Macromolecules

Volume 14, Number 5 September–October 1981

Photosensitized Cationic Polymerizations Using Dialkylphenacylsulfonium and Dialkyl(4-hydroxyphenyl)sulfonium Salt Photoinitiators

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Received April 23, 1981

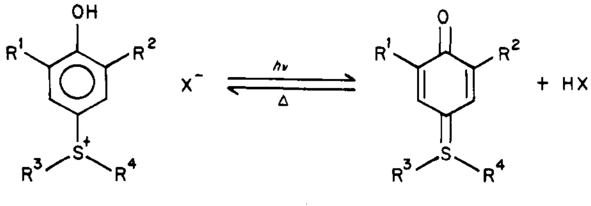
ABSTRACT: Aromatic hydrocarbons photosensitize the photolysis of dialkylphenacylsulfonium salts while aryl ketones photosensitize the photolysis of dialkyl(4-hydroxyphenyl)sulfonium salts. With these photosensitizer–photoinitiator combinations, it is possible to carry out long-wavelength (>320 nm) UV light cationic polymerization of epoxy and other monomers. The relative efficiencies of various photosensitizer–photoinitiator combinations are compared in the photopolymerization of limonene dioxide. Several mechanisms for the photosensitization are proposed and their relative merits discussed.

Introduction

As part of our continuing investigation of photoinitiated cationic polymerization, we have described the development of several photoinitiator classes, namely, diaryliodonium,[1] triarylsulfonium,[2] triarylselenonium,[3] dialkylphenacylsulfonium,[4] and dialkyl(4-hydroxyphenyl)sulfonium[5] salts. In all cases, photolysis of these onium salts produces Brønsted acids responsible for the initiation of cationic polymerization which proceeds thermally in subsequent dark steps. The first three photoinitiators differ markedly from the latter two with regard to the mechanism of their photolysis. Diaryliodonium, triarylsulfonium, and triarylselenonium salts undergo irreversible cleavage of a carbon–heteroatom bond on irradiation (eq 1). Dialkylphenacylsulfonium and dialkyl(4-hydroxyphenyl)sulfonium salts, on the other hand, reversibly photodissociate to give ylides and Brønsted acids (eq 2 and 3).

$$Ar_nZ^+X^- \xrightarrow{h\nu} Ar_{n-1}Z^{+\cdot} + Ar\cdot + X^- \qquad (1)$$

$$\mathrm{ArCOCH_2{-}\overset{+}{S}R^1R^2\ X^-} \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} \mathrm{ArCOCH{=}SR^1R^2} + \mathrm{HX} \qquad (2)$$



(3)

Since diaryliodonium, triarylsulfonium, and triarylselenonium salts absorb mainly at wavelengths below 300 nm, these compounds are not useful photoinitiators when irradiated at wavelengths above 300 nm. However, work in this laboratory has demonstrated that the photolysis of diaryliodonium salts may be photosensitized in the 400–500-nm region by acridine dyes,[6] while perylene and other polynuclear hydrocarbons are effective photosensitizers for the photolysis of triarylsulfonium salts.[7] Pappas and Jilek have suggested that an exciplex is formed between the excited dye and the aryl onium salt and that the exciplex decomposes chiefly by an electron transfer process.[8]

Photosensitization of the photolysis of dialkylphenacylsulfonium and dialkyl(4-hydroxyphenyl)sulfonium salts has not as yet been demonstrated. In view of the radically different course of the mechanisms of photolysis of these salts compared to the diaryliodonium, triarylsulfonium, and triarylselenonium photoinitiators, we thought it might be interesting to determine whether photosensitization is possible in these compounds and to speculate on the mechanisms involved.

Experimental Section

Reagents and Sulfonium Salts. Dialkylphenacylsulfonium[4] and dialkyl(4-hydroxyphenyl)sulfonium[5] salts were prepared and purified as described previously. Spectrograde solvents and photosensitizers were used as purchased from their suppliers. Limonene dioxide (dipentene dioxide) was a gift of SCM Corp. and was purified by distillation under nitrogen from calcium hydride.

Spectroscopic Studies. UV–visible absorption spectra were obtained with the aid of a Perkin-Elmer 575 spectrophotometer. Fluorescence and phosphorescence excitation, emission, and quenching studies were performed on a Perkin-Elmer MPF-44A spectrophotometer.

Photolysis and Polymerization Studies. Photolyses were conducted with a Hanovia 450-W medium-pressure mercury arc lamp equipped with a merry-go-round apparatus. Photopolymerization studies were conducted with a Perkin-Elmer DSC-2 differential scanning calorimeter fitted with a GE H3T7

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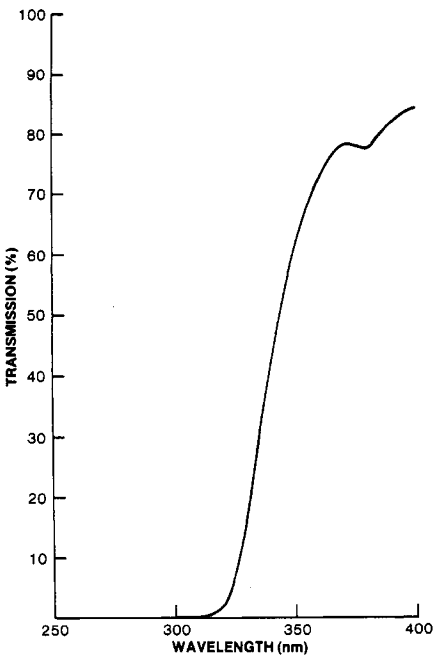


Figure 1. Transmission characteristics of the glass filter employed in the photosensitization studies.

medium-pressure mercury arc lamp and filter system as described previously.[10] Figure 1 shows the transmission characteristics of the glass filter used in these studies. Data collection and reduction were performed automatically by interfacing the DSC unit with a Spectra Physics computer processing unit.

The photosensitized polymerization of cyclohexene oxide (7-oxabicyclo[4.1.0]heptane) was carried out, with stirring, in a large capped Pyrex tube, employing a Hanovia 450-W medium-pressure Hg arc lamp. To 18.13 g (1.85×10^{-1} mol) of cyclohexene oxide were added 12.5 mL of CH_2Cl_2, 0.02 g (2×10^{-3} mol) of phenacyltetramethylenesulfonium hexafluoroarsenate, and 0.0025 g (3.9×10^{-4} mol) of perylene, and the mixture was irradiated for 1 h in a water bath at 25 °C. The polymer was precipitated into methanol containing 5% NH_4OH, filtered, washed with methanol, redissolved in CH_2Cl_2, and again reprecipitated into methanol. After the polymer was ground to a fine powder, it was exhaustively extracted with methanol for 3 days in a Soxhlet extractor and dried overnight in a vacuum oven at 60 °C. A pale yellow polymer (8.3 g) was obtained which, in CH_2Cl_2, had bands in the visible spectra at 415 and 437 nm due to the presence of the perylene nucleus.

Results and Discussion

Photosensitization Studies. Since the photolyses of dialkylphenacylsulfonium and dialkyl(4-hydroxyphenyl)sulfonium salts are reversible processes, direct observation of photosensitization in these compounds is experimentally difficult. In the past, we have made good use of differential scanning calorimetry (DSC) as a probe with which to detect the presence of photosensitization, to determine the active bands of the photosensitizer, and to directly measure the efficiency of photosensitized polymerizations.[6,7,9,10] On irradiation in the calorimeter, a sensitizing dye will cause photoinitiated polymerization of a bisepoxide, which can be detected as an exothermic peak in the recorder trace. Appropriate light filters are employed which permit the selection of bands absorbed by the photosensitizer and not by the photoinitiator. Limonene dioxide (dipentene dioxide) was chosen as the polymerizable substrate for these studies since it is readily purified and because its low vapor pressure at room temperature and high reactivity facilitate accurate DSC determinations.

The above-described techniques were used to screen a considerable number of candidate photosensitizers. A wide variety of polynuclear aromatic hydrocarbons are photosensitizers for the photolysis of dialkylphenacylsulfonium salts at wavelengths above 320 nm. Figure 2 shows plots of the heats of photopolymerization of limonene dioxide vs. irradiation time for phenacyltetramethylenesulfonium hexafluoroarsenate using equimolar concentrations of various aromatic hydrocarbons. Phenothiazene, a nonpolynuclear aromatic hydrocarbon, is also an active photosensitizer for dialkylphenacylsulfonium salts; however, the shape of its ΔH vs. irradiation time curve is considerably different from the others, indicating that additional factors, e.g., inhibition and termination reactions, may be playing important roles in this polymerization. The apparent slight delay in the start of the photopolymerization shown in Figure 2 is an artifact of the DSC method and appears to be related both to the response time of the instrument and to the heat transfer properties of the polymerizing epoxide. Under these conditions of irradiation, perylene is the best photosensitizer for dialkylphenacylsulfonium salts. Pyrene, anthracene, benzanthracene, and coronene are all approximately equally active, while tetracene is considerably less active than the others. Virtually no polymerization is noted in the blank, in which a photosensitizer is absent.

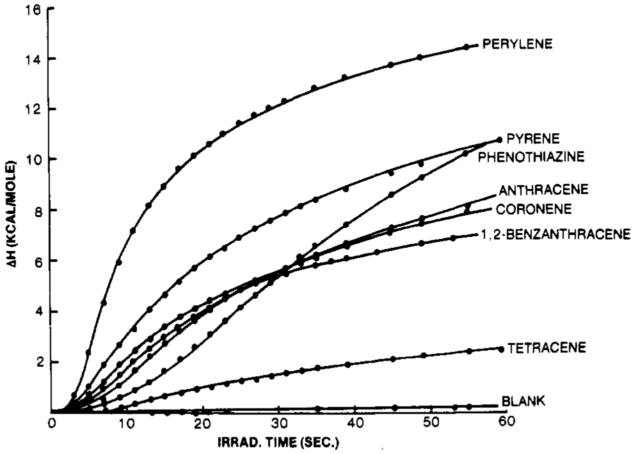


Figure 2. DSC study of the photopolymerization of limonene dioxide with phenacyltetramethylenesulfonium hexafluoroarsenate (5.2×10^{-5} mol) using various aromatic hydrocarbon photosensitizers (7.9×10^{-6} mol).

Similarly, photosensitizer screening studies were carried out for dialkyl(4-hydroxyphenyl)sulfonium salts. In contrast to the dialkylphenacylsulfonium salts, polynuclear aromatic hydrocarbons were not active photosensitizers for these compounds. Instead, aromatic ketones were observed to be excellent long-wavelength photosensitizers for these photoinitiators. Figure 3 gives plots of ΔH vs. irradiation time for the polymerization of limonene dioxide using dimethyl(3,5-dimethoxy-4-hydroxyphenyl)sulfonium hexafluoroarsenate and a number of different aromatic ketone photosensitizers.

Anthracene is a very effective photosensitizer for dialkylphenacylsulfonium salts. Figure 4 shows the results of a study of the anthracene-photosensitized polymerization of limonene dioxide comparing phenacyltetramethylenesulfonium salts with different counterions. The usual reactivity order $SbF_6^- > AsF_6^- > PF_6^-$ observed in diaryliodonium[1] and triarylsulfonium salts[2] is not observed in this case. Instead, as noted before in the unsensitized cases, the AsF_6^- salt is a more effective initiator than the corresponding SbF_6^- or PF_6^- compounds.[4]

Figure 5 shows a family of curves generated by measuring the rates of polymerization of limonene dioxide using

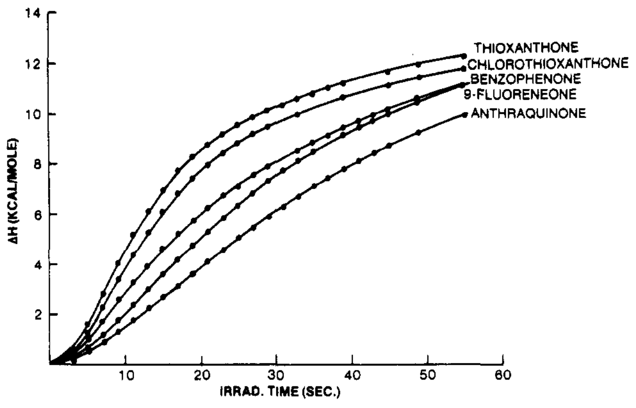


Figure 3. DSC study of the photopolymerization of limonene dioxide with dimethyl(3,5-dimethoxy-4-hydroxyphenyl)sulfonium hexafluoroarsenate (2.6×10^{-5} mol) using various aromatic ketone photosensitizers (1.95×10^{-5} mol).

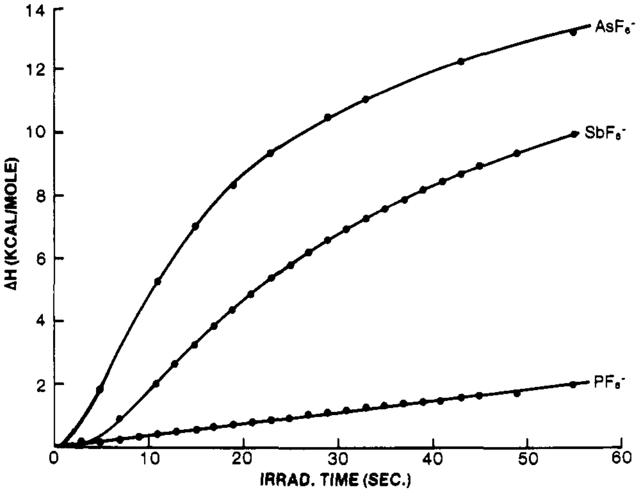


Figure 4. DSC study of the anthracene (1.9×10^{-5} mol) photosensitized polymerization of limonene dioxide with the same amounts (2.6×10^{-5} mol) of various phenacyltetramethylenesulfonium salts.

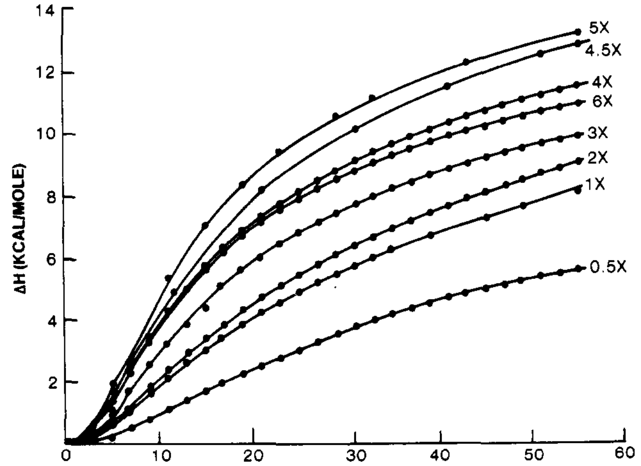


Figure 5. DSC study of the photosensitized polymerization of limonene dioxide with 5.2×10^{-5} mol of phenacyltetramethylenesulfonium hexafluoroarsenate using various concentrations of anthracene ($X = 7.9 \times 10^{-6}$ mol).

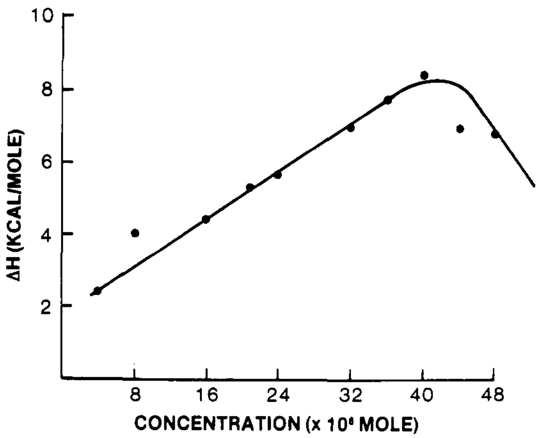


Figure 6. Effect of concentration of anthracene on the rate of polymerization of limonene dioxide (20-s irradiation; [phenacyltetramethylenesulfonium hexafluoroarsenate] = 5.2×10^{-5} mol).

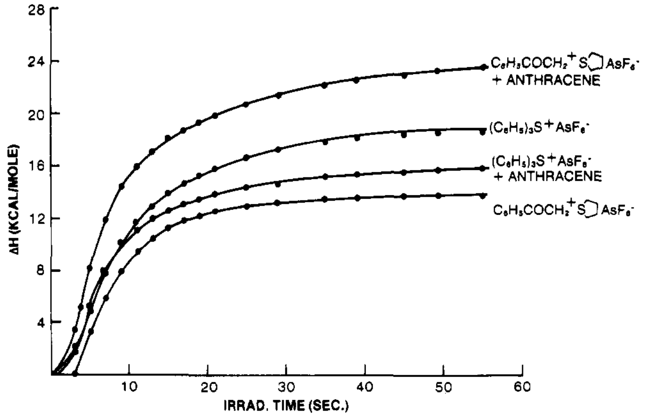


Figure 7. Comparison of the sensitized and unsensitized polymerization of limonene dioxide between triphenylsulfonium hexafluoroarsenate and phenacyltetramethylenesulfonium hexafluoroarsenate ([photoinitiator] = 5.2×10^{-5} mol; [anthracene] = 3.95×10^{-5} mol; unfiltered UV spectrum).

various concentrations of anthracene. In this case, the concentration of the photoinitiator, phenacyltetramethylenesulfonium hexafluoroarsenate, was arbitrarily chosen to be 5.2×10^{-5} mol/L. The optimum concentration of anthracene was determined by plotting the ΔH values determined at 20-s irradiation vs. concentration of anthracene as shown in Figure 6. This curve shows a maximum photosensitization effect at an anthracene concentration of 4.0×10^{-5} mol/L. As the anthracene concentration is further decreased, the rate of polymerization falls sharply. These effects are commonly observed and are similar to dye sensitization in silver halide emulsions.[11]

In Figure 7, triphenylsulfonium hexafluoroarsenate and phenacyltetramethylenesulfonium hexafluoroarsenate are compared with and without anthracene present in the photoinitiated cationic polymerization of limonene dioxide. An unfiltered mercury arc lamp was used in this study. Clearly, the higher rate observed with the optimally sensitized dialkylphenacylsulfonium salt points toward potential advantages in using this photosensitizer–photoinitiator combination. When anthracene was employed with the triphenylsulfonium salt, retardation of the polymerization was noted, due possibly to screening effects.

Photosensitized polymerizations employing either dialkylphenacylsulfonium or dialkyl(4-hydroxyphenyl)sulfonium salts are not restricted only to epoxide polymerizations but have been employed successfully in the cationic polymerization of such monomers as cyclic acetals, thiiranes, oxetanes, and vinyl ethers.

Mechanism of Photosensitization. The observation that, in every case where photosensitization was observed,

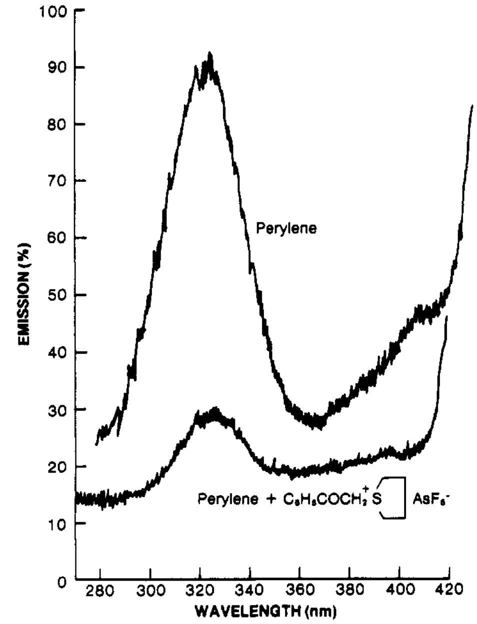


Figure 8. Quenching of perylene (2 × 10^{-4} mol) fluorescence emission at 435 nm by phenacyltetramethylenesulfonium hexafluoroarsenate (2 × 10^{-3} mol) in acetonitrile.

the sulfonium salt was found to quench the emission from the photosensitizer is a strong indication of an interaction between the onium salt and the excited state of the photosensitizer. Such an example is shown in the excitation spectrum of Figure 8, in which the fluorescence emission of perylene at 435 nm is monitored as a function of excitation wavelength. In this case, the fluorescence emission intensity is reduced by 70% on addition of the dialkylphenacylsulfonium salt. Emission quenching was not observed in those cases where photosensitization did not take place.

Similar behavior was noted in the quenching studies of thioxanthone with dimethyl(3,5-dimethoxy-4-hydroxyphenyl)sulfonium hexafluoroarsenate. Marked quenching of the phosphorescence (437 nm) emission was noted on addition of the sulfonium salt. Since aryl ketones undergo very efficient and rapid intersystem crossing to the lowest excited triplet state, most of their photochemistry arises from reactions of the triplet state. Our further observation that the phosphorescence of aryl ketones is strongly quenched by dialkyl(4-hydroxyphenyl)sulfonium salts suggests that photosensitization in this case involves the excited triplet state of the aryl ketone photosensitizer.

The simplest mechanism of photosensitization is that of classical energy transfer. This involves absorption of light by the photosensitizer to produce an excited species, P*, followed by energy transfer to the sulfonium salt, S, as shown in eq 4 and 5. The energy transfer process may

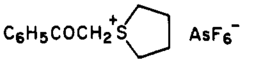
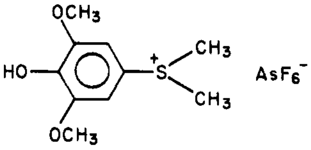
$$P \xrightarrow{h\nu} P^* \qquad (4)$$

$$P^* + S \rightarrow P + S^* \qquad (5)$$

occur either by resonance excitation energy transfer or by exchange energy transfer.[12] However, in either case, efficient energy transfer will occur only when the excitation energy of the photosensitizer is equal to or greater than the energy of the sulfonium salt. Energy transfer from the photosensitizer may involve either the singlet or triplet states.

In Table I are given the singlet and the triplet energies which have been determined for two different sulfonium salts.[13] Tables II and III give similar values for various polynuclear hydrocarbons which are photosensitizers for dialkylphenacylsulfonium salts and aryl ketones which photosensitize dialkyl(4-hydroxyphenyl)sulfonium salt photolyses. A comparison between the values shown in Tables I and II shows that the energetics for classical energy transfer are favorable (i.e., E_S or E_T of the photosensitizer > E_S or E_T of the dialkylphenacylsulfonium salt)

Table I
Excitation Energies of Sulfonium Salts

sulfonium salt[a]	E_S[b]	E_T
	82.4	71.5[c]
	80	70

[a] [Sulfonium salt] = 1 × 10^{-2} M. [b] Singlet excitation energies (kcal/mol) from fluorescence spectra in CH_3CN at room temperature. Excitation wavelength = 300 nm. [c] Triplet energies (kcal/mol) from phosphorescence spectra in 4:1 (v/v) EtOH-MeOH glass at 77 K. Excitation wavelength = 270 nm.

Table II
Singlet and Triplet Energies for Various Aromatic Hydrocarbon Photosensitizers[a]

photosensitizer	major absorption bands[b] λ_{max} (log ε)	E_S[c]	E_T[c]
anthracene	252 (5.12), 322 (3.47), 338 (3.77), 355 (3.90), 374 (3.85)	76.3	42.0
1,2-benzanthracene	300 (4.06), 315 (3.25), 345 (3.86), 360 (3.71), 384 (2.95)	74.5	44.1
coronene	370 (2.38), 389 (2.5), 402 (2.4), 410 (2.56), 428 (1.95)	66.7	54.4
perylene	290 (3.0), 385 (4.1), 407 (4.2), 434 (4.2)	65.8	35.1
phenothiazine	285 (3.29), 318 (3.66), 410 (2.62)		57.0
pyrene	195 (4.6), 240 (5.0), 270 (4.74), 330 (4.74)	76.9	48.1
tetracene	274 (5.1), 471 (4.0)	60.7	29.3

[a] E_S and E_T values from ref 14. [b] Spectra recorded in ethanol; see ref 15. λ_{max} in nm. [c] Values in kcal/mol.

Table III
Singlet and Triplet Energies for Various Aromatic Ketone Photosensitizers[a]

photosensitizer	major absorption bands[b] λ_{max} (log ε)	E_S[c]	E_T[c]
9,10-anthraquinone	250 (4.98), 270 (4.50), 325 (4.02)		62.4
benzophenone	252 (4.26), 335 (2.20)	75.4	68.6
2-chlorothioxanthone	220 (4.20), 260 (4.51), 293 (3.59), 304 (3.52), 386 (3.69)		
9-fluorenone	248 (4.81), 257 (5.04), 284 (3.49), 294 (3.59), 307 (3.35), 314 (3.25), 322 (3.14), 329 (3.04), 380 (2.47), 393 (2.44)		53.3
thioxanthone	257 (4.6), 264 (4.5), 285 (3.67), 299 (3.49), 280 (3.78)	80.5	65.5

[a] E_S and E_T values from ref 14. [b] Spectra recorded in ethanol; see ref 15. λ_{max} in nm. [c] Values in kcal/mol.

Scheme I

$$P \xrightarrow{h\nu} P^* \qquad (6)$$

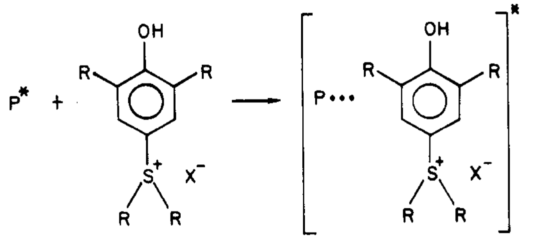
$$P^* + ArCOCH_2\overset{+}{S}R_2\ X^- \longrightarrow [P\cdots ArCOCH_2\overset{+}{S}R_2\ X^-]^* \qquad (7)$$

$$[P\cdots ArCOCH_2\overset{+}{S}R_2\ X^-]^* \longrightarrow P + ArCOCH_2\cdot + R_2S^{+\cdot}X^- \qquad (8)$$

$$R_2S^{+\cdot}X^- \xrightarrow{M} \text{polymer} \qquad (9)$$

Scheme II

$$P \xrightarrow{h\nu} P^* \qquad (10)$$



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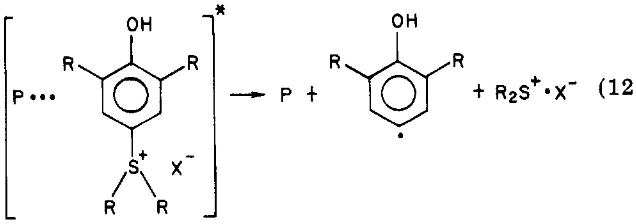

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$$R_2S^{+\cdot}X^- \xrightarrow{M} \text{polymer} \qquad (13)$$

only in the specific cases of anthracene, 1,2-benzanthracene, and pyrene. However, energy transfer in these cases would require interaction of the excited singlet states of the photosensitizer with the triplet state of the dialkylphenacylsulfonium salt. This is a spin-forbidden process and therefore highly improbable.[12] A similar argument drawn from the values in Tables I and III can be advanced for the improbability of direct energy transfer from aryl ketones to dialkyl(4-hydroxyphenyl)sulfonium salts. In addition, it should again be noted that since aryl ketones are known to undergo very rapid intersystem crossing to the excited triplet states, the probability that direct energy transfer will occur from the excited singlet of the aryl ketone to the excited triplet of the dialkyl(4-hydroxyphenyl)sulfonium salt is further decreased.

Another potential mechanism for photosensitization involves homolytic bond cleavage of the onium salt by means of an excited-state complex, or exciplex, of the photosensitizer and the sulfonium salt. Schemes I and II show this mechanism for the dialkylphenacylsulfonium and dialkyl(4-hydroxyphenyl)sulfonium salts, respectively.

In this mechanism, the excited-state photosensitizer shares its excitation energy within an exciplex and the energy is utilized for homolytic cleavage of a carbon–sulfur bond. The resulting sulfinium radical cation can then react with solvent or monomer (M) to generate the initiating species, probably the protonic acid, HX. Interestingly, previous to our investigations which demonstrated that the predominant process involved in the photolysis of dialkylphenacylsulfonium salts involves reversible ylide formation,[4] two groups[16,17] postulated a homolysis similar to that shown in eq 8 on the basis of the products formed after prolonged unsensitized photolysis.

Efficient photosensitized formation of a sulfinium cation radical requires that the excitation energy of the photosensitizer be greater than the dissociation energy of the carbon–sulfur bond of the sulfonium salts. Thus, aside from the factors which influence the efficiency of exciplex formation, this mechanism would predict that photosensitizers with excitation energies above the bond dissociation energy will be effective, whereas photosensitizers with excitation energies below the bond dissociation energy will be ineffective. Unfortunately, the bond dissociation energies of the above two sulfonium salts have not been determined. At the same time, there appears to be no correlation between the excitation energies of those compounds which are active photosensitizers and those which are not. A wide variety of potential photosensitizers having a broad range of excitation energies were screened for both types of sulfonium salts. The only correlation which could be made in these studies was on the basis of chemical type, i.e., aryl ketones on one hand and aromatic hydrocarbons on the other.

Scheme III

$$P \xrightarrow{h\nu} P^* \qquad (14)$$

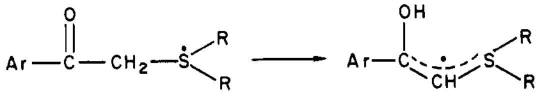
$$P^* + ArCOCH_2\overset{+}{S}R_2\ X^- \longrightarrow P^{+\cdot}X^- + ArCOCH_2\dot{S}R_2 \qquad (15)$$

$$P^{+\cdot}X^- \xrightarrow{M} \text{polymer} \qquad (16)$$

While the above arguments do not conclusively disprove photosensitized homolytic bond cleavage as the prime mechanism involved in the present photosensitization of sulfonium salts, taken together they suggest that it is rather unlikely.

A third alternative mechanism involves, as a key step, an electron transfer between the excited-state photosensitizer and the sulfonium salts. Scheme III shows a proposed electron transfer mechanism for the photosensitization of dialkylphenacylsulfonium salts.

The key feature of this reaction is that electron transfer between the photosensitizer and the dialkylphenacylsulfonium salt results in the generation of a cation radical species which ultimately initiates polymerization. The coproduct of the reaction is a highly resonance-stabilized sulfur radical species which probably eventually undergoes homolysis of a carbon–sulfur bond as shown in eq 17 and 18. A similar mechanism has been proposed by Pappas and Jilek for the photosensitized photolysis of diaryliodonium and triarylsulfonium salts.[8]



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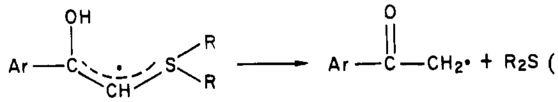

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It may be noted that the overall consequences of Scheme III are that of reduction for the sulfonium salt and oxidation for the photosensitizer. In concert with this observation is the wide recognition that electronic excitation dramatically changes the redox properties of reagents. Weller and co-workers have clearly demonstrated the relationship between the electron-donor or -acceptor ability of electronically excited aromatic hydrocarbons and the thermodynamic and kinetic characteristics of their reactions.[18,19] Schuster and co-workers have shown that the oxidation potential of an electronically excited state may be estimated by subtracting the excitation energy from the ground-state oxidation potential.[20] In Table IV are shown the calculated oxidation potentials for the excited states of the aromatic hydrocarbons used in this study. Thus, perylene, which is a good electron donor (reducing agent,

Table IV
Oxidation Potentials of Photosensitizers[a]

compound	E_{Ox},[b] V	E_S, kcal/mol	E_S, V	E^*_{Ox}, V
anthracene	−1.35	76.3	−3.31	−1.96
1,2-benzanthracene	−1.00	74.5	−3.23	−2.23
coronene	−1.23	66.7	−2.89	−1.66
perylene	−1.06	65.8	−2.85	−1.79
phenothiazine	−0.270 (−0.334)			
pyrene	−1.36	76.9	−3.33	−2.00
tetracene	−0.95	60.7	−2.63	−1.68

[a] All E_{Ox} values are assigned negative values by convention. [b] The oxidation values are taken from ref 21.

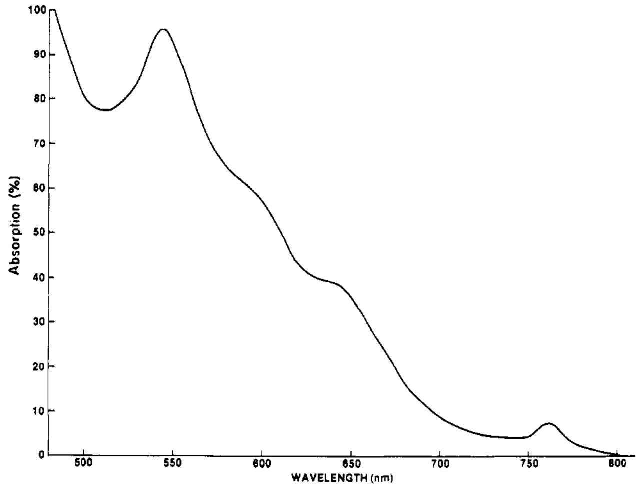
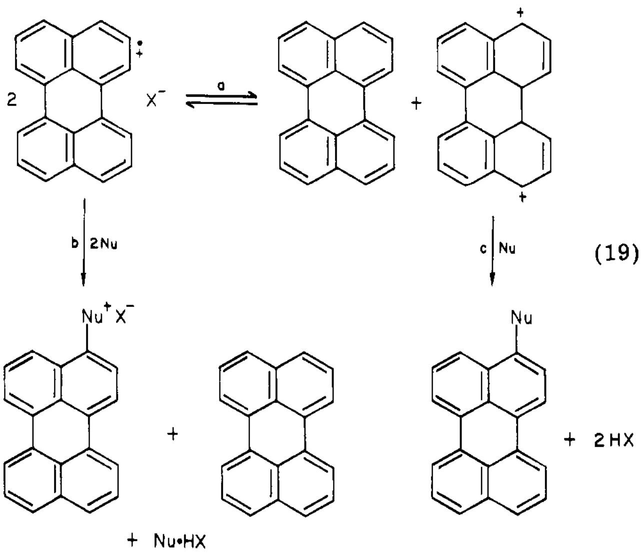


Figure 9. Visible spectrum of the photolysis of perylene (3.2×10^{-4} mol) and phenacyltetramethylenesulfonium hexafluoroarsenate (2×10^{-3} mol) in CH_2Cl_2.

Scheme IV



(19)

$E_{Ox} = -1.06$ V) in the ground state, is an even more powerful reducing agent, $E^*_{Ox} = -1.79$ V, in its excited state. Several workers have measured the enhanced reactivity of the excited state of various hydrocarbons in electron transfer reactions and have demonstrated that the rate of those reactions is a function of the oxidation potentials of the excited states.[22,23]

An additional consequence of Scheme III is that photosensitization results in irreversible photolysis of the dialkylphenacylsulfonium salt. This is in marked contrast to the nonphotosensitized photolysis which involves reversible ylide formation (eq 2). One would therefore predict that preirradiation in an inert solvent followed by addition of the polymerizable monomer would not result in polymerization, whereas in the photosensitized case, polymerization would take place. When 2.6×10^{-3} M solutions of phenacyltetramethylenesulfonium hexafluoroarsenate in CH_2Cl_2 were irradiated for 10 min, no polymerization was noted when styrene oxide was subsequently added. On the other hand, irradiation for 3 min in the presence of 3.9×10^{-4} M perylene followed by the dark addition of styrene oxide produced extremely vigorous polymerization. During irradiation, a deep blue solution was produced in the photosensitized case, suggestive of the presence of the perylene cation radical. The deep blue color was discharged immediately on addition of the epoxide. When the photolysis of a mixture of perylene and the dialkylsulfonium salt is carried out in CH_2Cl_2 and the ESR spectrum subsequently recorded, there is observed after 1–2-s irradiation the presence of a strong ESR band with considerable hyperfine splitting, indicating the generation of a long-lived organic radical. Perylene cation radical salts have been prepared and isolated as stable, well-characterized solids.[24,25] The visible absorption spectrum of the above photolysis mixture is shown in Figure 9. The bands at 547 and 761 nm correspond closely to those reported for the perylene cation radical.[25,26] Similarly, the photolyses of the other aromatic hydrocarbon photosensitizers shown in Table IV produce deep colors on irradiation in the presence of dialkylphenacylsulfonium salts, suggesting that the corresponding cation radicals were formed in these cases also.

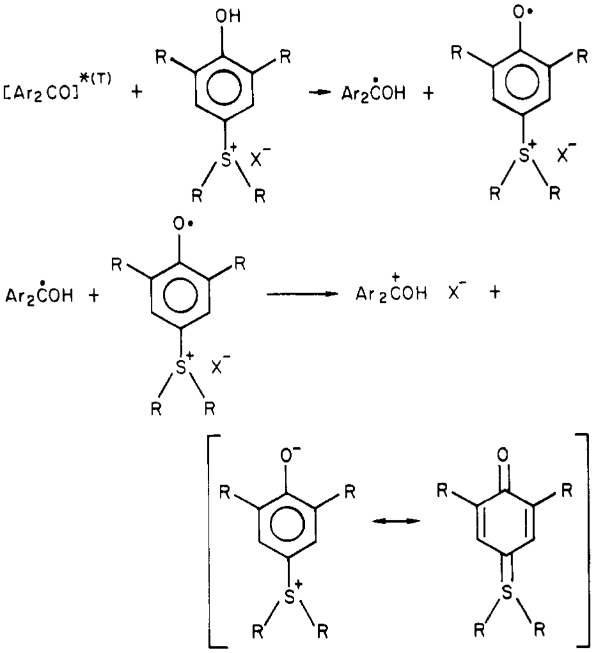
One of the consequences of Scheme III is that the photosensitizer cation radical rather than fragments from the photolysis of the sulfonium salt photoinitiator initiates cationic polymerization. Shine and co-workers have investigated the reactions of the perylene cation radical with typical nucleophiles and have observed products in which the nucleophile is bound to the perylene nucleus.[27] Scheme IV shows two possible mechanisms that have been proposed to account for the products which are formed. In the case where the nucleophile is a cationically polymerizable monomer, Scheme IV would predict that at least a portion of the polymer formed should have 3-perylenyl end groups. Indeed, when the perylene-photosensitized polymerization of cyclohexene oxide was carried out with phenacyltetramethylenesulfonium hexafluoroarsenate as the photoinitiator, the resulting polymer was found by visible spectroscopy to have perylene end groups bound to the polymer backbone. Similarly, Oberrauch, Salvatori, and Cesca[28] have recently used the stable perylene cation radical perchlorate to initiate the polymerization of various vinyl and heterocyclic monomers and have observed that perylene moieties are incorporated into the polymers.

Although phenothiazine is not a polynuclear hydrocarbon, it can likewise be regarded as an excited-state electron donor (reducing agent) for dialkylphenacylsulfonium salts. The reducing properties of phenothiazine are well-known[29] and its cation radical salts have been isolated.[30]

It must be pointed out that while the E^*_{Ox} values shown in Table IV allow one to predict which aromatic hydrocarbons will serve as photosensitizers for dialkylphenacylsulfonium salts, a simple comparison of the relative magnitudes of E^*_{Ox} does not allow the prediction of their relative efficiencies in photopolymerization. Other factors, such as the wavelength and magnitude of the absorption bands of the photosensitizer, the lifetime of their excited

Scheme V

$$\mathrm{Ar_2CO} \xrightarrow[n \to \pi^*]{h\nu} [\mathrm{Ar_2CO}]^{*(S)} \xrightarrow[\text{crossing}]{\text{intersystem}} [\mathrm{Ar_2CO}]^{*(T)} \qquad (20)$$



(21)

(22)

$$\mathrm{Ar_2\overset{+}{C}OH\ X^-} \longrightarrow \mathrm{Ar_2CO + HX} \qquad (23)$$

states, the wavelength of light used, and the efficiency of the reactive species in initiation, play a role in determining which photosensitizer–sulfonium salt combination will be most efficient in photoinitiated cationic polymerization.

Scheme V shows a proposed electron transfer mechanism for the photosensitization of dialkyl(4-hydroxyphenyl)sulfonium salts by aryl ketones. The hydrogen atom abstraction from phenols by triplet-state ketones to give phenoxy radicals (eq 21) is well documented in the literature.[31] This reaction has been shown to be favored by an exothermic heat of reaction when the activation energy of the ketone is $\lesssim$70 kcal/mol.[32] Our earlier observation of phosphorescence quenching of excited aryl ketones by the above sulfonium salts concurs with the known high quenching constants for the photochemical reaction of ketones by phenols.[33] In eq 22, the cation radical is further oxidized by the ketyl radical to the resonance-stabilized ylide. The protonated ketone then collapses to regenerate ketone and give the acid HX. It may be noted that in contrast to the process shown in Scheme III, which involves an overall reduction, Scheme V is an oxidation; however, photosensitization closely resembles the nonphotosensitized process with respect to the net products formed, i.e., an ylide and a Brønsted acid. Hence, the photosensitized process should also be reversible. It would, therefore, be predicted that preirradiation of an aryl ketone photosensitized photolysis of a dialkyl(4-hydroxyphenyl)sulfonium salt followed by addition of a polymerizable monomer should not result in polymerization. This conclusion has been confirmed experimentally. When the thioxanthone (3.9×10^{-3} M) photosensitized photolysis of dimethyl(3,5-dimethoxy-4-hydroxyphenyl)sulfonium hexafluoroarsenate (2.6×10^{-2} M) was performed in CH_2Cl_2 for 10 min, no observable change in the color of the solution was noted. On extinguishing the lamp and addition of styrene oxide, no polymerization was observed. While the above experiment does not conclusively prove that the mechanism shown in Scheme V is operating in this case, it does rule out the possibility of photosensitized bond cleavage (Scheme II) since this mechanism would predict that preirradiation followed by monomer addition should result in polymerization.

The involvement of charge transfer processes occurring between the photosensitizer and sulfonium salts together with the apparent high efficiency of photosensitization suggests the involvement of excited-state complexes (exciplexes). The observation of fluorescence and phosphorescence quenching of the photosensitizer excited states lends further credence to this possibility since quenching is often noted when exciplexes are observed. Attempts have not yet been made to look spectroscopically for the presence of an associated charge transfer band.

Acknowledgment. We thank A. Factor for assistance in obtaining the ESR spectra and P. Piacente for help in obtaining the fluorescence spectra.

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