Macromolecules 1983, 16, 864-870

# Structural and Mechanistic Studies on the Photolysis of Dialkylphenacylsulfonium Salt Cationic Photoinitiators

**James V. Crivello* and Julia L. Lee**

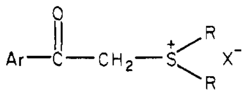
*General Electric Corporate Research and Development, Schenectady, New York 12301.*

*Received September 29, 1982*

ABSTRACT: A reinvestigation of the mechanism of photolysis of dialkylphenacylsulfonium salts showed that these reactions proceed through a Norrish II process involving the formation of a six-membered transition state. The effects of various structural modifications and substituents on the relative photolysis rates of these compounds were studied and related to their efficiencies in the photoinitiated cationic polymerization of a simple difunctional epoxy monomer.

## Introduction

Dialkylphenacylsulfonium salts, I, in which the anions, $X^-$, are of poor nucleophilic character, as, for example, $BF_4^-$, $AsF_6^-$, $SbF_6^-$, $PF_6^-$, etc., were reported in an earlier paper from this laboratory to be a new class of useful photoinitiators for cationic polymerization.[1] In a subsequent publication, we described the development of photosensitizers for these compounds that permit the extension of their photoresponse into the long-wavelength region of the ultraviolet spectrum.[2] The excellent photosensitivity of these photoinitiators together with their very good thermal stability makes them ideal photoinitiators for the polymerization of many types of cationically polymerizable monomers.



$$\mathrm{Ar{-}C(=O){-}CH_2{-}\overset{+}{S}R_2\ X^-}$$

I

In this paper we report further investigations into the mechanism of photolysis of these compounds and examine the effects of various structural changes on their photosensitivity.

## Experimental Section

**Preparation and Purification of Starting Materials.** Acetone-$d_6$, acetonitrile-$d_3$, benzene, and dimethyl-$d_6$ sulfoxide ($Me_2SO$-$d_6$) were spectrograde materials and were used as purchased from their suppliers. Epichlorohydrin was obtained from Aldrich Chemical Co. and purified by vacuum distillation from calcium hydride. Some of the $\alpha$-bromoalkyl aryl ketones (phenacyl bromides) were purchased from commercial sources and used without purification. Additional compounds of this type were prepared according to the literature by refluxing the alkyl aryl ketone with 1 equiv of cupric bromide in a 1:1 mixture of ethyl acetate and chloroform for 2 h.[5] Dialkylphenacylsulfonium salts were prepared as described earlier by combining equal molar amounts of the dialkyl sulfide and $\alpha$-bromoalkyl aryl ketone in acetone at room temperature.[1,6] Metathesis of the bromide salt was carried out in water containing a slight excess of $NaBF_4$ or $KAsF_6$. Purification of the sulfonium salts was accomplished by recrystallization, usually from ethanol. Table I gives the spectral characteristics and elemental analysis of the new compounds prepared during the course of this work and not previously reported elsewhere.

**Preparation of Dimethylsulfonium Phenacylide (II).** A modification of the method of Trost[8,9] was employed for this synthesis. Dimethylphenacylsulfonium bromide was freshly prepared by combining equimolar (0.4 mol) amounts of phenacyl bromide and dimethyl sulfide in 350 mL of acetone at 25 °C. An 80% yield of the desired sulfonium bromide was recovered in two crops after 2 days by suction filtration. The salt was thoroughly washed with diethyl ether and dried.

To a solution of 20 g of sodium hydroxide in 250 mL of water cooled to 5 °C was slowly added under nitrogen 26 g (0.1 mol) of the above sulfonium salt. After 2 h of stirring at 5 °C, the white crystalline ylide was obtained from the reaction mixture by filtration. There was obtained 8.6 g of crude ylide, which could be further purified by recrystallization from a mixture of chloroform and carbon tetrachloride. The melting point, 59–60 °C, and NMR spectral characteristics of this compound corresponded in all respects with data previously presented in the literature for the hydrated dimethylsulfonium phenacylide.

**Relative Photolysis Rate Studies.** Standard 0.2 M solutions of dialkylphenacylsulfonium salts were prepared in $Me_2SO$-$d_6$ and irradiated in quartz NMR tubes. Irradiations were carried out in a Rayonet apparatus (Southern New England Ultraviolet Co.) equipped with a merry-go-round sample holder and 16 RPR 3000-Å lamps. The sample tubes were periodically withdrawn and shielded from the light, and their $^1H$ NMR spectra were recorded on a Varian EM-390 spectrometer. Calculation of the percent photolysis was based on the decrease in the areas of the bands assigned to the protons adjacent to the positively charged sulfur in the sulfonium salt. Rate constants were obtained by plotting the data assuming pseudo-first-order kinetics. Relative rate constants were then determined from these data assuming the rate of photolysis of $PhCOCH_2S^+(CH_2)_4BF_4^-$ was equal to unity. Photolyses were conducted in air since rates obtained from the photolysis of exhaustively freeze–thaw degassed solutions were identical with those run in air.

**Quantum Yield Measurements.** Quantum yield measurements were conducted by using standard benzophenone–benzhydrol actinometry.[3] Equimolar (0.1 M) solutions of benzhydrol and benzophenone in benzene were irradiated in 13-mm-diameter quartz tubes fitted with rubber septums. The Rayonet apparatus described previously was employed for the irradiations. After irradiation, the samples were analyzed for residual benzophenone by GC using a Hewlett-Packard 5840A gas chromatograph equipped with a flame ionization detector and a $^1/_8$ in. × 6 ft XE-60 column. $n$-Decane was added to the sample prior to analysis as an internal standard. A light intensity of $1.38 \times 10^{19}$ einsteins was obtained. Photolyses of 0.2 M solutions of dialkylphenacylsulfonium salts were conducted with the same equipment described above. The disappearance of starting sulfonium salt was followed by NMR analysis of the solutions in the same manner as described for the photolysis rate determinations. In the spectrum, the aromatic protons served as an internal standard.

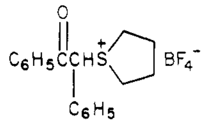
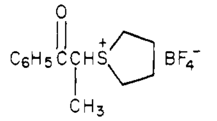
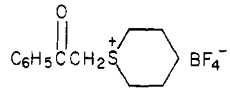
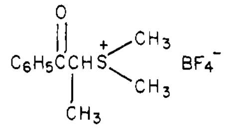
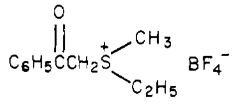
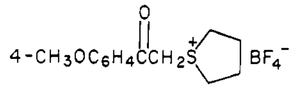
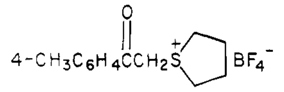
**Photoinitiated Polymerization of Epichlorohydrin.** To each 13-mm-diameter quartz tube was added 2.0 g ($2.16 \times 10^{-2}$ mol) of freshly distilled epichlorohydrin and $2.16 \times 10^{-4}$ mol of the dialkylphenacylsulfonium salt photoinitiator shown in Table III. The tubes were flushed with nitrogen and sealed with a rubber serum cap. The samples were then irradiated in a merry-go-round holder with a 450-W Hanovia mercury arc lamp. After 60 min of irradiation, the polymerizations were terminated by injecting 2 mL of 5% $NH_4OH$ solution in methanol. To each solution was added 1 mL of $n$-decane as an internal standard, and the solutions were analyzed for residual monomer by GC, using a $^1/_8$ in. × 6 ft Carbowax 1540 column.

## Results and Discussion

**Mechanistic Studies.** The mechanism shown in Scheme I was proposed earlier to account for the photoinduced hydrogen–deuterium isotope exchange that

0024-9297/83/2216-0864$01.50/0

Table I
Properties of Dialkylphenacylsulfonium Salts

| structure | mp, °C | UV $\lambda_{max}$, nm ($\epsilon$) | elemental anal. | | | |
|---|---|---|---|---|---|---|
| | | | | % C | % H | % S |
|  | 157.0–157.5 | 255 (11 475)<br>315 (2 063) | calcd<br>found | 58.38<br>58.30 | 5.14<br>5.30 | 8.65<br>8.77 |
|  | 122.5–123.0 | 250 (12 780)<br>280 (2 940) | calcd<br>found | 50.65<br>50.54 | 5.52<br>5.67 | 10.39<br>10.58 |
|  | 118.5–119.0 | 248 (10 890)<br>290 (4 507) | calcd<br>found | 50.65<br>50.76 | 5.52<br>5.64 | 10.39<br>10.47 |
|  $C_6H_5COCH(CH_3)\overset{+}{S}(CH_3)_2\ BF_4^-$ | 127.5–128.0 | 250 (12 240)<br>280 (2 400) | calcd<br>found | 46.81<br>47.06 | 5.32<br>5.45 | 11.35<br>11.75 |
|  $C_6H_5COCH_2\overset{+}{S}(CH_3)(C_2H_5)\ BF_4^-$ | 109.0–111.0 | 248 (10 600)<br>290 (4 000) | calcd<br>found | 46.80<br>47.05 | 5.32<br>5.49 | 11.35<br>11.49 |
|  | 216.0–218.0 (dec) | 222 (9 150)<br>287 (18 000) | calcd<br>found | 48.15<br>47.99 | 5.25<br>5.29 | 9.88<br>10.06 |
|  | 180 (dec) | 260 (14 400)<br>300 (3 800) | calcd<br>found | 50.65<br>50.84 | 5.52<br>5.49 | 10.39<br>10.58 |

occurs when dialkylphenacylsulfonium salts are irradiated in acetone-$d_6$.[1]

When the sulfonium salt Ia is irradiated, a resonance-stabilized ylide, phenacylidinedimethylsulfurane (II), and the acid HX, which is solvated by acetone-$d_6$ (eq 1) are generated. Since dialkylphenacylsulfonium salts can be prepared by reaction of II with protonic acids at room temperature, this reaction is reversible.[4] In acetone-$d_6$, protonation results in hydrogen–deuterium exchange in the methyl groups of the solvent as depicted in eq 3 and 4. At the same time, the deuterio acid, $DBF_4$, is also formed. Addition of $DBF_4$ to ylides II and IV generates sulfonium salts III and V, in which the protons bonded to the carbons attached to the sulfur atom are scrambled with deuterium (eq 4 and 5).

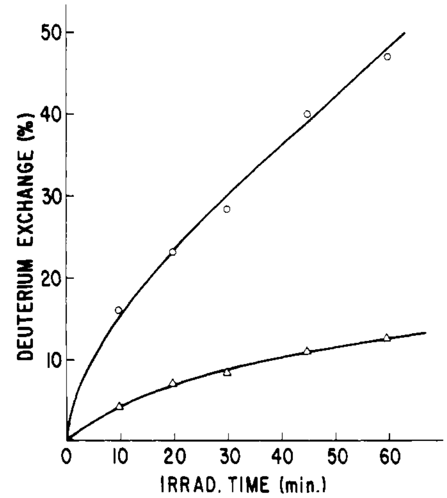
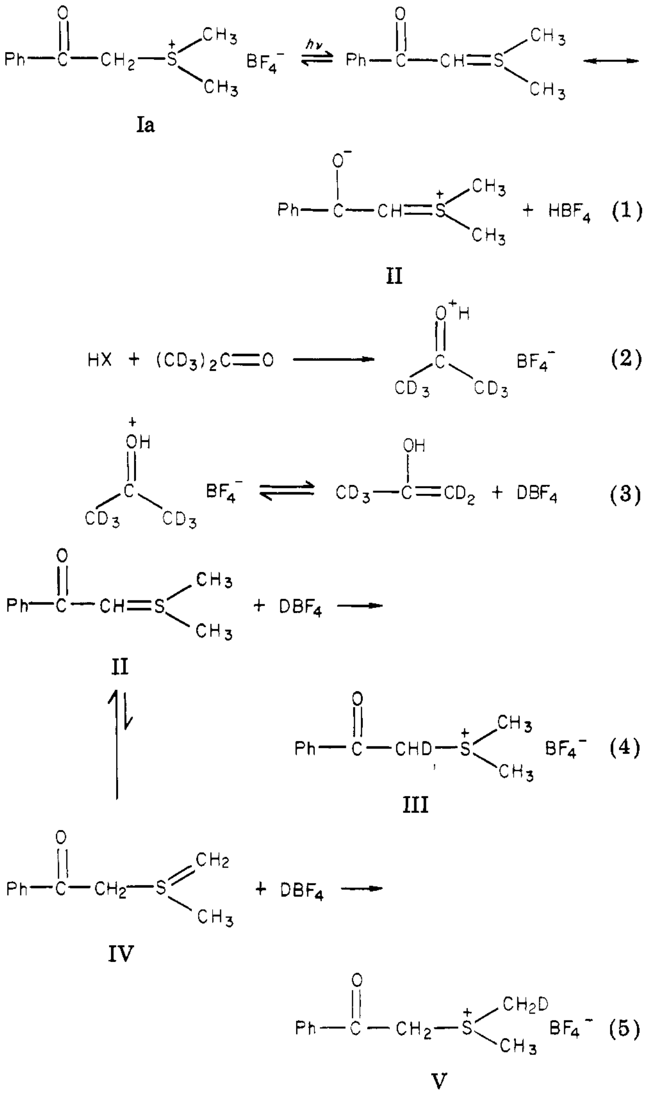


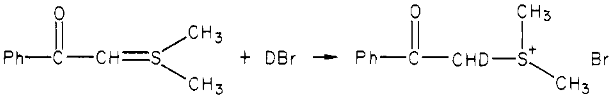
**Figure 1.** Comparison of the rates of photoinduced deuterium exchange of the methyl (○) and methylene (△) protons in dimethylphenacylsulfonium tetrafluoroborate (0.2 M) in $Me_2SO$-$d_6$ using 300-nm light.

We have been critically reexamining the above mechanism in light of recent investigations. While the photolysis of dialkylphenacylsulfonium salts does yield both protonic acids and ylides II and IV, the mechanism depicted in Scheme I involving a simple deprotonation of the sulfonium salt does not appear to be the major process. Evidence for this conclusion is derived from several observations. When the photolysis of dimethylphenacylsulfonium tetrafluoroborate is carried out in acetone-$d_6$ or $Me_2SO$-$d_6$,[7] isotopic exchange is observed to occur more rapidly at the methyl positions in the sulfonium salt than at the methylene positions. Figure 1 shows the hydrogen–deuterium exchange that has occurred at each of these positions as a function of irradiation time. However, on the basis of the mechanism shown in Scheme I it would be predicted that isotopic exchange should take place at a slower rate at the methyl than at the methylene positions. The rationale for this conclusion is the following. Because ylide II is resonance stabilized and therefore of lower energy than ylide IV, the equilibrium between the two compounds should lie far to the side of ylide II. Reaction with $DBF_4$, therefore, should give predominantly sulfonium salt III. Instead, sulfonium salt V and other similar salts resulting from deuterium exchange at the methyl groups are the major products. Further, when ylide II was prepared by treatment of the corresponding sulfonium bromide with base, only ylide II (cis and trans isomers) could be observed by $^1H$ NMR.[9] The presence of ylide IV was not detected. The equilibrium mixture of the two ylide forms (eq 4 and 5) must therefore contain less than 5% ylide IV, i.e., the

Scheme I



limit of detection by NMR analysis. Treatment of ylide II with DBr (eq 6) gave exclusive deuterium incorporation in the methylene positions to give Ib, again confirming that ylide II is thermodynamically the most stable species and, therefore, cannot be the origin of products derived from ylide IV. Clearly, another mechanism is required to resolve these discrepancies.

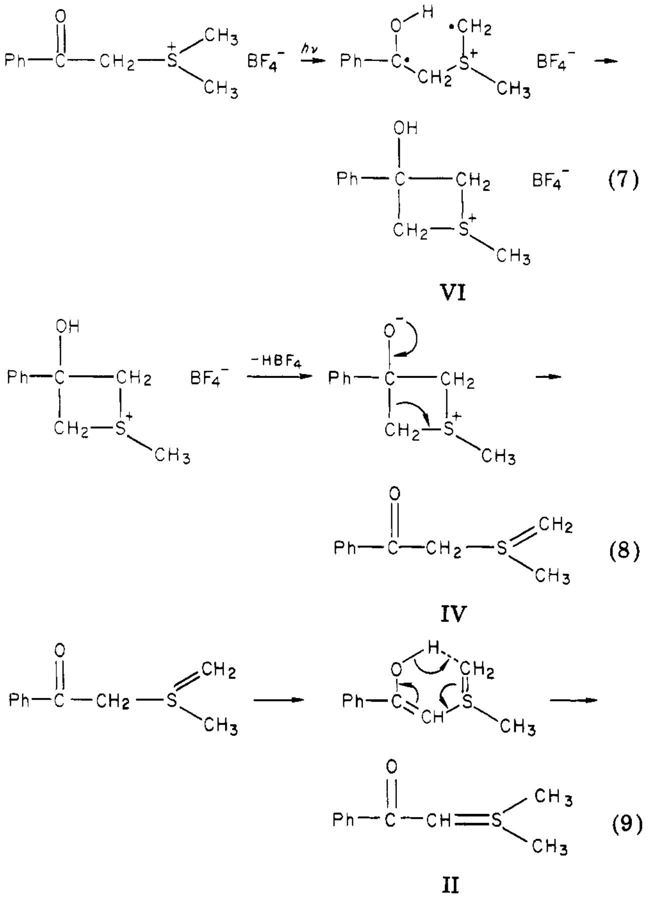


$$PhC(=O)CH{=}S(CH_3)_2 + DBr \rightarrow PhC(=O)CHD{-}S^+(CH_3)_2\ Br^- \quad (6)$$

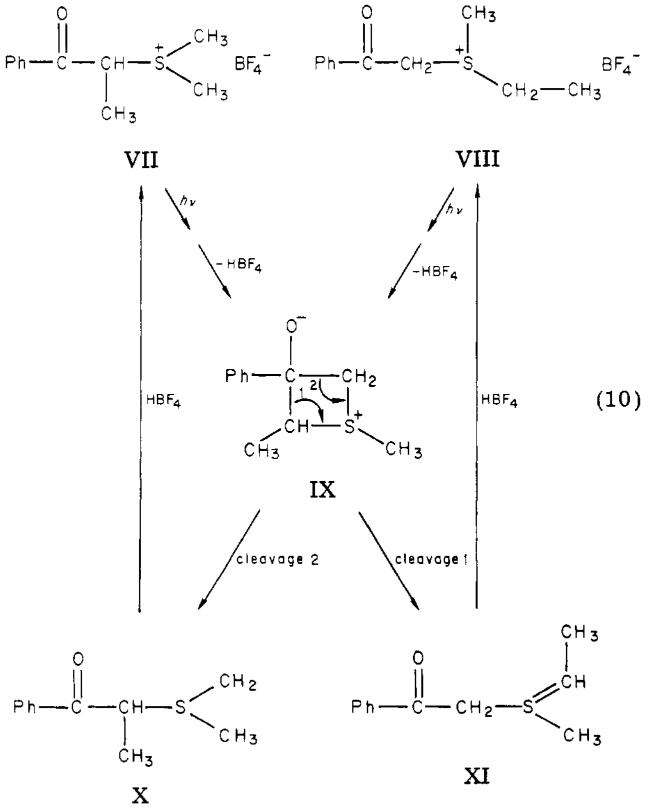
II Ib

An alternate potential mechanism for the photolysis of dialkylphenacylsulfonium salts is depicted in Scheme II. In the first step of this mechanism (eq 7), the carbonyl oxygen of the photoexcited sulfonium salt abstracts a hydrogen atom from one of the methyl groups in a six-membered transition state. Ring closure occurs through a discrete diradical species to produce the four-membered cyclic intermediate VI. This reaction is directly analogous to the well-known Norrish II photolysis of aliphatic ketones in which cyclobutanols are produced.[10,11] Deprotonation of VI followed by ring opening in the manner shown would give ylide IV. Proton transfer via another six-membered transition state (eq 9) converts ylide IV to isomeric ylide II. Thus, ylide IV is the kinetic product of the photolysis, and since protonation is generally a rapid process, this ylide would be trapped preferentially to give sulfonium salt V. Some portion of ylide IV, however, would be converted as shown in eq 9 to give the thermodynamically more stable II, which is trapped as III.

Scheme II



Scheme III



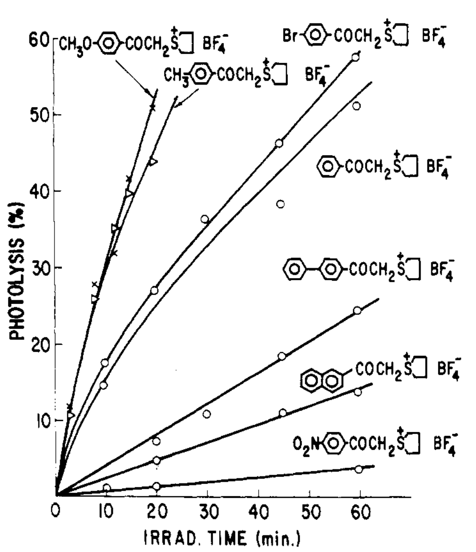
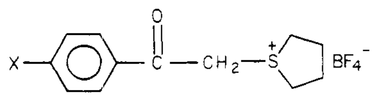


**Figure 2.** Photolysis of various para-substituted dialkylphenacylsulfonium salts (0.2 M) in $Me_2SO$-$d_6$.

Table II
Rate Constants for the Photolysis of Para-Substituted Dialkylphenacylsulfonium Salts



| X | $k_X$,[a] $s^{-1}$ | $K_{rel}$ |
|---|---|---|
| H | $1.7 \times 10^{-4}$ | 1.0 |
| $CH_3$ | $3.6 \times 10^{-4}$ | 2.1 |
| $CH_3O$ | $5.5 \times 10^{-4}$ | 3.2 |
| Br | $1.9 \times 10^{-4}$ | 1.1 |
| $C_6H_5$ | $8.6 \times 10^{-5}$ | 0.51 |
| $NO_2$ | $1.5 \times 10^{-5}$ | 0.08 |
| $C_{10}H_7$[b] | $4.8 \times 10^{-5}$ | 0.28 |

[a] Determined in $Me_2SO$-$d_6$ with 300-nm light at a constant intensity of approximately $1.38 \times 10^{19}$ einsteins.
[b] $2$-$C_{10}H_7COCH_2{}^+S(CH_2)_4BF_4{}^-$.

Several experiments were designed to test the validity of Scheme II. In Scheme III is shown the basis for these experiments. If the mechanism given in Scheme II is correct, isomeric sulfonium salts VII and VIII should give the same common cyclic intermediate, IX. Ring opening of IX may then proceed by pathways 1 and 2 to generate ylides X and XI. Reaction of these ylides with $HBF_4$ regenerates sulfonium salts VII and VIII, respectively.[12] The overall result is that irradiation of either pure VII or VIII should generate a mixture of the two sulfonium salts VII and VIII. However, when this experiment was attempted, interconversion of sulfonium salts VII and VIII was not observed. Even when steric considerations are involved to distinguish between the cyclic intermediates produced by irradiation of sulfonium salts VII and VIII, it is difficult to rationalize the above results.[13] On prolonged irradiation, typical Norrish II cleavage products are produced, with VII yielding propiophenone and VIII yielding acetophenone exclusively. Thus, while the mechanism shown in Scheme II involving a four-membered cyclic intermediate would satisfactorily explain the results of the isotopic exchange studies, it cannot be reconciled with the above-mentioned isomerization experiments and therefore must be discarded.

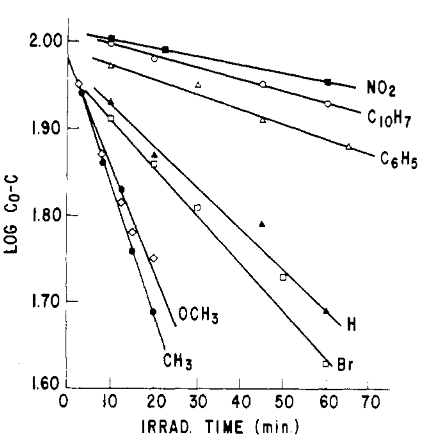


**Figure 3.** First-order rate plots for the photolysis of para-substituted dialkylphenacylsulfonium salts (0.2 M) in $Me_2SO$-$d_6$ ($C_{10}H_7 = 2$-$C_{10}H_7COCH_2{}^+S(CH_2)_4BF_4{}^-$).

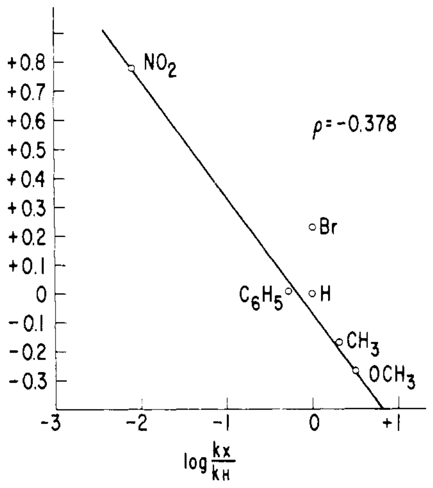


**Figure 4.** Least-squares Hammett plot for the photolysis of para-substituted dialkylphenacylsulfonium salts (correlation coefficient 0.943, $\rho$ (slope) = $-0.378$).

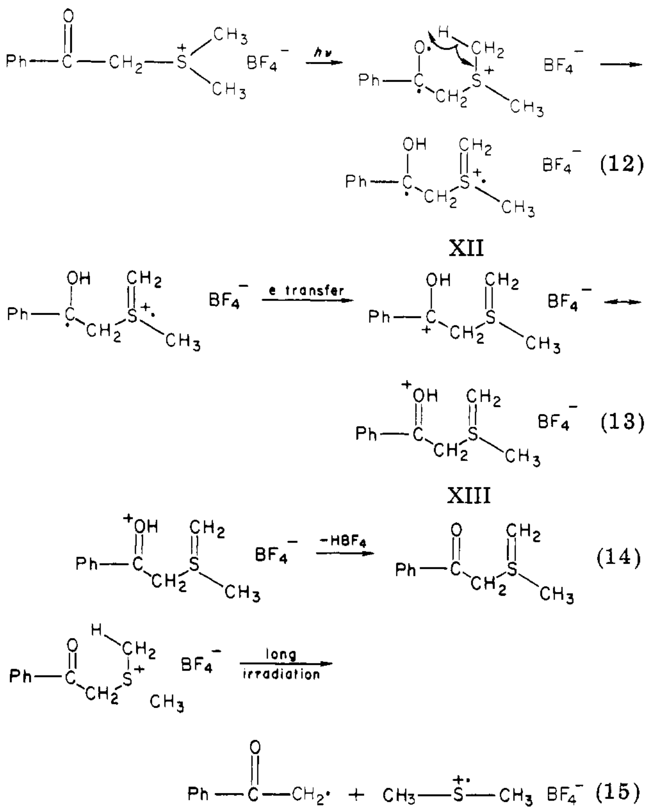
A study of the photolysis rates of various substituted dialkylphenacylsulfonium salts provided some highly pertinent mechanistic information. Although the UV absorption characteristics of these salts are similar, they exhibit markedly different photolysis rates as shown in Figure 2. Straight-line correlations were obtained when the same data were plotted according to first-order kinetics as depicted in Figure 3. Table II gives the rate constants obtained from the kinetic plots as well as the relative rates $K_{rel}$, where $K_{rel} = k_X/k_H$. Figure 4 shows a Hammett analysis of the data in which log $K_{rel}$ is plotted against the substituent constant, $\sigma$, according to the equation[14]

$$\log K_{rel} = \rho\sigma \tag{11}$$

An excellent straight-line correlation was obtained for the data, suggesting a strong dependence of the photolysis rates on the electronic character of the substituent. The reaction constant, $\rho$, calculated from the slope of the line was $-0.378$, indicating that there is a considerable accumulation of positive character at the reaction site in the transition state during the reaction.

Based on the above considerations, the mechanism shown in Scheme IV is proposed. In this mechanism, hydrogen abstraction by a typical Norrish II process generates the radical, cation-radical pair XII, which undergoes facile internal electron transfer due to their proximity to give the cation XIII. While in Scheme IV the hydrogen abstraction and electron-transfer processes are written as separate steps for clarity, they may in fact occur simultaneously.[15] Alternatively, there is considerable justification from the literature to consider a hydride abstraction by the polarized photoexcited ketone to produce XIII directly. Huyser and Neckers have demonstrated that

Scheme IV



(12) XII (13) XIII (14) (15)

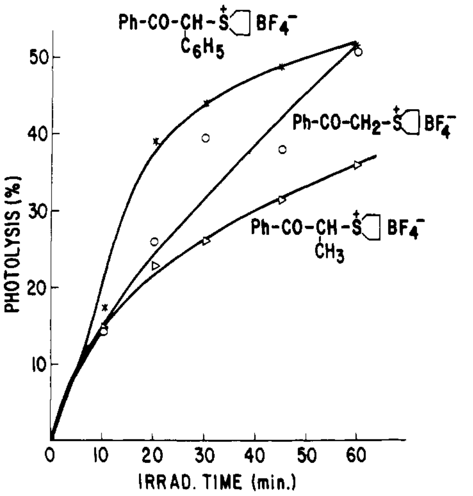
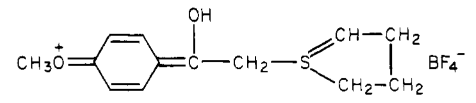


**Figure 5.** Photolysis of $\alpha$-substituted phenacyltetramethylenesulfonium salts (0.2 M) in Me$_2$SO-$d_6$.

polarized ketones play an important role in photoinduced hydrogen-transfer reactions.[16] Similarly, Ireland and Wyatt have conclusively shown on the basis of p*K* measurements that aromatic ketones are much stronger bases in their excited state than in the ground state.[17]

The observation that electron-releasing para substituents have an accelerating effect on the photoinduced hydrogen–deuterium exchange can be rationalized on the basis that such substituents would be expected to stabilize intermediate XIII by enhancing charge dispersal as shown in XIV. On the other hand, electron-withdrawing para substituents should have a retarding effect since they increase positive charge density at the carbonyl.



XIV

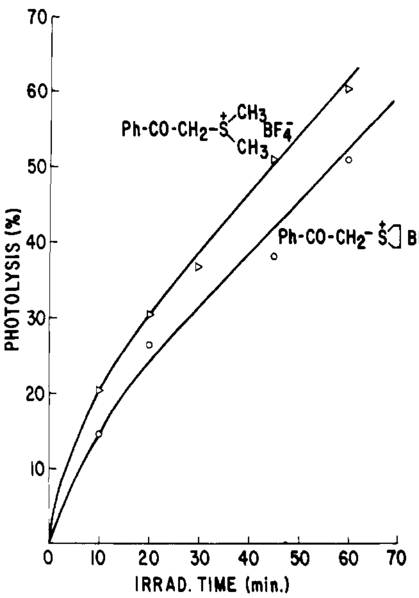
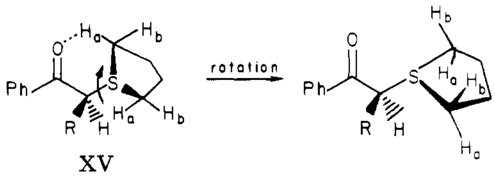


**Figure 6.** Comparison between the photolysis of 0.2 M Me$_2$SO-$d_6$ solutions of PhCOCH$_2$S$^+$(CH$_3$)$_2$BF$_4^-$ and PhCOCH$_2^+$S(CH$_2$)$_4$BF$_4^-$.

**Effects of Structure on the Photosensitivity of Dialkylphenacylsulfonium Salts.** In addition to the above study of the effects of various substituents on the aromatic rings of dialkylphenacylsulfonium salts on their photolysis rates, a similar study was conducted to investigate the influence of other structural modifications in the cation portion of these compounds.

Figure 5 shows a comparison of the photolysis rates of sulfonium salts bearing methyl and phenyl groups attached at the $\alpha$-carbon with the photolysis rate of the unsubstituted sulfonium salt. A faster initial photolysis rate was observed in the case of the phenyl-substituted compound, which can be partially ascribed to the ability of this group to stabilize the resulting ylide. The introduction of a methyl group has the opposite effect due to its destabilizing effect on the ylide. Examination of molecular models suggests that the bulky phenyl and methyl groups sterically hinder rotation about the carbon–sulfur bond, $\alpha$, as shown in eq 16. This would tend to force the alkyl groups into conformations such as XV, which are favorable for proton abstraction by a Norrish II process. By the same token, rotamer XVI would be disfavored due to the 1,3 steric interaction of the R group and the protons on the two carbon atoms attached to sulfur in the five-membered ring. The combination of the above two effects results in an overall increased photolysis rate for the $\alpha$-phenyl-substituted sulfonium salt and a slight decrease in photolysis rate for the $\alpha$-methyl compound as compared to the unsubstituted compound. Both of the photolyses for the substituted salts appear to slow appreciably at high conversions. This effect appears to be an artifact and is due to the intense darkening that occurs on photolysis of those solutions.



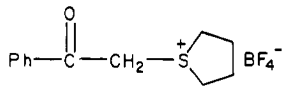
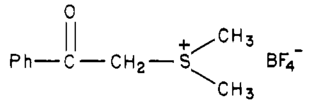
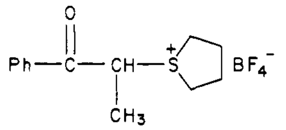
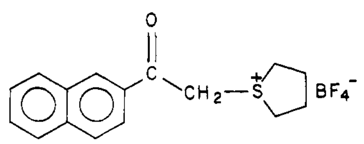
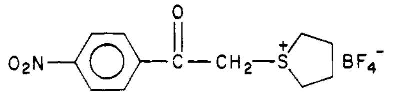
(16)

XV

XVI

A comparison of the photolysis rates of two different dialkylphenacylsulfonium fluoroborates is shown in Figure

Table III
Photoinitiated Cationic Polymerization of Epichlorohydrin[a]

| photoinitiator | % conv to polymer |
|---|---|
|  | 28 |
|  | 28 |
|  | 15 |
|  | 19 |
|  | 22 |

[a] Irradiations were carried out for 60 min using a 450-W Hanovia Hg arc lamp on solutions of 2.16 × $10^{-4}$ mol of photoinitiator dissolved in 2.16 × $10^{-2}$ mol of epichlorohydrin.

6. The rate of photolysis of the dimethyl-substituted compound is approximately 0.4 times faster than the compound bearing the five-membered aliphatic ring. This was initially surprising since the abstraction of secondary protons is generally regarded as more facile than the abstraction of primary protons. Again an examination of models of the two compounds and eq 16, where R = H provides a plausible explanation for these observations. In the case of the dimethylphenacylsulfonium salt, both methyl groups are free to rotate about the carbon–sulfur bond and thus all six protons are available for abstraction by a Norrish II process. In contrast, only the two methylene protons, $H_a$, on the side of the ring facing the carbonyl group are available for abstraction in the phenacyl tetramethylene salt. The remaining two protons, $H_b$, cannot be abstracted since they are held rigidly by the ring in conformations that preclude their participation in the required six-membered transition state. Pyramidal inversion at sulfur, which would interconvert the $H_a$ and $H_b$ protons, is known to be slow at room temperature[18,19] and probably does not occur within the lifetime of the excited state. On a statistical and conformational basis, therefore, proton abstraction is favored for dimethyl-substituted salt.

Quantum yield measurements of the photolysis of phenacyltetramethylenesulfonium tetrafluoroborate and hexafluoroarsenate at 313 nm gave values of 0.32 and 0.41, respectively. These values are somewhat higher than those obtained for the corresponding triphenylsulfonium salts ($\Phi$ = 0.1–0.2) at the same wavelength.[20] Despite their higher quantum yields of photolysis, dialkylphenacylsulfonium salts are less efficient as photoinitiators for cationic polymerizations than the analogous triphenylsulfonium salts. One reason for the difference between these two compounds is the presence of the thermal back-reaction in the former compounds, which continually depletes the solution of the acid initiator. In contrast, triarylsulfonium salts undergo irreversible photolysis. The initiating efficiency of dialkylphenacylsulfonium salts is further reduced by the presence of the ylide, which can serve as both a chain terminator and chain-transfer agent.[1]

**Photoinitiated Cationic Polymerization of Epichlorohydrin.** The effects of modifying the structure of the cation in dialkylphenacylsulfonium salts were studied in relation to the efficiency with which they photoinitiated the cationic polymerization of epichlorohydrin. Table III shows the data obtained in this study. Only broad trends in efficiency of these photoinitiators can be distinguished from the results of this study.

As predicted from Figure 2, the sulfonium salts bearing 4-nitrophenyl and 2-naphthyl groups were the least photosensitive compounds and gave poorest conversion to polymer. Although on the basis of the photolysis rates (Figure 6) dimethylphenacylsulfonium tetrafluoroborate photolyzes 0.4 times faster than the corresponding phenacyltetramethylenesulfonium salt, they both appear to give approximately equal conversions of epichlorohydrin to polymer. Significantly lowered yields of polymer are obtained for the less photosensitive ($\alpha$-methylphenacyl)tetramethylenesulfonium salt than for the parent compound in which the $\alpha$-methyl group is absent.

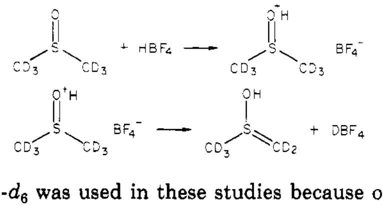
## Conclusions

Dialkylphenacylsulfonium salts are a series of readily prepared and useful photoinitiators for cationic polymerization whose photosensitivity may be easily manipulated by the introduction and modification of substituents at various sites within the molecule. Using such schemes, one may obtain a threefold increase in photosensitivity in optimally substituted sulfonium salts over the parent unsubstituted compounds. The effects of various substituents correlate well with what has been predicted on the basis of the proposed mechanism for the photolysis of these compounds.

**Registry No.** $CH_3$-$p$-$C_6H_4COCH_2S^+(CH_2)_4BF_4^-$, 85629-03-4; $CH_3O$-$p$-$C_6H_4COCH_2S^+(CH_2)_4BF_4^-$, 85629-05-6; Br-$p$-$C_6H_4COCH_2S^+(CH_2)_4BF_4^-$, 71967-55-0; $C_6H_5$-$p$-$C_6H_4COCH_2S^+(CH_2)_4BF_4^-$, 71967-60-7; $C_6H_5COCH_2S^+(CH_2)_4BF_4^-$, 71967-51-6; $C_6H_5COCH_2S^+(CH_3)_2BF_4^-$, 24806-57-3; $C_6H_5COCH(CH_3)S^+CH_2)_4BF_4^-$, 85629-07-8; 2-$C_{10}H_7COCH_2S^+(CH_2)_4BF_4^-$, 71967-58-3; $NO_2$-$p$-$C_6H_4COCH_2S^+(CH_2)_4BF_4^-$, 71967-53-8; $C_6H_5COCH(C_6H_5)S^+(CH_2)_4BF_4^-$, 85629-09-0; $C_6H_5COCH_2S^+(CH_2)_5BF_4^-$, 85629-10-3; $C_6H_5COCH(CH_3)S^+(CH_3)_2BF_4^-$, 85629-12-5; $C_6H_5COCH_2S^+(CH_3)(C_2H_5)BF_4^-$, 85629-13-6; epichlorohydrin, 106-89-8.

## References and Notes

(1) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2877.
(2) Crivello, J. V.; Lee, J. L. *Macromolecules* **1981**, *14*, 1141.
(3) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 125.
(4) Johnson, A. W. "Ylid Chemistry"; Academic Press: New York, 1966; p 315.
(5) King, L. C.; Ostrum, G. K. *J. Org. Chem.* **1964**, *29*, 3459
(6) Boeme, H.; Krause, W. *Chem. Ber.* **1949**, *82*, 426.
(7) Acid-induced isotopic exchange in $Me_2SO$-$d_6$ occurs in an analogous manner to that in acetone-$d_6$; i.e.



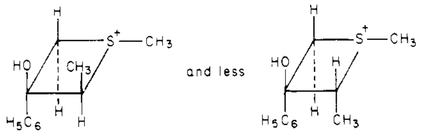
$Me_2SO$-$d_6$ was used in these studies because of its excellent transmission characteristics at 300 nm and because it readily dissolves dialkylphenacylsulfonium salts.
(8) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138.
(9) Trost, B. M. *J. Am. Chem. Soc.* **1966**, *88*, 1587.

(10) Yang, N. C.; Yang, D. H. *J. Am. Chem. Soc.* **1958**, *80*, 2913. Yang, N. C.; Morduchowitz, A.; Yang, D. H. *Ibid.* **1963**, *85*, 1017.

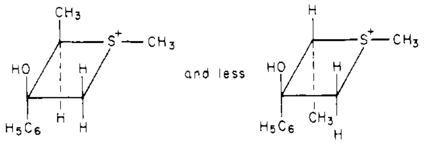
(11) Yates, P.; Szabo, A. G. *Tetrahedron Lett.* **1965**, 485.

(12) Ylides X and XI can also undergo prototropic rearrangement as shown in eq 9 to shift the carbon–sulfur double bond to the position $\alpha$ to the carbonyl. However, reaction of these new ylides with $HBF_4$ would also be expected to give sulfonium salts (VII and VIII).

(13) On the basis of minimization of steric hindrance, photolysis of VII would be expected to give mainly



and photolysis of VIII mainly



(14) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt, Reinhart and Winston: New York, 1959; p 220.

(15) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin Cummings Publishing Co.: Menlo Park, 1978; p 384.

(16) Huyser, E. S.; Neckers, D. C. *J. Am. Chem. Soc.* **1963**, *85*, 3641.

(17) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1968**, *12*, 188.

(18) Darwish, D.; Hui, S. H.; Tomilson, R. *J. Am. Chem. Soc.* **1968**, *90*, 5631.

(19) Scartazzini, R.; Mislow, K. *Tetrahedron Lett.* **1967**, 2719.

(20) Crivello, J. V.; Lam, J. H. W. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 977.

---

# Structure–Property Relationships of Polyacetylene/Polybutadiene Blends

**Michael F. Rubner,* Sukant K. Tripathy, Jacque Georger, Jr., and Patricia Cholewa**

*GTE Laboratories, Inc., Waltham, Massachusetts 02254.* *Received August 27, 1982*

ABSTRACT: Polymer blends of polyacetylene and *cis*-1,4-polybutadiene of various compositions were prepared and examined. The resulting blends were characterized by infrared spectroscopy, thermal analysis, and X-ray diffraction techniques. The blends were found to exist as two-phase systems consisting of crystalline polyacetylene and amorphous polybutadiene. The mechanical properties of the blends were found to be a function of the blend composition, with low polyacetylene compositions exhibiting rubbery elastic properties and high polyacetylene compositions behaving more plastic-like. Doping the blends with electron acceptors such as iodine and ferric chloride resulted in electrical conductivities in the 10–100 $\Omega^{-1}$ $cm^{-1}$ range. For blends containing 40–60% polyacetylene, the conductivity could be further enhanced by stretching the blend prior to doping. Results suggest that this phenomenon is a complex process of stress-induced ordering that is taking place in the polyacetylene phase. Varying the composition of the blend allowed a range of mechanical and electrical properties to be obtained that thus extend the useful properties of polyacetylene.

## Introduction

Polyacetylene has been the subject of many recent research activities. This is primarily due to the unique electrical properties manifested by polyacetylene when it is exposed to electron-donating or electron-withdrawing dopants.[1] Typically, polyacetylene is prepared in the form of a film or as a powder. However, the material is insoluble, intractable, and infusible, and, although reasonable mechanical properties are observed[2] when it is maintained in an inert atmosphere, upon exposure to ambient conditions, polyacetylene quickly becomes brittle. For these reasons, morphological modification of polyacetylene and its characterization have been difficult. Additionally, lack of processibility and stability are the major stumbling blocks in finding suitable applications for this fascinating material.

Attempts have been made to improve the undesirable mechanical properties without compromising the electrical properties via synthetic techniques. For example, copolymers of polyacetylene with phenylacetylene[3] and methylacetylene[4] have been prepared and characterized. This was carried out with the hope that while the unchanged structure of the polymer backbone will result in unaltered electrical properties, the side groups will impart the required processing advantage. The resultant materials were indeed found to have some processing advantages (soluble copolymers can be obtained with phenylacetylene) over the homopolymer; however, this was accomplished only with significant decrease in the electrical conductivity. While this behavior is not well understood, it is speculated that the electrical properties are very sensitive to the arrangement of chains and order in the polymeric "microdomains".[5] Interestingly, Galvin and Wnek recently reported[6] that films consisting of polyacetylene blended with polyethylene remained tough and flexible after prolonged exposure to air. Yet the films could be doped to conductivities of about 10 $\Omega^{-1}$ $cm^{-1}$. Obviously, a detailed study of polyblends can make a significant impact on the understanding of the nature of electrical transport in these materials and the structural requirements thereof.

In our laboratory we are presently carrying out these investigations with the polyblends of polyacetylene with an elastomer. In this paper we report on polyblends in which the elastomeric component is *cis*-1,4-polybutadiene. The selection of an elastomer as a component of the blend can be rationalized at two levels. First, the contrast between the rubbery nature of polybutadiene and the polycrystalline nature of polyacetylene can be exploited to gain information on morphology, structure, and the physical properties of the blend. Also, by blending with a flexible polymer having a low $T_g$, a full range of blend compositions can be obtained. Second, the excellent mechanical properties of polyblends containing a rubbery component are well-known, and therefore a similar enhancement of properties would be expected in the case of a polyacetylene blend. In other words, polyacetylene/elastomer blends not

0024-9297/83/2216-0870$01.50/0