with trifluoroacetophenone and acetone occur through energy transfer involving the triplet state [12] and the triplet energy of iodonium salts are found to be around 269 kJ mol^{-1}. The triplet sensitized decomposition of diaryliodonium salts proceeds by heterolytic cleavage mechanism, which gives aryliodonium radical cation and aryl radical. The triplet energy of triarylsulphonium salts has been found to be about 315 kJ mol^{-1} by phosphorescence spectroscopy [13]. Triplet sensitizers like acetone, acetophenone, 1-indanone [14,15] sensitize the triarylsulphonium salts by energy transfer involving the triplet state. Photosensitization of iodonium salts with benzophenone and acetophenone are mediated by hydrogen donors. The excited state of the benzophenone abstracts hydrogen from the H-donors and thereby producing radical, which in turn reduce the diaryliodonium salts involving radical chain mechanism [4]. Triarylsulphonium salts do not undergo such type of decomposition, due to their more negative reduction potentials.

Acridinedione dyes are new family of laser dyes, which operate in the blue green region with efficiencies comparable to that of coumarin-102 [16]. The dye can function as both electron donor and acceptor and their electrochemical [17], photophysical [18,19] and excited state reaction have been investigated [20]. Acridinedione sensitized decomposition of onium salts involves electron transfer reaction with high barrier for the solvent reorganization energy [21]. Consequently, the efficiency of photodecomposition is lower in protic solvents compared to non-protic solvents. Timpe et al. [22] reported radical polymerization of methyl methacrylate which is based on the decahydroacridinedione and onium salts combinations as photoinitiator. In this study, we have prepared diaryliodonium salts (DPI-1–7) and triphenylsulphonium salts (type-I, type-II and type-III) with different substituents. The excited state reaction of these onium salts with decahydroacridinedione dyes have been studied using fluorescence and laser flash photolysis studies. Photosensitization involves the electron transfer from the excited decahydroacridinedione to the onium salts. Electron transfer is confirmed by the detection of ADD enol radical cation and the diarylsulphinium radical cations in the laser flash photolysis. Steady photolysis of the onium salts produces Brönsted acid and the quantum yields of acid release by direct and sensitized decomposition of onium salts were determined. The quantum yield of acid release in each process was used to determine practical efficiency of iodonium salt or sulphonium salt/ADD combinations as the photoinitiators for the cationic polymerization and the details of the excited state reactions are discussed.

2. Experimental details

2.1. Materials

Acridinedione dyes have been synthesized by the procedure reported in the literature [17]. Diphenyliodonium salts (1–7) and triarylsulphonium salts (type-I, type-II and type-III) with various substituents (Fig. 1) have been prepared by the procedure reported in literature [4,23,24]. All solvents used are HPLC grade obtained from Qualigens, India.

2.2. Absorption and fluorescence spectra

The absorption spectra were recorded using Hewlett-Packard 8542A diode array spectrophotometer. The fluorescence quenching experiments were carried out using a Perkin-Elmer spectrofluorimeter. For all the quenching experiments, the ADD concentration was adjusted to have an absorbance of 0.1 and concentration of quenchers was normally in the order of 10^{-3}–10^{-1} M.

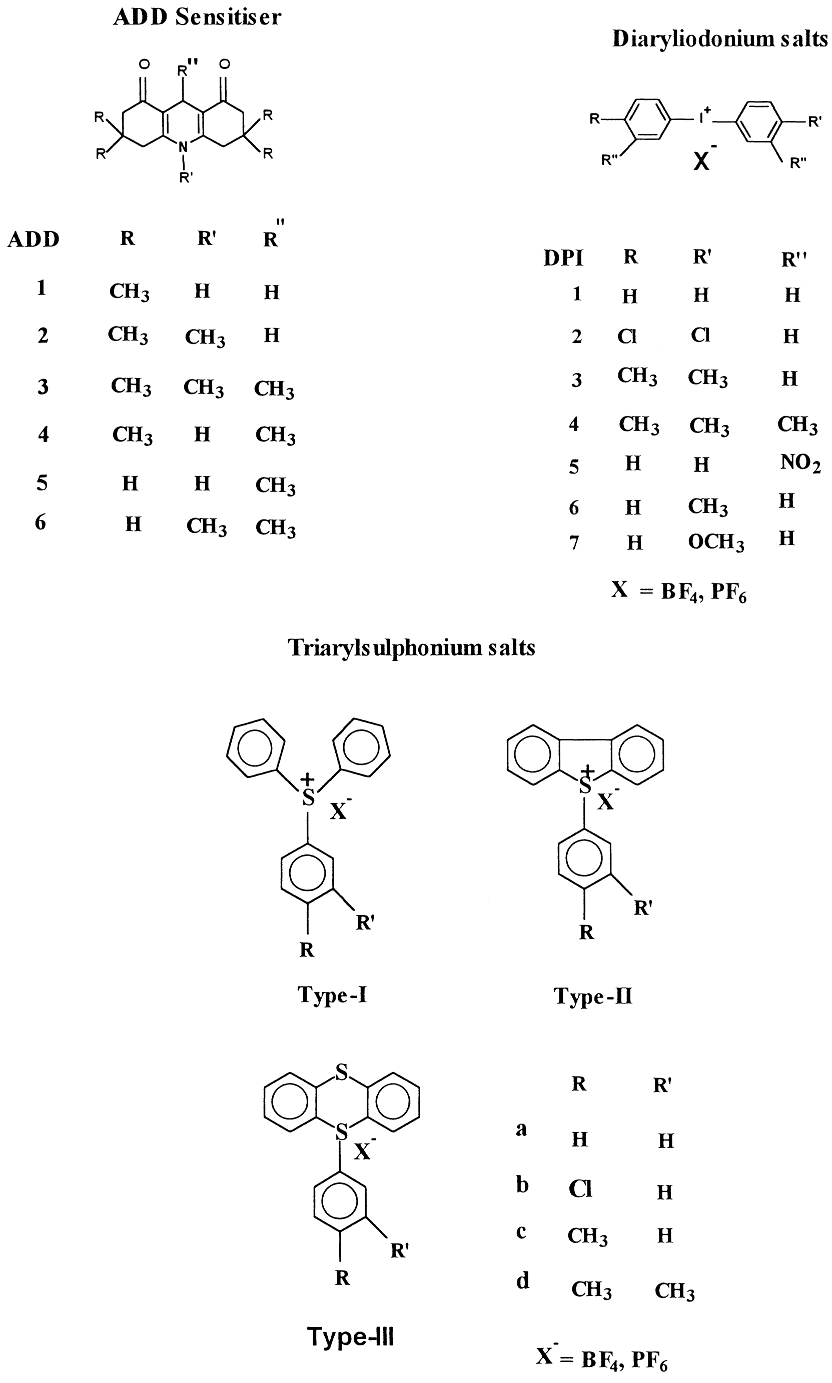
2.3. Laser flash photolysis

Transient spectra and triplet quenching experiments were carried out using nanosecond laser flash photolysis. For laser excitation using third (355 nm) and fourth (266 nm) harmonics output from Quanta Ray GCR-2 (Spectra Physics, USA) Nd-YAG laser with a pulse width of 8 ns was used in right-angled geometry and with a 1 cm pathlength cell. The signals were detected using a 250 W pulsed xenon lamp, a Czerny–Turner monochromator and R-928 PMT. The signals were captured in a Hewlett-Packard 54201A digital storage oscilloscope. Kinetic analysis were carried out using the software described elsewhere [25]. For all the studies the solutions were deaerated by purging argon gas (30 min) prior to the experiments.

2.4. Quantum yield of acid release

The quantum yield of acid release by the iodonium and sulphonium salt solution on photolysis was determined with help of pH indicator sodium bromophenol blue. The band at 595 nm is due to the basic form of the indicator and change in absorbance at 595 nm was used to monitor the amount of acid release on photolysis.

For direct photolysis 254 nm mercury pen ray lamp was used. For sensitized photolysis 420 nm light from 300 W xenon lamp (ILC Technology, USA) was isolated using glass



ADD	R	R'	R''
1	CH_3	H	H
2	CH_3	CH_3	H
3	CH_3	CH_3	CH_3
4	CH_3	H	CH_3
5	H	H	CH_3
6	H	CH_3	CH_3

DPI	R	R'	R''
1	H	H	H
2	Cl	Cl	H
3	CH_3	CH_3	H
4	CH_3	CH_3	CH_3
5	H	H	NO_2
6	H	CH_3	H
7	H	OCH_3	H

$X = BF_4, PF_6$

	R	R'
a	H	H
b	Cl	H
c	CH_3	H
d	CH_3	CH_3

$X^- = BF_4, PF_6$

Fig. 1. Structure of ADD sensitizers and the onium salts.

Table 1
Photophysical and electrochemical parameters of ADD sensitizers in methanol

Sensitizer	$E^{ox}_{1/2}$ vs. AgCl	Singlet lifetime (ns)	Singlet state energy (kcal mole^{-1})	Triplet lifetime (μs)	Triplet state energy[15] (kcal mole^{-1})
ADD-1	0.97	5.2	69.5	1.5	53.29
ADD-2	0.91	4.4	66.4	3.2	51.48
ADD-3	1.05	5.8	67.23	25.7	52.86
ADD-4	1.18	5.7	68.68	18.0	54.05
ADD-5	1.17	5.4	69.51	19.9	–
ADD-6	1.05	5.1	71.6	24.6	–

filters. The intensity of light was measured using ferrioxalate actinometry [26] for both the cases.

3. Results and discussion

3.1. Excited state reactions of diaryliodonium salts with ADD in methanol

3.1.1. Singlet state reactions

Some of the selected acridinedione dyes having low oxidation potential (below 1.02 V versus Ag/AgCl) undergo ground state reaction with iodonium salts. The oxidation potential [17] and the singlet state parameters [18,19] of the ADD dyes are given in Table 1. ADD-1 and ADD-2 have lower oxidation potential and show ground state reaction. The absorption spectra of ADD-3, ADD-4, ADD-5 and ADD-6 were unchanged on addition of iodonium salts, indicating the absence of ground state reaction. The fluorescence of ADD was effectively quenched by iodonium salts and the absence of any new peak in the emission spectrum excludes the exciplex formation. The quenching constants (k_q) were determined using the Stern–Volmer equation and the plots are linear upto 70% quenching of fluorescence intensity.

$$\frac{I_0}{I} = 1 + k_q \tau [Q] \tag{1}$$

where I_0 and I are the fluorescence intensity of ADD in the absence and in the presence of iodonium salts. Q is the concentration of iodonium salts and τ is the fluorescence lifetime of ADD in the absence of iodonium salts. The singlet quenching constants are close to the diffusion-controlled limit and are given in the Table 2. The observed quenching constants correlate with the reduction potential of iodonium salts except in the case of 3,3′-dinitrodiphenyliodonium (DPI-5) salt that may be due to the charge transfer interaction of –NO_2 group present in the iodoinium salt.

The diffusion rate constant was calculated using the Somoluchowski equation

$$k_d = \frac{4\pi RDN}{1000} \tag{2}$$

where R is the collision radius, D is the sum of the diffusion coefficient of the fluorophore and quencher and N is the Avogadro's number. The collision radii is the sum of the molecular radii of fluorophore and quencher and it can be calculated from PC MODEL Version-4. The diffusion coefficient of quencher and ADD dyes were calculated from Stokes–Einstein equation

$$D = \frac{kT}{6\pi \eta R} \tag{3}$$

where k is the Boltzmann constant and η is the solvent viscosity.

The k_d value calculated as above is in the order of $1.2 \times 10^{10}\,M^{-1}\,s^{-1}$. The quenching constants are varying from 0.4×10^{10} to $0.9 \times 10^{10}\,M^{-1}\,s^{-1}$ (except DPI-5). The observed quenching constants are lower than the calculated k_d value, which exemplify that all the collisions are not fruitful collisions and the quenching efficiency of iodonium salt is varying from 40 to 85%.

The mode of quenching can be attributed to electron or energy transfer. Quenching through singlet–singlet energy transfer is ruled out because of the higher singlet energy of iodonium salts. The free energy change for electron transfer quenching can be calculated using the Rehm–Weller expression

$$\Delta G_{et} = E_{1/2\,oxid} - E_{1/2\,red} - E^0 + C \tag{4}$$

where $E_{1/2\,oxid}$ is the oxidation potential of acridinedione, $E_{1/2\,red}$ is the reduction potential of iodonium salts, E^0 is the singlet energy of the sensitizer obtained from the intersection point of the absorption and emission spectra of ADD and C is the coulombic term. Since the ADD is neutral the C term is negligible. The reduction potential of iodonium salts [27,28] are in the same order, the calculated ΔG_{et} values are negative and very similar in magnitude. The k_q value increases as the ΔG_{et} becomes more negative and most of the data points lie in the plateau region of the Rehm–Weller plot. Due to this a clear Rehm–Weller approach of photoinduced electron transfer could not be observed. Further support for the electron transfer arises from the direct observation of radical intermediates in the laser flash photolysis studies.

Table 2
Singlet quenching constants (k_q^S) and ΔG_{et} of ADD by iodoniumm salts in methanol

Iodonium salt	Reduction potential[23] (V) vs. SCE	$k_q^S \times 10^{-10}$, $M^{-1}\,s^{-1}$ (ΔG_{et}, kcal mole^{-1})			
		ADD-3	ADD-4	ADD-5	ADD-6
1	−0.193	0.68 (−48.67)	0.75 (−47.12)	0.92 (−48.12)	0.86 (−53.04)
2	−0.200	0.69 (−48.51)	0.81 (−46.96)	0.98 (−48.08)	0.77 (−52.88)
3	−0.192	0.46 (−48.69)	0.59 (−47.17)	0.83 (−48.20)	0.51 (−53.06)
4	−0.192	0.44 (−48.69)	0.53 (−47.12)	0.61 (−48.2)	0.56 (−53.06)
5	−0.205	3.04 (−48.38)	3.49 (−46.84)	4.12 (−47.90)	4.71 (−52.75)
6	−0.18	0.49 (−48.82)	0.65 (−47.28)	0.64 (−48.30)	0.57 (−53.20)
7	−0.19	0.48 (−48.74)	0.63 (−47.19)	0.72 (−48.25)	0.55 (−53.11)

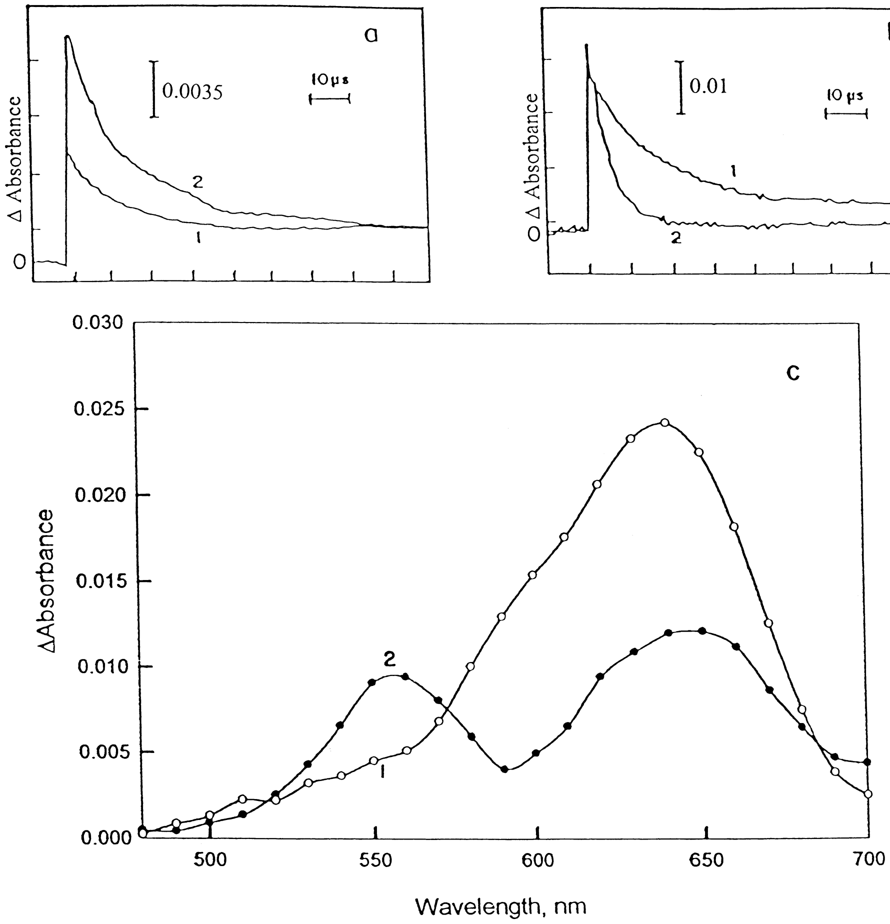


Fig. 2. Transient absorption spectra of ADD-3 recorded at 5 μs after the laser pulse in methanol ($\lambda_{ex} = 355$ nm). (a) Transient decay monitored at 550 nm. (1) Transient decay of 1×10^{-4} M ADD-3. (2) Transient decay of 1×10^{-4} M ADD-3 and 1×10^{-3} M DPI-1. (b) Triplet monitored at 640 nm. (1) Triplet decay of 1×10^{-4} M ADD-3. (2) Triplet decay of 1×10^{-4} M ADD-3 and 1×10^{-3} M DPI-1. (c) (1) Transient absorption spectrum of 1×10^{-4} M ADD-3. (2) Transient absorption spectrum of 1×10^{-4} M ADD-3 and 1×10^{-3} M DPI-1.

3.1.2. Triplet state reactions

Laser excitation of ADD in methanol leads to a long lived triplet state and the triplet lifetime are given in Table 1. The triplet absorption spectrum exhibits a maximum at 630 nm (Fig. 2). In addition to singlet quenching diphenyliodonium salts were found to interact with the triplet state of ADD. Addition of diphenyliodonium salts to ADD in methanol reduces the lifetime of the triplet state. The bimolecular quenching constant k_q^T was evaluated from a plot of triplet decay rate constant of the ADD versus the concentration of iodonium salts using Stern–Volmer treatment. The triplet quenching constants obtained are given in Table 3. Iodonium salts quench the singlet excited state of acridinedione with a rate constant close to the diffusion controlled limit, but the quenching of the triplet excited state is slow, which is a common trend in electron transfer reactions where the excited singlet state shows higher reactivity than the triplet state [29].

3.1.3. Radical cation of ADD

Quenching of both triplet and singlet states result in the formation of a new transient absorption in the region of 540–560 nm (Fig. 2). Acridinedione dyes can be also considered as NADH analog and the mechanism of photo-oxidation of NADH model compounds has been extensively studied [30]. NADH radical cations formed as an intermediate in the oxidation reaction NADH $\rightleftarrows$ NAD$^+$ following a mechanism based on sequential electron–proton–electron transfer [31]. Recently, Marcinek et al. [32] reported that the radical cation generated from the NADH model compounds un-

Table 3
Rate constant for the the triplet quenching of ADD by iodonium salts in methanol

Iodonium salt	$k_q^T \times 10^{-7}$, M^{-1} s^{-1} (ΔG_{et}, kcal mole^{-1})			
	ADD-3	ADD-4	ADD-5	ADD-6
1	4.5 (−34.29)	5.25 (−32.50)	25.4	15.8
2	32 (−34.13)	28.1 (−32.34)	58.3	55.5
3	4.2 (−34.32)	5.21 (−32.52)	10.5	12.5
4	2.3 (−34.32)	4.98 (−32.52)	11.3	8.7
5	48.6 (−34.01)	51.4 (−32.22)	58.7	60.3
6	4.5 (−34.56)	3.7 (−32.80)	11.2	13.4
7	3.2 (−34.18)	3.53 (−32.43)	14.5	12.5

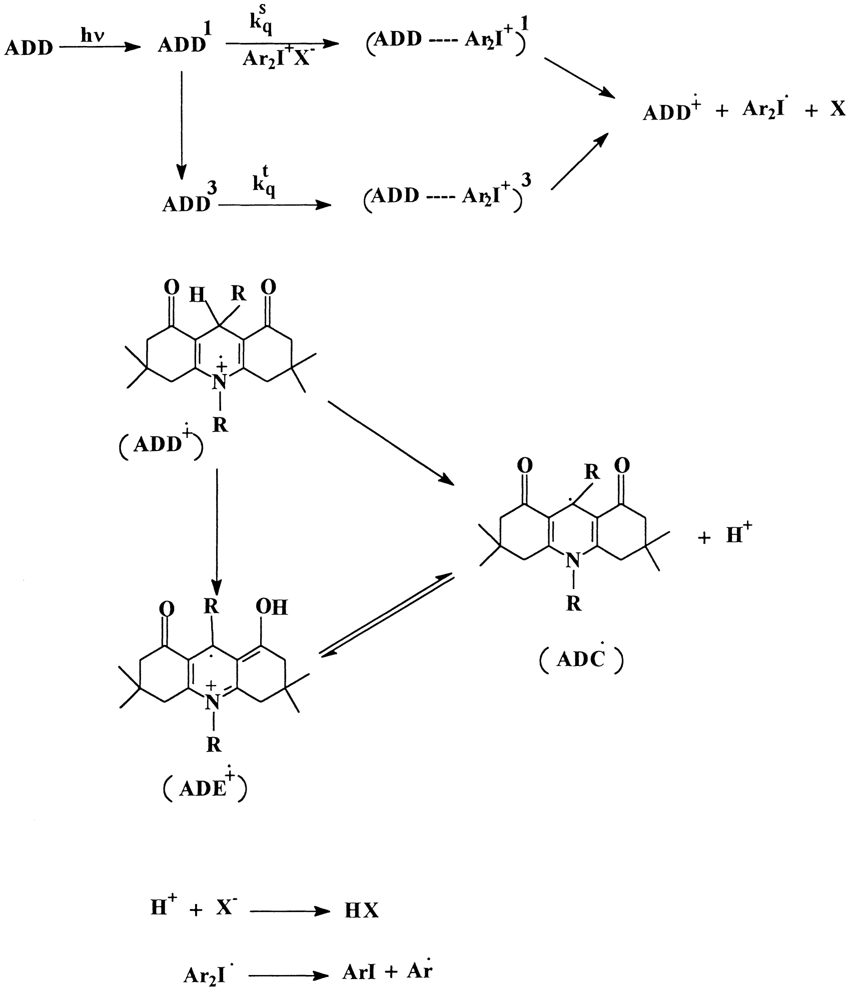
dergoes spontaneous keto–enol tautomerization. The oxygen atom in the acridinediones are in favorable geometry for the keto–enol tautomerization in the corresponding radical cations [33] and in solution the primarily formed keto radical cations tautomerize in less than 1 ns to the corresponding enol radical cations which has transient absorption at 550 nm region. The 550 nm transient is assigned as enol-radical cation of ADD and is in agreement with the findings and conclusions of Marcinek et al. [32]. The absorption spectrum of radical cation formed by the interaction of ADD with diphenyliodonium salts recorded at 5 μs after the laser pulse is shown in Fig. 2. The transient observed at 550 nm shows long lifetime component (Fig. 2a) which does not decay even at 90 μs after the laser excitation. This is due to the formation of stable product tetrahydroacridinedione, which is the photochemical oxidation product of acridinedione [34]. Steady photolysis of ADD in presence of iodonium salts enhance the formation of the tetrahydroacridinedione.

3.1.4. Mechanism of photosensitization

An electron is transferred from the excited state of ADD to iodonium salt resulting in the formation of radical cation ($ADD^{+\bullet}$) and diaryliodine radical ($Ar_2I^\bullet$) (Scheme 1). The radical cation $ADD^{+\bullet}$ undergoes tautomerization to form enol radical cation $ADE^{+\bullet}$ which is characterized by transient absorption at 550 nm in the laser flash photolysis. The observation of enol radical cation ($ADE^{+\bullet}$) provides the strong evidence for electron transfer process. The resulting acridinedione radical cations ($ADD^{+\bullet}$ and $ADE^{+\bullet}$) react with the nucleophile ($X^- = BF_4^-$ and PF_6^-) to produce Brönsted acid and carbon centred radical ($ADC^\bullet$). The diaryliodine radical is dissociated into iodobenzene and phenyl radical. In the sensitized decomposition of iodonium salts, the super acid (H^+) is coming from the deprotonation of the both keto and enol cation radicals of ADD and the quantum yield of super acid formation will be discussed in the later section.

3.2. Excited state reactions of triarylsulphonium salts with ADD in acetonitrile

Three types of sulphonium salts have been prepared and used in this investigation. Presence of one or more substituents like Cl or CH_3 on one of the rings causes a very



Scheme 1.

Table 4
Reduction potential, singlet quenching constants and free energy change for electron transfer between ADD and triarylsulphonium salts in acetonitrile

Triphenylsulphonium salts		Reduction potential (V) vs. Ag/AgCl	ADD-1		ADD-2		ADD-3	
			$k_q \times 10^{-10}$ ($M^{-1}\,s^{-1}$)	ΔG (kcal $mole^{-1}$)	$k_q \times 10^{-10}$ ($M^{-1}\,s^{-1}$)	ΔG (kcal $mole^{-1}$)	$k_q \times 10^{-10}$ ($M^{-1}\,s^{-1}$)	ΔG (kcal $mole^{-1}$)
Type-I	a	−1.35	0.93	−16.00	1.29	−13.86	0.61	−10.21
	b	−1.37	0.98	−15.54	1.27	−13.39	0.76	−9.75
	c	−1.38	0.62	−15.31	0.69	−13.16	0.40	−9.52
	d	−1.37	0.53	−15.54	0.92	−13.39	0.26	−9.75
Type-II	a	−0.67	1.24	−31.68	1.47	−29.54	1.11	−25.89
	b	−0.53	1.31	−34.91	1.77	−32.76	1.25	−29.12
	c	−0.61	1.08	−33.06	1.26	−30.92	0.88	−27.28
	d	−0.54	1.21	−34.68	1.70	−32.53	0.88	−28.89
Type-III	a	−0.53	1.40	−34.91	0.75	−32.76	0.68	−29.12
	b	−0.65	1.51	−32.14	1.08	−29.99	0.71	−26.35
	c	−0.64	0.78	−32.37	0.87	−30.23	0.58	−26.58
	d	−0.65	1.33	−32.14	0.77	−29.99	0.57	−26.35

little shift in the absorption characteristic of the sulphonium salts (type-I). Structural modification by bonding the adjacent aromatic rings together to give a sulphonium salts of type-II or by introducing a bridging sulphur atom between the two phenyl rings to give sulphonium salts of type-III extends the spectral absorption towards long wavelength.

3.2.1. Fluorescence quenching studies

Fluorescence of ADD dyes were quenched by the triphenylsulphonium salts. On addition of sulphonium salts there is no change in the absorption of ADD indicating that the absence of ground state reaction. The quenching rate constants are in the diffusion limit. The reduction potential for the

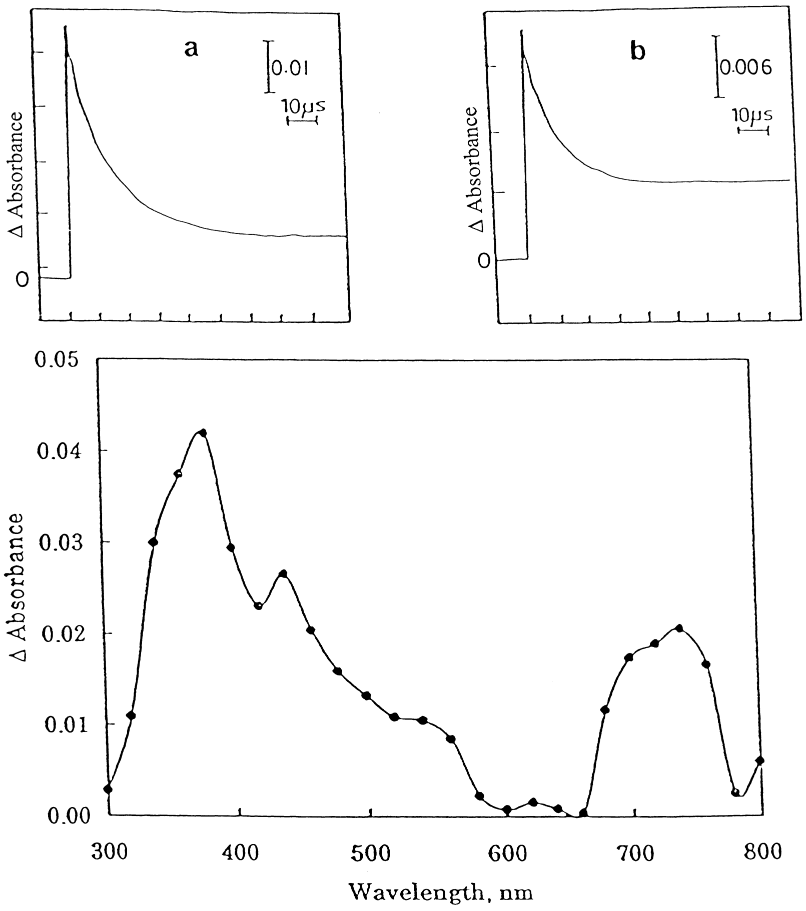


Fig. 3. Transient absorption spectrum of TPS-Ia (5×10^{-5} M) on excitation with 266 nm recorded 500 ns after the laser pulse in deaerated acetonitrile. (a) Transient decay monitored at 380 nm. (b) Transient decay monitored at 740 nm.

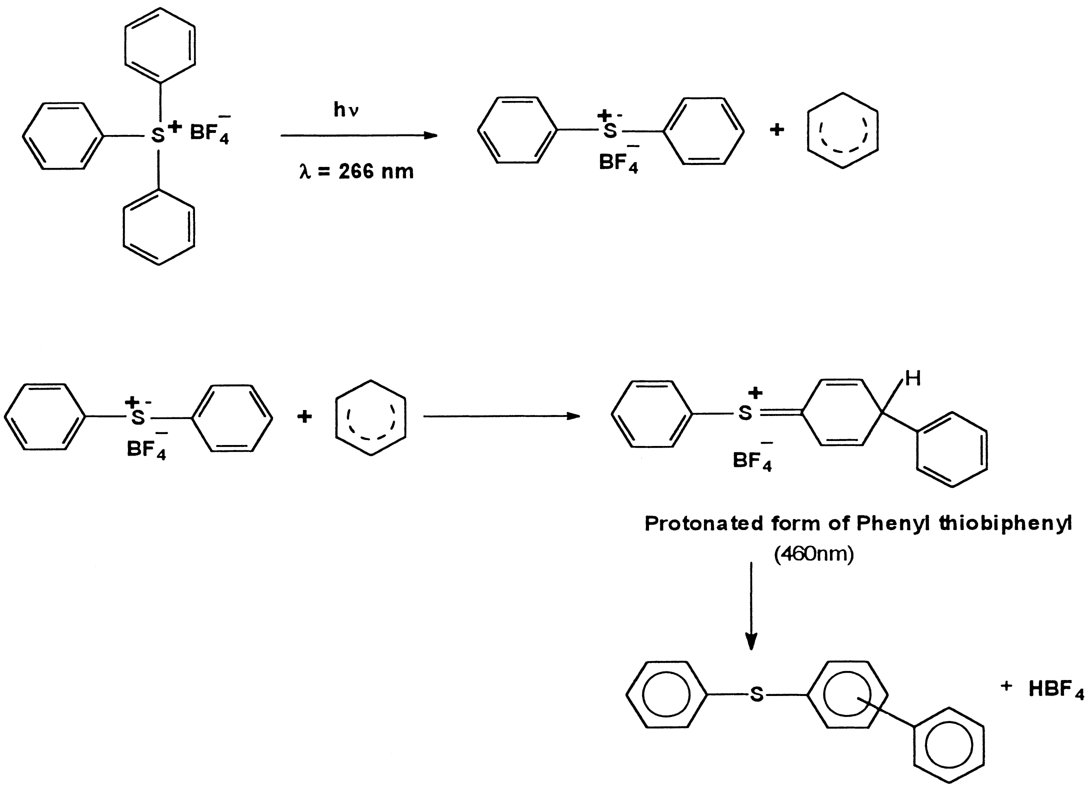
substituted sulphonium salts were determined by cyclic voltammetry. The reduction potential of sulphonium salts versus Ag/AgCl are given in Table 4. The free energy change for the electron transfer was calculated using Rehm–Weller equation and ΔG_{et} values are negative. The values of quenching constants and free energy change are given in Table 4. The absence of a more complete set of values precludes an analysis based on the Rehm–Weller approach for photoinduced electron transfer. Nevertheless, the quenching efficiency increases with decrease in the reduction potential of the sulphonium salts indicating that the quenching occurs through photoinduced electron transfer. Decrease in the quenching constants with increase in the oxidation potential of the ADD sensitizer also supports the photoinduced electron transfer.

3.2.2. Laser flash photolysis studies

The transient absorption spectrum of TPS-I on excitation with 266 nm is shown in Fig. 3. The spectrum shows peaks at 380, 440, and 740 nm. In the literature, several [35] groups have thoroughly studied and reported that the transients in the region of 380 and 740 nm are due to the diphenylsulphinium radical cation and the 440 nm transient is assigned to the protonated form of phenyl thiobiphenyl. Photodecomposition of sulphonium salts occur as a result of the photoexcitation of an electron from the π molecular orbital localized on the phenyl groups to the σ^* molecular orbital localized on the C–S bond producing the C–S bond cleavage. The homolytic cleavage of C–S bond yields diphenylsulphinium radical cation and phenyl radical pair which can either undergo cage escape reactions to give diphenylsulphinium radical cation and phenyl radical or undergo incage reactions to give the isomeric phenylthiobiphenyls [36] (Scheme 2).

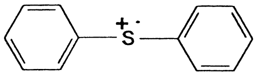
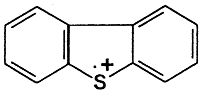
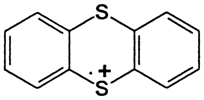
Substituted sulphonium salts in the TPS-I series exhibited similar transient absorption characteristics indicating that the presence of chloro or methyl in one of the phenyl ring of the sulphonium salts does not affect the transient absorption characteristics of the intermediates. Laser flash photolysis of TPS-II and TPS-III sulphonium salts shows corresponding sulphinium radical cation absorption and are given in Table 5. The transient absorption spectrum of TPS-IIIa is shown in Fig. 4. The spectrum shows a transient maximum at 480 nm along with a shoulder at 540 nm region. The short lived 480 nm transient is ascribed to the triplet of the TPS-IIIa, since it was quenched by oxygen and the long lived transient at 540 nm is attributed to the thianthrenium radical cation. Literature [37] reports of thianthrenium radical cation formation in acidic medium and its absorption spectra supports the observation of 540 nm transients as thianthrenium radical cation.

Transient absorption spectrum of ADD-1 in the presence of TPS-Ia in acetonitrile on excitation at 355 nm, shows transient maxima (Fig. 5) at 340, 470, 620 and 720 nm. The 470 and 620 nm transients are also observed in the absence of TPS-Ia and these transients are attributed to the anion radical [38] and triplet [18,19] absorptions of ADD-1, respectively. The transient at 720 nm are similar to the transient obtained on 266 nm excitation of TPS-Ia indicating that these tran-



Scheme 2.

Table 5
Triarylsulphinium radical cation structure and its transient absorption maximum

Sulphonium salts	Radical cation structure	Radical cation absorption
TPS-I	 Diphenyl sulphinium Radical Cation	380 and 740 nm
TPS-II	 Dibenzothiophenium Radical Cation	380 and 760 nm
TPS-III	 Thianthrenium Radical Cation	540 nm

sients are due to diphenylsulphinium radical cation [34]. The observation of transient due to diphenylsulphinium radical cation intermediate at 720 nm region can be attributed to the oxidation of diphenylsulphide ($E^{\mathrm{ox}}_{1/2} = 1.26$ V, Ag/AgCl) by the ADD radical cation. Triplet lifetime of the acridinedione dyes are unaffected by the sulphonium salts. The diarylsulphinium radical cations were also observed in the air-equilibrated solution of ADD where the triplet of ADD was effectively quenched by oxygen. These results indicate that the singlet state of acridinedione dyes alone is involved in the photosensitization of triphenylsulphonium salts.

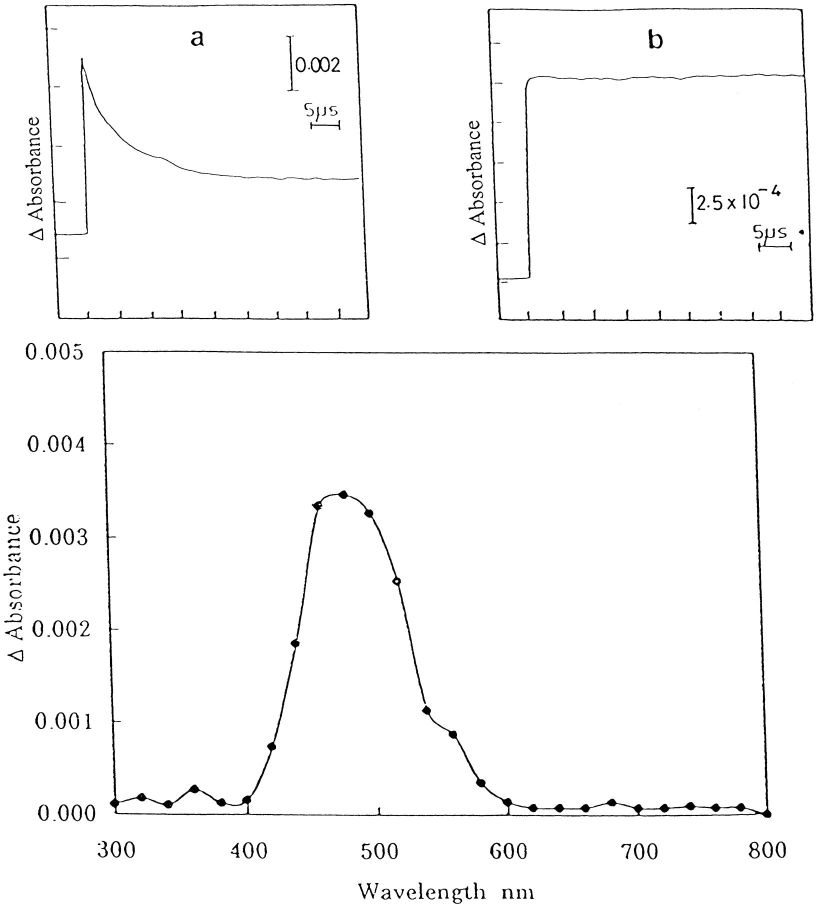


Fig. 4. Transient absorption spectrum of TPS-IIIa (1×10^{-4} M) on excitation with 266 nm recorded 5 μs after the laser pulse in deaerated acetonitrile. (a) Transient decay monitored at 480 nm. (b) Transient decay monitored at 540 nm.

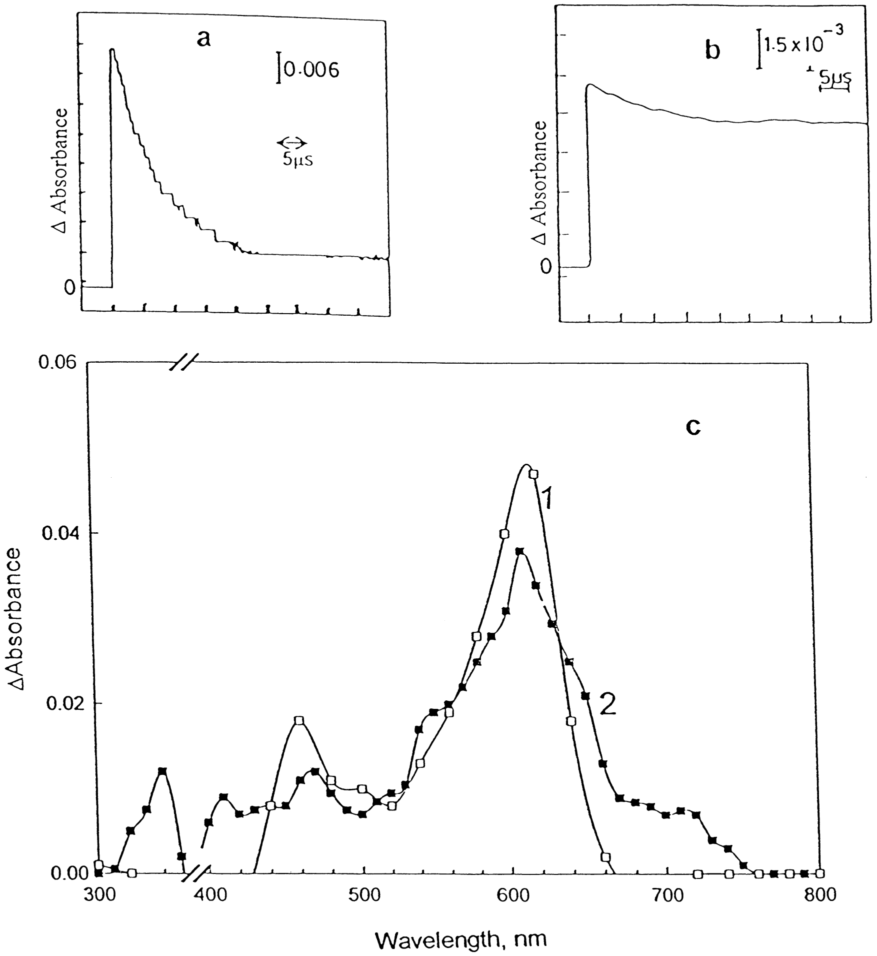


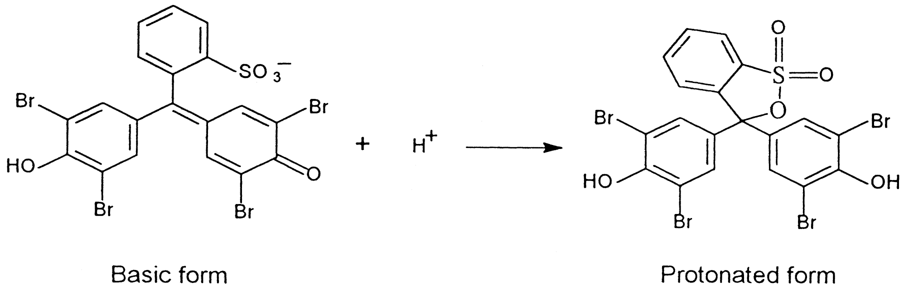
Fig. 5. Transient absorption spectra of ADD-1 (1×10^{-5} M) recorded at 2 μs after the laser pulse in acetonitrile ($\lambda_{ex} = 355$ nm). (a) Transient decay of ADD-1 monitored at 620 nm. (b) Transient decay of ADD-1 and 5×10^{-4} M of TPS-Ia monitored at 720 nm. (c): (1) Transient absorption spectrum of ADD-1; (2) transient absorption of ADD-1 in the presence of TPS-Ia.

The mechanism of photosensitization of triphenylsulphonium salts is given in Scheme 3. Singlet state of ADD dyes react with sulphonium salts by electron transfer mechanism. Electron transfer from ADD to TPS results in the formation of triarylsulphuranyl radical and radical cation of ADD. The triphenylsulphuranyl radical rapidly decomposes to give the diarylsulphide and phenyl radical. The radical cation of ADD undergoes tautomerization to enol form which is discussed already in the diaryliodonium salts. The transient absorption spectrum of ADD in presence of sulphonium salts exhibit a shoulder in 550 nm region (Fig. 5) which is due to the formation of enol radical cation. Unlike iodonium salts the transient absorption due to the enol radical cation of ADD could not be seen clearly due to the following reasons: (1) the triplet absorption of ADD around 620 nm dominates in the transient absorption spectrum of ADD and sulphonium salts over the enol cation radical [18,19,31] and (2) electron transfer reaction between the enol cation radical and diaryl sulphide makes it difficult to observe. In order to support for the second possibility, the enol radical cation generated by the excited state reactions of ADD with diphenyliodonium salts was made to react with diphenylsulphide and we observe that the absorbance of enol radical cation decreases. This confirms the reaction between the enol radical cation and diarylsulphide. Oxidation of diaryl sulphide by the enol radical cation of ADD occurs within the cage to give the diaryl sulphinium cation radical and acridinedione. The observation of radical cation of thianthrene [37] in the ADD sensitized photolysis of TPS-III (Fig. 6) strongly supports the electron transfer mechanism.

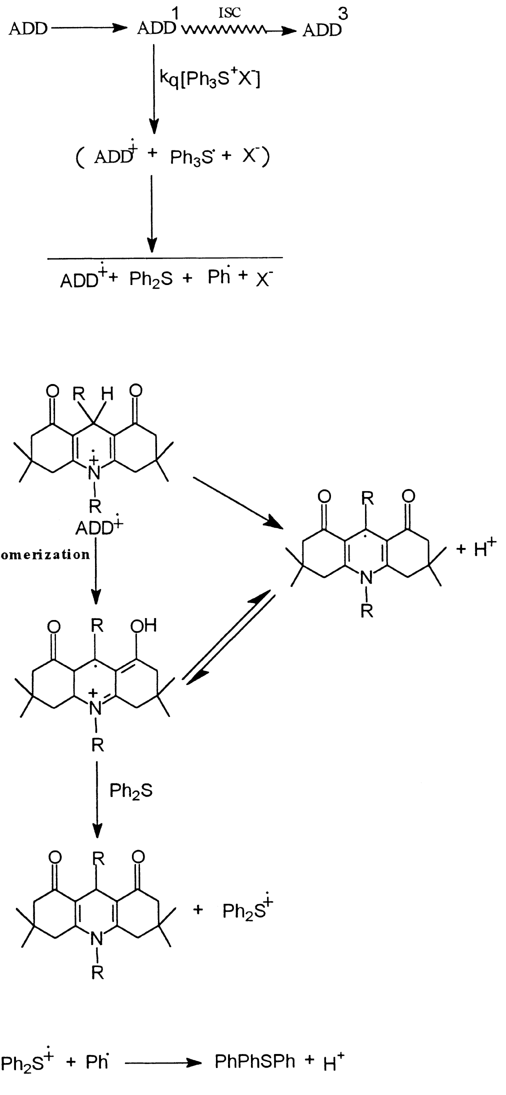
3.3. Steady photolysis and quantum yield of photoacid release

Steady photolysis of onium salts in the presence of acridinedione has been carried out using 366 nm light. On photolysis the solution acidity increases. Steady photolysis was also carried out without sensitizer. Due to the tail absorption of diaryliodonium salts, they can undergo photodecomposition even in the absence of sensitizer at 366 nm. Triarylsulphonium salts do not undergo any such decomposition without sensitizer at this wavelength.

The quantum yield of acid release in the solution on photolysis was measured using sodium bromophenol blue, which has absorption maximum at 595 nm. The absorption of sodium bromophenol was decreased on photolysis of solution containing onium salts, ADD and sodium bromophenol blue. This is due to the release of acid into the solution by the onium salts.



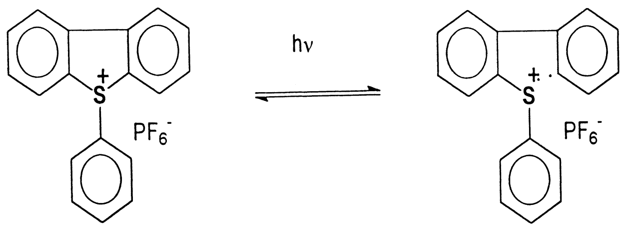
Steady photolysis experiments have been carried out using 254 nm light without ADD. The quantum yield of acid release for all the iodonium and sulphonium salts, both direct and sensitized process are given in Tables 6 and 7. In the case of iodonium salts, 420 nm light was used for the quantum yield of acid release determination because of the self decomposition of iodonium salts at 366 nm radiation.



Scheme 3.

Diphenyliodonium salts have higher quantum yield of acid release than the other substituted iodonium salts. This indicates that the substituted diaryliodonium salts are less reactive than the diphenyliodonium salt. Diaryliodonium salts have lower quantum yield of acid release on sensitization compared to direct decomposition. This may be due to the difference in the mechanism of decomposition. On irradiation of diaryliodonium salts in the excited singlet state undergoes heterolytic cleavage [39] to form iodobenzene and phenyl cation or ISC to triplet state, which can compete with the cleavage reactions because of the iodine heavy atom enhancement of the ISC rate. The triplet state can undergo homolysis to form a triplet radical pair, phenyl radical and the iodobenzene radical cation (Scheme 4). The process by which the protonic acids arises are (1) phenyl cation and iodobenzene or phenyl radical and iodobenzene radical cation can recombine to form iodobiphenyls and protons, (2) reactions of phenyl cation with solvents and monomer. In the case of sensitised decomposition of iodonium salts, there is only one way by which the protonic acid arises is from the radical cation of the sensitizer, which is given in Scheme 1. Consequently, the quantum yield of acid release is decreased on sensitization.

Among the triarylsulphonium salts, type-I have higher quantum yield of acid release compared to that of type-II and type-III sulphonium salts, although the latter have better absorption characteristics. This has been attributed to the cyclic structure of the sulphonium salts of type-II and type-III on photolysis the reactive fragments formed by photolytic cleavage of the C–S bonds are held in close proximity to one another. This would be expected to facilitate recombination and result in the decrease in the quantum yield of acid release.



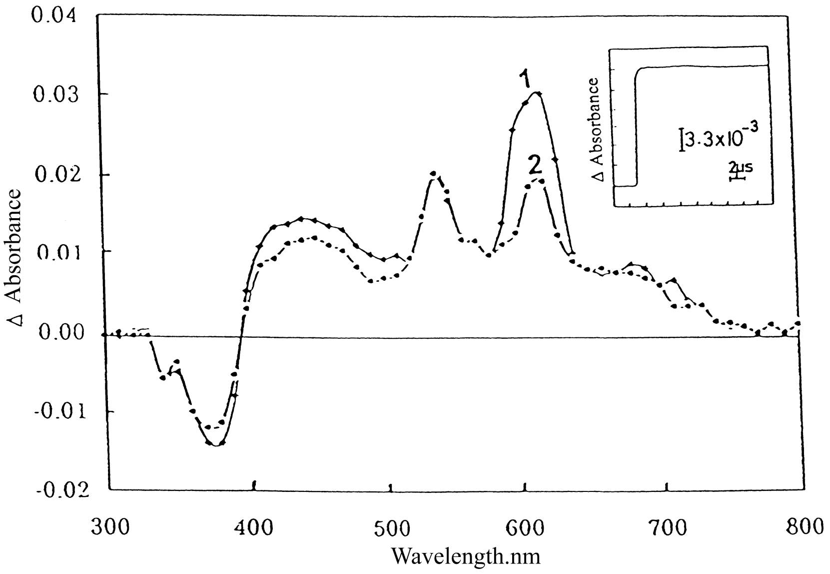


Fig. 6. Transient absorption spectra of ADD-1 (1×10^{-5} M) and TPS-IIIa (5×10^{-4} M) in acetonitrile recorded at (1) 3 and (2) 10 μs after the laser pulse in acetonitrile ($\lambda_{ex} = 355$ nm). Inset shows the transient decay monitored at 540 nm.

Table 6
Quantum yield of photoacid release on photolysis of iodonium salts[a]

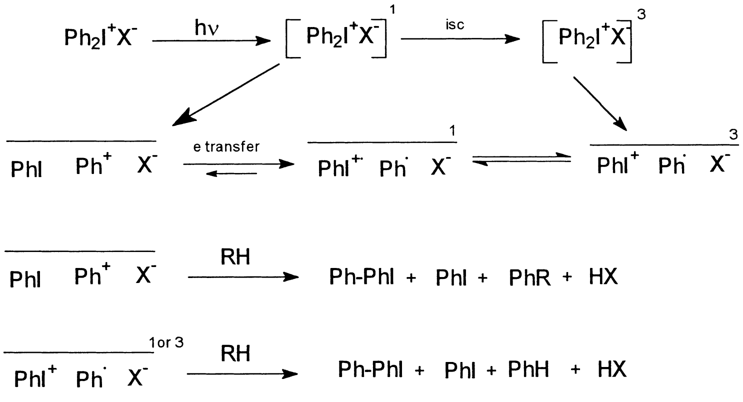
DPI	Direct photolysis ($\lambda = 254$ nm)	ADD sensitised photolysis ($\lambda = 422$ nm)			
		ADD-3	ADD-4	ADD-5	ADD-6
1	0.49	0.15	0.13	0.23	0.21
2	0.1	0.04	0.04	0.04	0.05
3	0.23	0.01	0.08	0.10	0.13
4	0.13	0.03	0.03	0.10	0.11
5	0.11	0.04	0.03	0.08	0.07
6	0.11	0.03	0.03	0.03	0.05
7	0.12	0.02	0.02	0.03	0.03

[a] Estimated error (from replicate determinations) ± 15%.

Table 7
Quantum yield of photoacid release on photolysis of sulphonium salts[a]

Triarylsulphonium salts		Direct decomposition ($\lambda_{ex} = 254$ nm)	Sensitized photolysis ($\lambda_{ex} = 366$ nm)		
			ADD-1	ADD-2	ADD-3
Type-I	a	0.66	0.50	0.49	0.46
	b	0.69	0.53	0.52	0.50
	c	0.88	0.55	0.54	0.53
	d	0.70	0.48	0.49	0.45
Type-II	a	0.27	0.18	0.17	0.16
	b	0.27	0.18	0.18	0.17
	c	0.25	0.16	0.15	0.14
	d	0.24	0.14	0.13	0.13
Type-III	a	0.30	0.25	0.24	0.23
	b	0.31	0.25	0.24	0.23
	c	0.35	0.23	0.22	0.22
	d	0.32	0.22	0.21	0.21

[a] Estimated error (from replicate determinations) ± 8%.



Scheme 4. Direct photolysis of diaryliodonium salts

3.4. *Effect of oxygen on the quantum yield of acid release*

Quantum yield measurements have been carried out in air-equilibrated and argon saturated conditions. In the case of diaryliodonium salts in methanol under argon saturated condition, the quantum yield of acid release is approximately three times higher than that in air equilibrated conditions. This may be due to radical chain mechanism in which phenyl radical abstracts hydrogen from methanol, producing hydroxy methyl radical which further reduce the diphenyliodonium salts. Phenyl radical is the principal chain carrier and is regenerated. Such free radical chain process is favored in absence of oxygen. In acetonitrile, the quantum yield of acid release is close to methanol and there is no effect of oxygen on quantum yield of acid release. There is no hydrogen abstraction by phenyl radical in acetonitrile that prevents the radical chain mechanism (Scheme 5).

There is no change in the quantum yield of acid release of triarylsulphonium salts in the presence of air and argon saturated condition in methanol as well as acetonitrile. This is due to the more negative reduction potential of triarylsulphonium salts which cannot be reduced by the phenyl radical.

4. Conclusion

The spectral sensitivity of diaryliodonium and triarylsulphonium salts can be extended to visible light using acridinedione as sensitizer. Sensitization occurs through electron transfer which is proved by the detection of the intermediates like radical cation of ADD and diarylsulphinium radical cation. Both singlet and triplet states are involved in the electron transfer between the ADD and diaryliodonium salts. Singlet state is only involved in the electron transfer between ADD and triarylsulphonium salts. In the sensitized decomposition of diaryliodonium salts the proton is released from radical cation of ADD. The quantum yield of acid release is higher for the triarylsulphonium salts as compared to diaryliodonium salts. The spectral sensitization of onium salts by ADD was not as effective as that of the direct decomposition of onium salts, the use of longer wavelength in addition to the UV radiation will help in giving a synergistic effect of the polymerization processes.

$$\dot{Ph} + CH_3OH \longrightarrow \dot{C}H_2OH + PhH$$

$$\dot{C}H_2OH + Ph_2I^+ \longrightarrow {}^+CH_2OH + Ph_2I^\bullet$$

$$Ph_2I^\bullet \longrightarrow PhI + \dot{Ph}$$

$$^+CH_2OH \longrightarrow HCHO + H^+$$

Scheme 5.

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