

# DECOMPOSITION OF PHENYL-AZO-TRIPHENYLMETHANE (PAT) BY AMMONIUMYL CATION RADICAL SALTS

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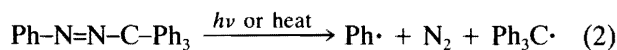
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## INTRODUCTION

Compounds with the structure R-N=N-R' decompose either thermally or photochemically to yield nitrogen and the radicals R· and R'·; these radicals, under appropriate conditions can act as polymerization initiators. A combination of organic radical and an oxidant such as onium salts with complex metal halide anions, can participate in redox processes that lead to the oxidation of electron donor radicals R· to the corresponding carbocations R<sup>+</sup>; the latter can be used to promote cationic polymerization [1]. The overall processes may be represented as shown in Equation (1).

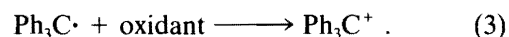


The expected products of decomposition of phenyl-azo-triphenylmethane (PAT) thermally or photochemically to give a triphenylmethyl radical, nitrogen gas, and a phenyl radical are shown in Equation (2).

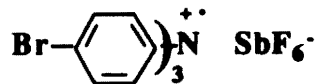


Triphenylmethyl (Ph<sub>3</sub>C·) is a relatively stable free radical and functions only as a chain initiator, at low concentrations. With large quantities of (Ph<sub>3</sub>C·), chain growth is restricted and low molecular-weight polymers are obtained, as an excess amount of (Ph<sub>3</sub>C·) will result in radical recombination or termination of the growing chains with vinyl-type monomers [2]. Triphenylmethyl radical has been

shown to undergo oxidation to Ph<sub>3</sub>C<sup>+</sup>, and the latter has been used as a cationic polymerization initiator [1, 3, 4]:



Support for the proposed electron transfer oxidation of the organic radical was readily obtained by spectroscopic and product analysis studies of the reaction of PAT with the stable *para*-substituted triphenylammoniumyl cation radical **1**:



**1**

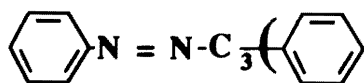
Since some of the radicals obtained from the decomposition of PAT are relatively stable and can take part in "side reactions", it seemed appropriate to evaluate quantitatively the amount of each product obtained from the reaction of PAT with **1** in an attempt to investigate the mechanism of this reaction and to test the use of **1** in converting the terminating triphenylmethyl radical to the corresponding cation in free radical polymerizing systems and thus improve the efficiency of PAT as a free radical initiator.

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## EXPERIMENTAL

Phenylazotriphenylmethane **2** was prepared according to the method of Cohen and Wang [5]. The crude solid was recrystallized from methylene chloride with the addition of absolute ethanol. The product of m.p. 110°C was obtained with 50% yield. Elemental analysis for (PAT)  $C_{25}H_{20}N_2$ : *Calculated*: C = 86.17%, H = 5.78%, N = 8.04%; *Found*: C = 86.25%, H = 5.8%, N = 8.11%.



2

The cation radical salt was prepared as reported in the literature [6]; the counter ion  $SbF_6^-$  was obtained by using  $AgSbF_6$  and iodine in  $CH_2Cl_2$ . The salt obtained as solid has m.p. 190–92°C;  $\lambda_{max} = 725$  nm;  $\epsilon_{max} = 7.6 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup>. Elemental analysis for **1**:  $C_{18}H_{12}Br_3NSbF_6^-$ . *Calculated*: C = 30.11%, H = 1.69%, N = 1.95%; *Found*: C = 30.45%, H = 1.74%, N = 1.95%.

The product analysis of the reaction of PAT with the cation radical **1** was followed by a gas liquid chromatographic technique; separation was achieved on 3% O.V. 225 supelcoport (100–120 mesh) column at 30°C; the detector temperature was 100°C. 1,2-Dichloromethane was purified and dried

over  $CaH_2$  and fractionally distilled through a Vigreux column.

## RESULTS AND DISCUSSION

Figure 1 shows that the obtained triphenylmethyl cation has a double maximum at 410 and 438 nm, characteristic of the  $Ph_3C^+$  cation, with an  $\epsilon_{max} = 3.9 \times 10^4$  l mol<sup>-1</sup> cm<sup>-1</sup> in dichloromethane; while the azo compound (PAT) showed a  $\lambda_{max}$  at 420 nm,  $\epsilon_{max} = 204$  l mol<sup>-1</sup> cm<sup>-1</sup> in  $CH_2Cl_2$ .

Figure 2 shows the absorption spectrum of the ammoniumyl cation radical salt (**1**). The absorption spectrum of the reaction mixtures at different concentrations of the cation radical salt (**1**) in the range ( $9.2 \times 10^{-5}$ – $2.76 \times 10^{-4}$ ) are shown in Figure 3.

As it can be seen from Table 1 about 65% average yield of carbocations was obtained when an equimolar quantity of ammoniumyl salt and PAT were used.

Table 2 shows the amount of benzene obtained from the analysis of the reaction. In each of these reactions, chlorobenzene was produced in about 5%, which is explained by the reaction between the phenyl radical and the solvent. The above results show the amount of benzene obtained from the analysis of the reaction mixture. However, it has been found that when the reaction mixture was left in laboratory conditions (25°C and normal laboratory light) for 24 hours the amount of benzene was increased to 70%.

Table 1.

No.	Concentration of PAT M	Concentration of $Ar_3\dot{N}^+X^-$ M	Concentration of $Ph_3C^+X^-$ M	$\frac{[Ph_3C^+X^-]}{[Ar_3\dot{N}^+X^-]}$ %
A	$2.76 \times 10^{-4}$	$2.76 \times 10^{-4}$	$1.79 \times 10^{-4}$	65
B	$2.76 \times 10^{-4}$	$2.45 \times 10^{-4}$	$1.47 \times 10^{-4}$	60
C	$2.76 \times 10^{-4}$	$2.07 \times 10^{-4}$	$1.23 \times 10^{-4}$	59
D	$2.76 \times 10^{-4}$	$1.57 \times 10^{-4}$	$6.15 \times 10^{-5}$	39
E	$2.76 \times 10^{-4}$	$9.20 \times 10^{-5}$	$2.56 \times 10^{-5}$	28

Table 2.

Concentration of PAT M	Concentration of $Ar_3\dot{N}^+X^-$ M	Concentration of Benzene M	$\frac{[Benzene]}{[Ar_3\dot{N}^+X^-]}$ %
$5 \times 10^{-4}$	$5 \times 10^{-4}$	$1.5 \times 10^{-4}$	29.8
$3.33 \times 10^{-4}$	$6.66 \times 10^{-4}$	$1.85 \times 10^{-4}$	27.62

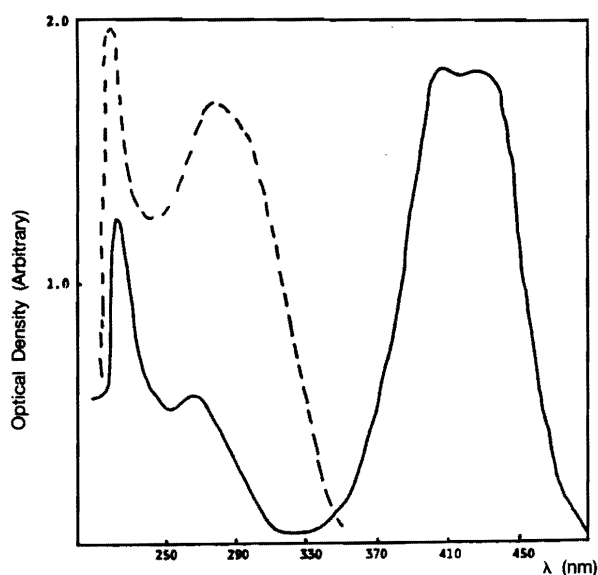
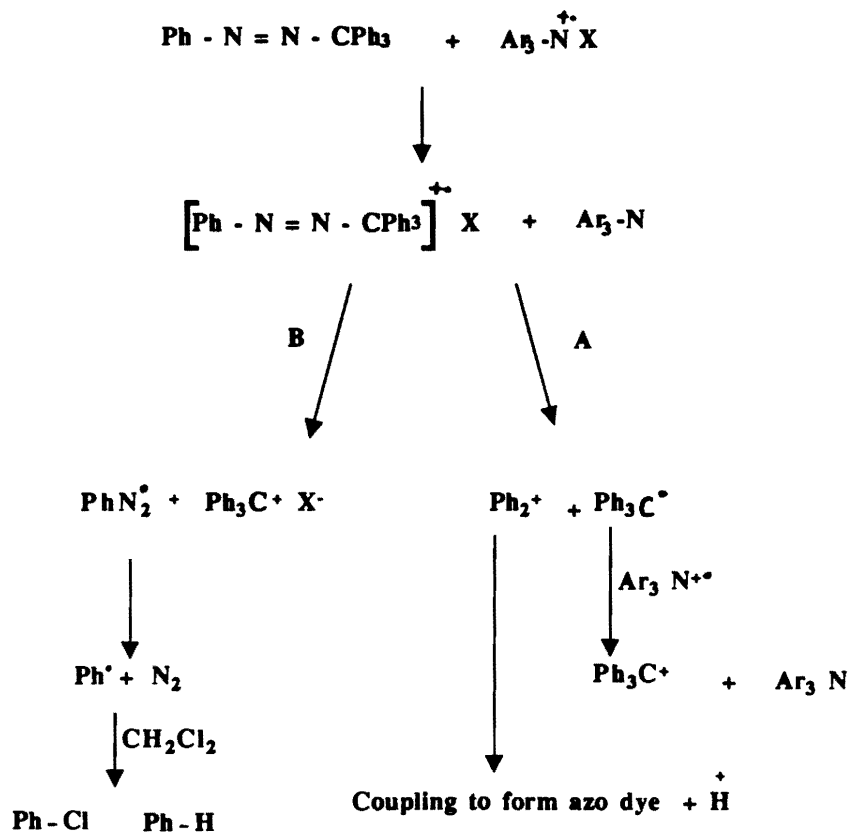


Figure 1. Absorption Spectra of (—)  $\text{Ph}_3\text{C}^+ \text{SbF}_6^-$ , and (----)  $\text{Ph-N=N-CPh}_3$ , in  $\text{CH}_2\text{Cl}_2$ .

The evidence from both the spectroscopic (Table 1) and the gas liquid chromatography quantitative studies of the reaction products (Table 2) suggest the following pathways for the reaction mechanism (Scheme 1).

Reaction pathway A suggests that for the production of one mole of  $\text{Ph}_3\text{C}^+ \text{X}^-$  two mole of  $\text{Ar}_3\text{N}^+ \text{X}^-$  are required. However, reaction pathway B suggests that one mole of  $\text{Ph}_3\text{C}^+$  is produced per mole of  $\text{Ar}_3\text{N}^+ \text{X}^-$  which is shown in Figure 2, explain reaction path B. While mechanistic features for each pathway of the reaction have been shown in Scheme 1, it is extremely probable that both pathways (A&B) can operate at the same time since the maximum amount of  $\text{Ph}_3\text{C}^+$  cation obtained is not exceeding 65% and the amount of benzene obtained is only about 30%. Support for pathway A was readily obtained, by carrying out the reaction between tris-(*p*-bromophenylamine) and *p*-chlorophenyldiazonium



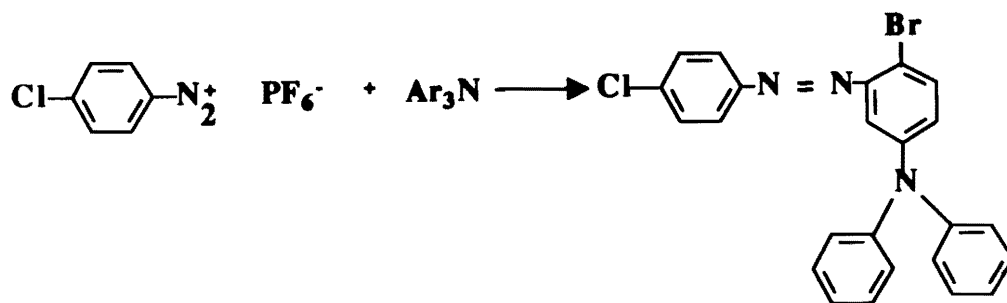
Scheme 1.

hexafluorophosphate in dichloromethane. The results obtained from the infrared and absorption spectrum of the reaction product, showed  $\text{-N=N-}$  stretching frequency at  $1590\text{ cm}^{-1}$  (Figure 4) and absorption between  $380\text{--}550\text{ nm}$  (Figure 5) suggests the azo dye is formed as shown in Scheme 2.

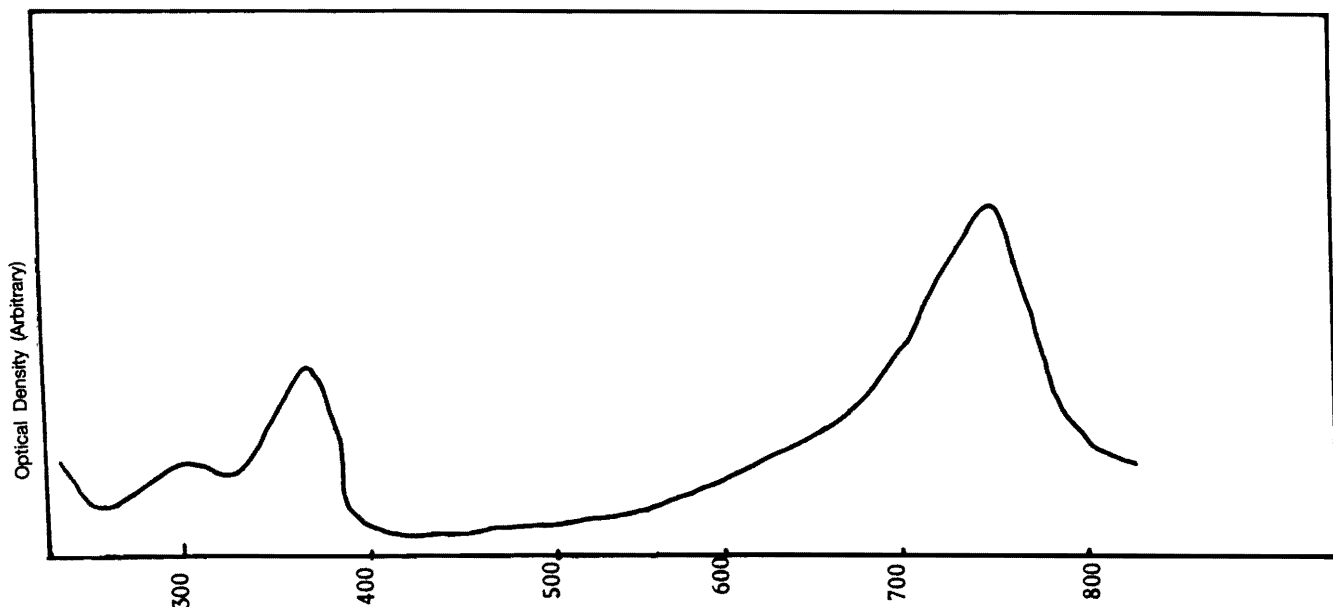
Further support for the reaction pathway A was obtained from the following experiment. Reaction between the ammoniumyl salt **1**, ( $10^{-3}\text{ M}$ ) and PAT ( $10^{-3}\text{ M}$ ) was carried out in  $\text{CH}_2\text{Cl}_2$  at room temperature. The reaction mixture was shaken with an aqueous alkali solution (10%), and then the organic layer was separated, washed with water and dried over calcium chloride. Removal of the solvents by a rotary evaporator yields a yellow oily product

which gives the visible absorption spectrum in  $\text{CH}_2\text{Cl}_2$  shown in Figure 5 and the infrared stretching frequency of the azo group at  $1590\text{ cm}^{-1}$ . Thus, there is a good reason to expect less than a 1:1 correspondence between  $\text{Ph}_3\text{C}^+$  and  $\text{Ar}_3\text{N}^+$  in the spectroscopic studies of the reaction product (Table 1), because PAT is always in excess compared to the cation radical salt **1** and because of the competition of pathway A, which suggests the requirement of two moles of  $\text{Ar}_3\text{N}^+\text{X}^-$  to produce one mole of  $\text{Ph}_3\text{C}^+$ .

Whilst the fate of  $\text{Ph}^\cdot$  or  $\text{PhN}_2^\cdot$  is yet unknown in a chain polymerization reaction, these data will serve to indicate the efficiency of the cationic salt ( $\text{Ph}_3\text{C}^+$ ) in free radical polymerization initiated by PAT.



Scheme 2

Figure 2. Absorption Spectrum of Salt in  $\text{CH}_2\text{Cl}_2$ .

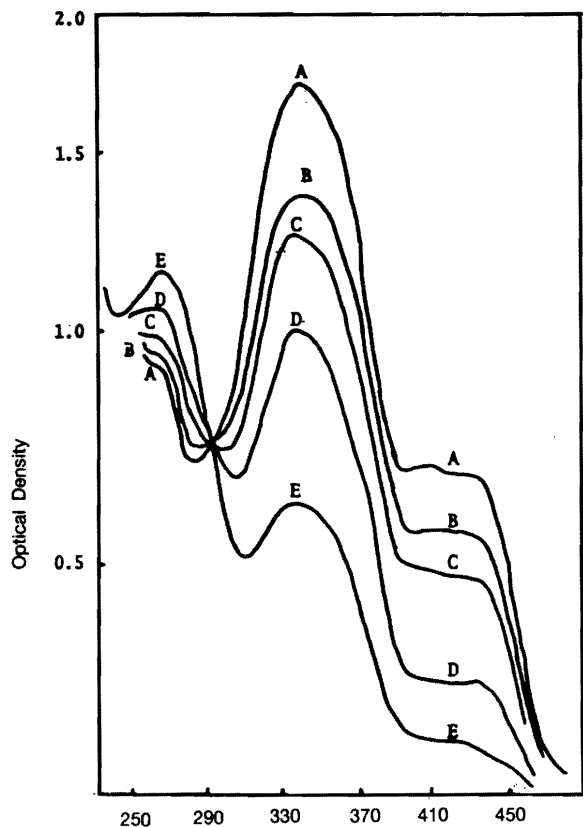


Figure 3. Absorption Spectra of the Reaction Mixtures, at Different Concentrations of the Cation Radical Salt and Fixed Concentration of PAT, in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$  (see Table 2).

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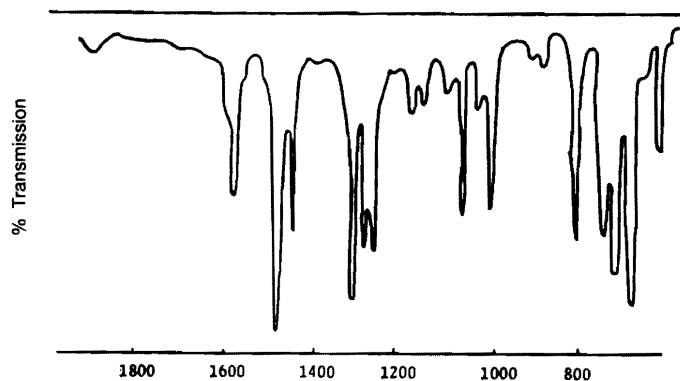


Figure 4. Infrared Spectrum of the Reaction Product in  $\text{CH}_2\text{Cl}_2$ .

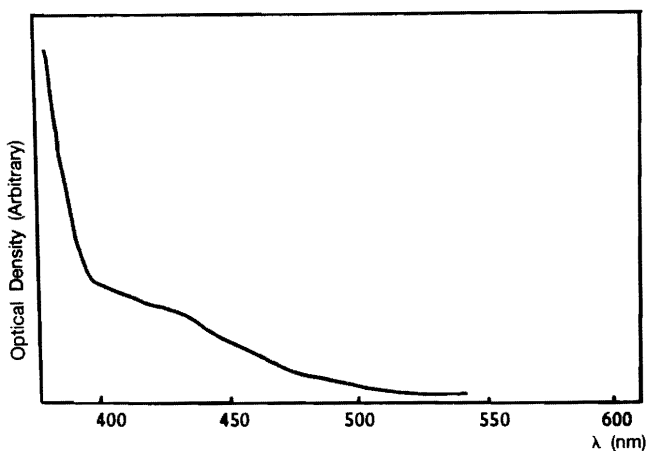


Figure 5. Absorption Spectrum of the Reaction Product in  $\text{CH}_2\text{Cl}_2$ .

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Paper Received 10 April 1989; Revised 29 May 1989.



## **ANNOUNCEMENTS**