

**SUBSTITUTED TRIPHENYLMETHYL CARBOCATIONS.
I. PHOTO INITIATED CATIONIC POLYMERIZATION OF THE**

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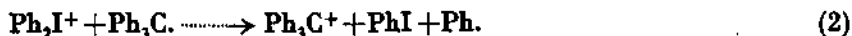
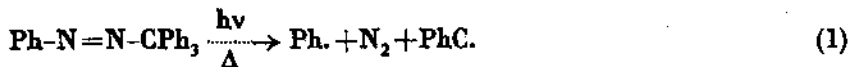
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SUMMARY

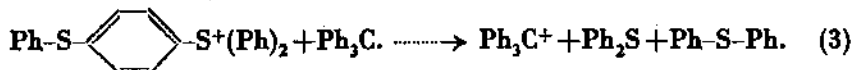
Triphenyl, diphenyl-*p*-tolyl and diphenyl-*o*-hydroxyphenyl methyl carbocations have been obtained by the U.V. irradiation of the solutions of the related azo compounds and $\text{Ph}_2\text{I}^+ \text{PF}_6^-$ or $\text{Ph-S-} \langle \text{benzene ring} \rangle \text{-S}^+ (\text{Ph})_2 \text{PF}_6^-$ in methylene chloride. Interrelations of triphenylmethyl radicals and cationic polymerization and the possibility of termination are considered on the basis of experimental data.

INTRODUCTION

Phenylazotriphenylmethane (PAT) may be decomposed thermally and photochemically to give a triphenylmethyl radical and a phenyl radical (Eq. 1). Subsequent oxidation of triphenylmethyl radical with the aid of onium salts such as diaryliodonium ($\text{Ar}_2\text{I}^+\text{X}^-$) and triaryl sulphonium ($\text{Ar}_3\text{S}^+\text{X}^-$) and silver salts with complex metal halide anions like PF_6^- , SbF_6^- , BF_4^- , (Eq. 2-3) provides formation of Ph_3C^+ which has been shown to be convenient initiator for cationic polymerization of alkyl vinyl ethers and cyclic ethers¹⁻⁴.



or:



$\text{Ph}\cdot$ and $\text{Ph-S-Ph}\cdot$ radicals abstract hydrogen from solvent or monomer.

In continuation of these studies, we now report the synthesis of two new azo compounds (phenyl azo diphenyl p-toly methane and phenyl azo diphenyl-o-hydroxyphenyl methane) in order to produce corresponding carbocations with the aid of iodonium of sulfonium salt by U.V. irradiation and test their effect in cationic polymerization of tetrahydrofuran (THF).

EXPERIMENTAL

Materials

THF and CH_2Cl_2 were purified by the conventional drying and distillation procedures. Phenylazotriphenylmethane (PAT), diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$) and diphenyl sulfonidiphenyl sulphide hexafluoro phosphate were prepared as described elsewhere⁵⁻⁷.

Diphenyl-p-toly chloromethane was prepared by reacting dry HCl with diphenyl-p-toly carbinol, which was also prepared in our laboratory from starting materials according to the established procedure⁸.

Phenyl azo diphenyl-p-tolymethane (M_3 -PAT) was prepared by refluxing diphenyl-p-toly chloromethane (20 g) and phenylhydrazine (15 ml) in 100 ml absolute ether for 1.5 hours. After cooling at room temperature, phenylhydrazine hydrochloride occurred from the reaction was filtered. Then 20 ml saturated NaHCO_3 and 8 ml H_2O_2 (35 %) were added to this filtered solution and stirred for 10 hours at room temperature. The ethereal solution washed with 5 % NaOH and distilled water, dried over MgSO_4 and then the solvent was evaporated. The product induced to crystallize from CH_2Cl_2 and ethanol. 4.2 gr of phenylazo diphenyl-p-tolymethane was eventually obtained (m.p. : 101°C, NMR : δ 2.18 Me, 7.1 phenyl).

Phenylazo-o-hydroxy diphenyl methane (HO-PAT) : Diphenyl-o-hydroxyphenyl carbinol, which was prepared by reacting methyl salicylate and phenyl magnesium bromide, was first reacted with dry HCl in absolute ether. Diphenyl-o-xyphenylchloro methane (20 g) was reacted with phenylhydrazine (15 ml). Then, the reaction was completed using the same procedure as described above. The crude product was crystallized from CH_2Cl_2 and ethanol leading to the azo compound (m.p. : 118°C, NMR : δ 9.0 OH, 7.5 phenyl).

Photolysis Studies

Photolysis were conducted with Phywe 55W mercury lamp. Appropriate solutions of given type of the azo compound and the cationic salt contained in 15 mm pyrex glass tubes with quartz side-arm were degassed in the usual manner before irradiation. Absorption measurements were performed after transferring the irradiated solutions to 1 mm quartz cell.

Polymerization Procedures

Bulk THF, containing given type of the azo compound and the cationic salt in 15 mm pyrex vessels were degassed in the usual manner. The samples were first irradiated at 1 cm from the U.V. lamp for ten minutes, then kept in a thermostat at 40°C in the absence of light. Polytetrahydrofuran was precipitated into distilled water containing a little amount of base.

RESULTS AND DISCUSSION

In the previous studies¹⁻⁴, we have made good use of the absorption spectra of pH_3C^+ as a probe with which to detect the presence of photoactivation and measure the efficiency of promoted polymerization. Formation of Ph_3C^+ and subsequent oxidation will initiate polymerization of THF at appropriate conditions.

Glass tubes were used in order to prevent absorption by the sulfonium or the iodonium salt. Figure 1 shows absorption characteristics of the sulfonium and iodonium salts and three types of triphenylmethyl cations. Both salts exhibit very weak absorption around glass cut-off region in addition to the usual strong absorption below 300 nm.

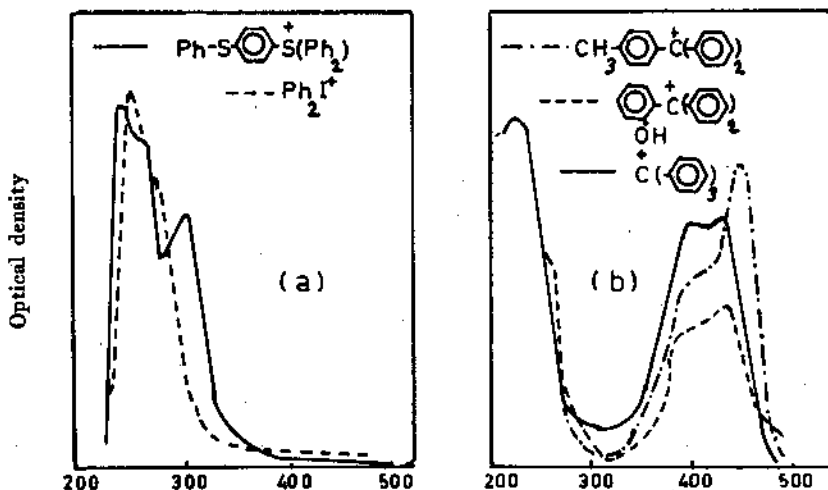



Figure 1 — U.V. Absorption spectra of (a) the cationic salts, (b) triphenyl methyl carbocations.

Tables I, II and III give data for a series of photolysis of the sulfonium and the iodonium salt in the presence of PAT, Me-PAT and HO-PAT, respectively. In these experiments, optical densities were measured wavelengths at which maximum absorption of corresponding carbocations were obtained. Substitution by OH group decreased the rate of formation of the carbocation as CH_3 group increased compared with the unsubstituted compound. Similar

behaviour was observed by *Cohen et al.*⁹, who studied the effects of structure on the decomposition of substituted phenyl azo triphenyl methanes and the formation of free radicals.

Table I — Photolysis of the cationic salts and PAT in methylene chloride

[Ph-S-  -S+(Ph2)] = 10 ⁻³ M			[Ph2I ⁺] = 10 ⁻³ M		
[PAT] · 10 ³ M	Irrad. time (min)	O.D.	[PAT] · 10 ³ M	Irrad. time (min)	O.D.
1.0	0.5	0.62	1.00	2	0.28
	1.0	0.74		4	0.48
	1.5	0.58		6	0.65
0.8	0.5	0.75		8	0.70
	1.0	0.88	10	0.66	
	1.5	0.78	0.75	2	0.33
0.5	0.5	0.58		4	0.55
	1.0	0.72		6	0.53
	1.5	0.60		8	0.75
0.4	0.5	0.65	10	0.63	
	1.0	0.70	0.50	3	0.53
	1.5	0.55		5	0.64
0.2	0.5	0.45		7	0.65
	1.0	0.50	0.25	3	0.46
	1.5	0.35		5	0.48
	2.5	0.20			

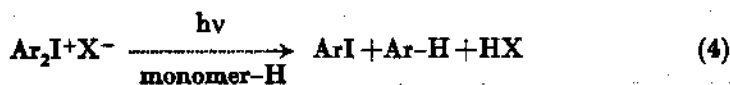
Maximum yield of carbocations was obtained after 1-2 minutes of irradiation when the sulfonium salt is used as oxidising salt while longer irradiation times were necessary for the iodonium salt. We have also observed that conversion of triphenylmethyl group to corresponding carbocation with [PAT] to the certain concentration from which point a marked reduction was observed in the apparent rate of conversion and additional salt supply increases the efficiency of the azo compounds.

Polymerization of THF was readily achieved using either the sulfonium salt or the iodonium salt in the presence of the azo compounds. The effect of the azo compound and relative efficiency of different initiating salts are shown in Tables IV and V.

Table II — Photolysis of the cationic salts and Me-PAT in methylene chloride

$[\text{Ph-S-} \langle \text{benzene ring} \rangle \text{-S}^+(\text{Ph})_2] = 10^{-3} \text{ M}$			$[\text{Ph}_2\text{I}^+] = 10^{-3} \text{ M}$			
[Me-PAT] · 10 ³ M	Irrad. time (min)	O.D.	[Me-PAT] · 10 ³ M	Irrad. time (min)	O.D.	
1.0	0.5	1.16	1.00	1	0.26	
	1.0	1.38		3	0.58	
	1.5	1.38		5	0.86	
	2.5	1.16		7	1.03	
	4.5	1.06		9	1.16	
	8.5	0.84		11	1.22	
0.8	0.5	0.98		13	1.28	
	1.0	1.40		15	1.26	
	1.5	1.32		17	1.25	
0.6	0.5	1.16		0.75	2	0.57
	1.0	1.44			4	0.92
	1.5	1.31			6	1.02
0.4	0.5	0.92			8	1.17
	1.0	1.20	10		1.25	
	1.5	1.04	12		1.22	
	2.0	0.84	0.50	2	0.65	
0.2	0.5	0.61		4	0.86	
	1.0	0.77		6	0.95	
	1.5	0.68		8	1.00	
	2.0	0.58		10	0.97	
	2.5	0.50		0.25	2	0.62
	4.5	0.39	4		0.66	
8.0	0.28					

High conversion to polytetrahydrofuran in the absence of the azo compounds confirms that the efficient emission of the lamp is around glass cut off region where the cationic salts have a tailed absorption band. Even at this wavelength absorption by the cationic salt is reasonably high and provides the formation of suitable species for initiation of cationic polymerization¹⁰. (e.g. for $\text{Ar}_2\text{I}^+\text{X}^-$)



The powerful protonic acid, HX, protonates the monomer, subsequent addition of monomer molecules to the protonated monomer species results in chain growth.

Table : III — Photolysis of the cationic salt and HO-PAT in methylene chloride

$[\text{Ph-S} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C}_6\text{H}_4 \text{S}^+ \text{-(Ph)}_2] = 10^{-3} \text{ M}$			$[\text{Ph}_2\text{I}^+] = 10^{-3} \text{ M}$			
[HO-PAT] · 10 ³ M	Irrad. time (min)	O.D.	[HO-PAT] · 10 ³ M	Irrad. time (min)	O.D.	
1.0	0.5	0.54	1.0	2.5	0.50	
	1.0	0.73		5.0	0.72	
	1.5	0.73		7.5	0.80	
	2.5	0.59		10.0	0.80	
	4.5	0.58		0.75	3.0	0.54
	9.0	0.51			5.0	0.68
0.8	0.5	0.60	0.50	7.0	0.68	
	1.0	0.63		2.0	0.18	
	1.5	0.57		4.0	0.32	
0.6	0.5	0.42	0.25	6.0	0.42	
	1.0	0.60		8.0	0.40	
0.4	0.5	0.32	0.25	2.0	0.24	
	1.0	0.42		4.0	0.28	
	1.5	0.38		5.0	0.26	
	3.0	0.30				
0.2	0.5	0.36				
	1.0	0.32				
	1.5	0.22				
	2.0	0.15				

As it can be seen from the results, all types of the azo compound decrease the efficiency of the cationic salt and this may result from the consumption of some amount of the salt to oxidise triphenylmethyl radical. Although Ph_3C^+ is known to be a convenient initiator for cationic polymerization, this diversion may cause a reduction in the rate of polymerization. Slight increase in PAT concentration, then, provides higher conversion to polytetrahydrofuran indicating efficiency of Ph_3C^+ as an initiator up to the certain level. However, recently the termination effect of PAT at high concentrations was observed¹¹ in thermally initiated polymerization of THF utilizing diphenyliodonium salt.

Table : IV — Photoinitiated polymerization of THF utilising

$[\text{Ph-S} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_4 \\ \diagdown \end{array} \text{-S}^+ (\text{Ph})_2] = 5 \times 10^{-3} \text{ M}$ in the presence of the azo compounds

[PAT] $\times 10^3$ (M)	[Me-PAT] $\times 10^3$ (M)	[OH-PAT] $\times 10^3$ (M)	Conversion %	$[\eta]$
—	—	—	28.7	4.4
0.25	—	—	22.3	—
0.5	—	—	25.5	3.1
1.0	—	—	18.8	—
3.0	—	—	16.8	—
5.0	—	—	12.6	2.4
—	0.25	—	23.3	—
—	0.5	—	23.1	3.3
—	3.0	—	16.3	—
—	5.0	—	11.1	—
—	—	0.25	19.6	—
—	—	0.5	18.4	2.9
—	—	3.0	11.9	—
—	—	5.0	4.4	—

Table : V — Photoinitiated polymerization of THF utilising $[\text{Ph}_2\text{I}^+] = 5 \times 10^{-3} \text{ M}$ in the presence of the azo compounds

[PAT] $\times 10^3$ (M)	[Me-PAT] $\times 10^3$ (M)	[HO-PAT] $\times 10^3$ (M)	Conversion (%)	$[\eta]$
—	—	—	25.6	—
0.25	—	—	18.2	—
0.5	—	—	20.9	2.8
1.0	—	—	20.4	—
5.0	—	—	12.7	2.4
—	0.25	—	20.1	—
—	0.5	—	16.2	3.1
—	1.0	—	27.2	—
—	5.0	—	7.3	—
—	—	0.25	12.4	—
—	—	0.5	12.7	2.7
—	—	1.0	13.7	—
—	—	5.0	1.5	—

In this polymerization, active centres were produced by thermal activation of PAT. Triphenylmethyl radicals are known to be stable free radicals and function as terminator at high concentrations in vinyl polymerizations. More recently Yağcı et al¹², reported that the efficiency of PAT as a free radical initiator may be improved by converting triphenyl methyl radical to the corresponding cations with the aid of diphenyliodonium salt.

While our results do not conclusively disprove the activation effect of phenylazotriphenyl methanes; taken together they suggest the involvement of termination by the azo compound, when direct initiation by cationic salt is predominant in the system.

Future studies will describe the involvement of termination in both activated and direct initiation of cationic polymerization.

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