# The Reaction Between Trityl Hexachloroantimonate and 1,2-Dimethoxy-4-(1-Propenyl)-Benzene

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SUMMARY

Reactions between triphenylmethyl hexachloroantimonate and 1,2-dimethoxy-4-(1-propenyl) benzene in methylene dichloride were studied by liquid chromatography, n.m.r. and visible spectroscopy. The system is characterised by slow initiation, shown to proceed through an addition reaction, and propagation only to the dimer stage, enabling simple analysis of the initiation kinetics. Similarities between this system and the anethole-trityl salt system were observed including initiation rate constants on the order of $10^{-3} dm^3. mol^{-1}. sec^{-1}$ and the development of a chromophore at 545 nm which is probably due to a side reaction of the propagating cation.

INTRODUCTION

A previous publication concerning the cationic polymerization of anethole initiated by triphenylmethyl hexafluoroantimonate in methylene dichloride indicated that the kinetics of this system are relatively complex (ROONEY, 1978). Slow initiation and the existence of at least one major termination reaction prevent simple analysis. In the present work experiments designed to shed light on the mechanism of the initiation reaction were conducted with a model for anethole, 1,2-dimethoxy-4-(1-propenyl)-benzene (DPB). The presence of a second methoxy group on the ring in a position meta to the vinyl group does not appear to influence the reactivity of the double bond appreciably. This observation is not surprising since methoxy groups are classified as ortho-para directors. However the reactivity of the ring towards electrophilic substitution is altered to the extent that intramolecular chain termination appears to occur rapidly enough to prevent polymerization. Consequently the interaction between trityl salts and DPB consists of slow initiation followed by addition of a second monomer unit and then by chain transfer. A kinetic termination step also occurs, possibly linked with the appearance of a chromophore. The absence of polymerization permits more careful study of the initiation mechanism and more accurate estimation of the initiation rate constant than is possible with the anethole-trityl salt system.

EXPERIMENTAL

DPB (Aldrich) was washed with aqueous NaOH and aqueous $FeSO_4$, dried over calcium chloride and distilled from molecular sieves under vacuum through a Vigreux column. The fraction boiling at 109.5–110.5°C under 0.15mm Hg

pressure was collected and stored over calcium hydride.    Spectroscopic and gas-liquid chromatographic analyses indicated that the monomer consisted of approximately 94% trans isomer with 6% cis isomer.

$^1$H NMR (CDCl$_3$): $\delta$ = 1.84 (d; CH$_3$),
3.83(S;OCH$_3$), 5.7-6.2(m;$\beta$-H),6.27(S; $\alpha$-H),
6.7-7.0 (m; aromatic H).

Cyclic dimers of DPB were synthesized by adding an excess of methanesulfonic acid to a 0.06 mol. dm$^{-3}$ solution of DPB in methylene dichloride (CH$_2$Cl$_2$) and allowing the mixture to react for several hours.   The products isolated by evaporation were subjected to spectroscopic and chromatographic analyses.   Liquid chromatograms showed a single peak.   The molecular weight corresponding to this peak was 409 on a polystyrene calibration (theoretical molecular weight = 356).    The proton magnetic resonance spectrum was similar to that observed for the cyclic dimer of anethole(HIGASHIMURA,1981) with respect to the shifts of the methyl group protons and the aromatic protons and the splitting of the peak ascribed to the methoxy protons.

$^1$H NMR (CDCl$_3$): $\delta$ = 1.00 (t; CH$_3$), 1.12 (d; CH$_3$) 2.01, 2.65(m; aliphatic H), 3.70,3.77,3.85 (s;OCH$_3$), 6.42-7.0 (m,aromatic H).

Other materials were purified by conventional techniques.

Reactions between triphenylmethyl hexachloroantimonate and DPB in CH$_2$Cl$_2$ were monitored in 1 and 10mm quartz UV cells attached to a mixing vessel. Spectra were scanned on a Perkin Elmer Model 124 Spectrophotometer.   The concentration of the trityl cation was estimated from the absorbance at 435nm.   Blank runs showed that under experimental conditions (Ph$_3$CSbCl$_6$ concentration = 4 x 10$^{-4}$ mol.dm$^{-3}$) diminution of this peak was negligible in the absence of monomer.    All reactions were conducted at room temperature.

Reactions were quenched with dilute piperidine/CH$_2$Cl$_2$ solutions or with moist solvent.   Products were isolated by evaporation.   Liquid chromatograms were obtained on a Waters Model 244 unit with $\mu$-Styragel or Corasil columns.

RESULTS:

Polymerization of DPB was not observed in any experiment.   Gas-liquid chromatography indicated that only about 5% of the monomer was consumed in kinetic runs, resulting in the formation of two compounds of slightly longer retention time than the unconverted DPB.

Immediately after mixing the monomer and initiator solutions a red colour appeared and increased in intensity as the reaction progressed.   Repeated scanning of the visible spectrum revealed the development of a peak at 545nm together with the diminution of the initiator peaks (See Figure 1).

In kinetic runs,for which the initial monomer concentration ($[M]_0$) was varied from 0.31 to 0.66 mol.dm$^{-3}$ and the initiator concentration ($[I]_0$) from approximately 10$^{-3}$ to 10$^{-4}$ mol.dm$^{-3}$, half-lives for the consumption of initiator were in the range 5 to 20 minutes.
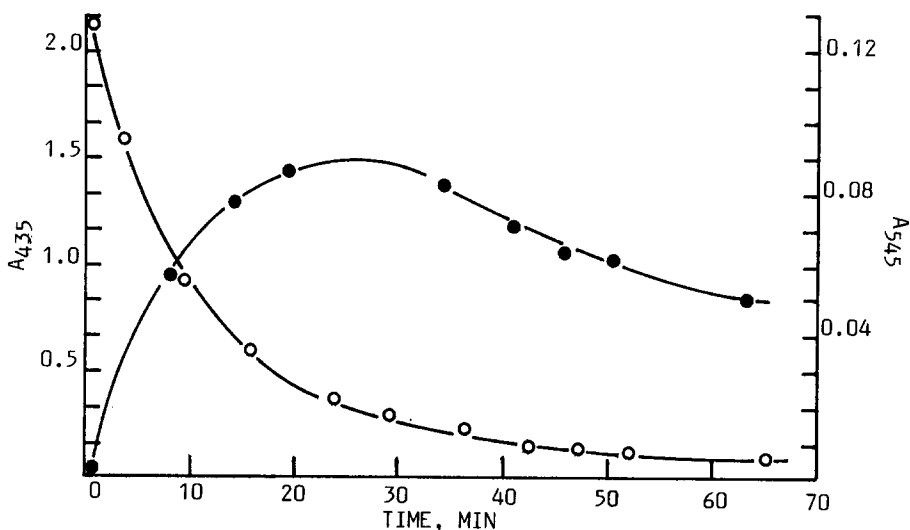
Fig.1. Changes in absorbances at 435(O) and 545(●)nm during the reaction of DPB($[M]_o$ = 0.66 mol.dm$^{-3}$) and $Ph_3SCbCl_6$ ($[I]_o$ = 5.6 x 10$^{-4}$ mol.dm$^{-3}$)

Synthetic experiments were conducted in which high concentrations of initiator (10$^{-1}$ mol.dm$^{-3}$) were treated with amounts of DPB ranging from equimolar to a threefold excess. In these runs consumption of monomer was virtually complete. Chromatographic analyses of the quenched reaction mixture showed only a few products (see Figures 2 and 3).
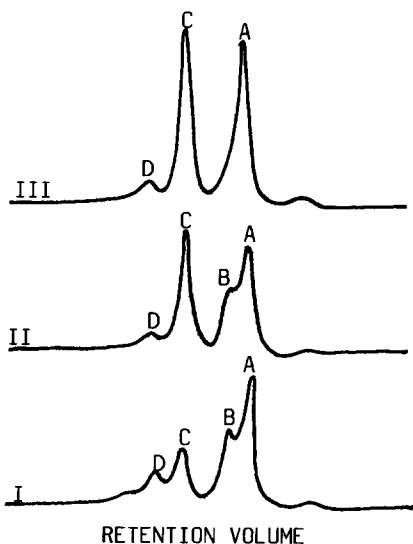


RETENTION VOLUME

Fig. 2 Liquid chromatograms of the reaction products of DPB ($[M]_o$ = 0.075 mol.dm$^{-3}$) and $Ph_3CSbCl_6$($[I]_o$= 0.043 mol.dm$^{-3}$) at different reaction times: I = 5 min, II = 45 min, III = 120 min

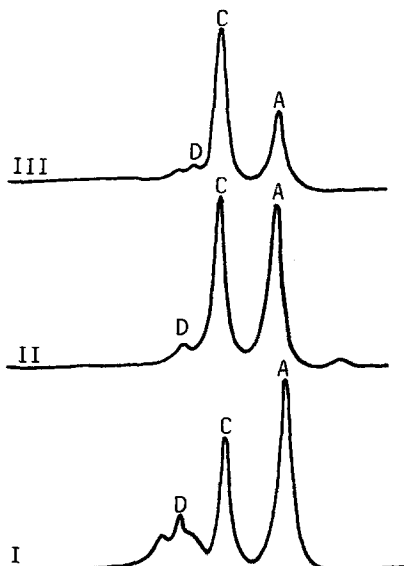FIG.3. Liquid chromatograms of the reaction products of
Ph₃CSbCl₆ and DPB at different DPB/Ph₃CSbCl₆ mole
ratios: I = 1,II = 1.8, III = 3

Peaks were identified by enhancement with known samples, and by fraction-
ation followed by NMR measurements. In figure 2 peaks A and B were found
to be trityl residues and unnreacted DPB respectively. Peak C was ident-
ified as the cyclic dimer of DPB. The NMR spectrum of peaks C and D
(obtained by separating the initial mixture into higher (C and D) and lower
(A and B) molecular weight products on a liquid chromatograph) reveals the
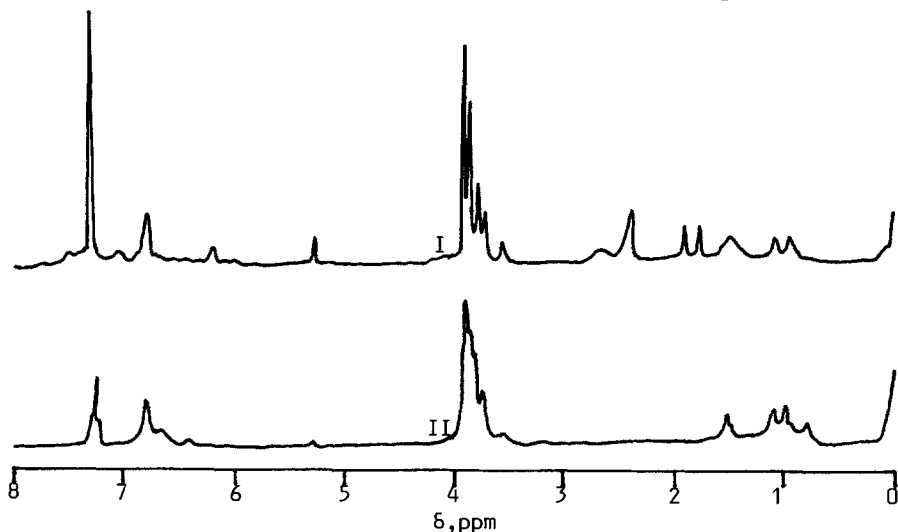presence of trityl groups and cyclic dimer, as shown in Figure 4.



FIG.4.NMR spectra of reaction products of DPB ($[M]_0$ = 0.075 mol.dm$^{-3}$)and
Ph₃CSbCl₆($[I]_0$ = 0.043 mol.dm$^{-3}$)after 5 minutes reaction time. I =
entire product mixture,II = higher molecular weight products only

Semilogarithmic plots of the initiator absorbance as a function of time
were linear over most of the conversion range (see Figure 5), and first-
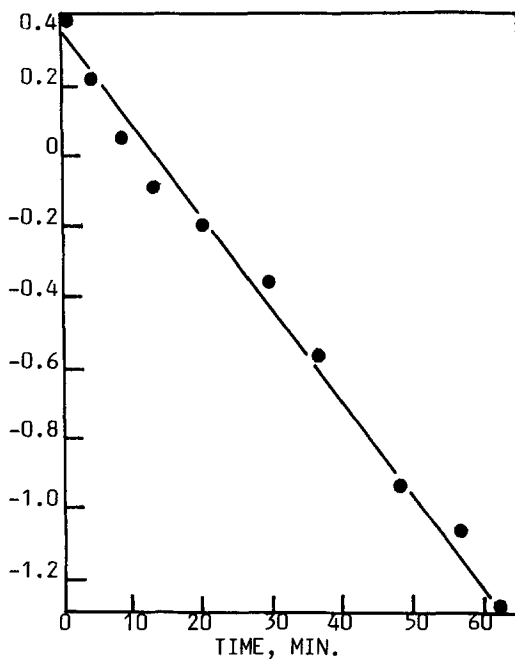


FIG.5.First-order plot of initiator absorbance
as a function of time for the reaction of
DPB ($[M]_0$ = 0.31 mol.dm$^3$)and Ph$_3$CSbCl$_6$
($[I]_0$ = 3.8 x 10$^{-4}$ mol.dm$^{-3}$)

order rate constants derived from the slopes of the plots are shown in
Table 1.

TABLE  1
RATE CONSTANTS OF INITIATION FOR THE DPB-Ph$_3$CSbCl$_6$ System
IN METHYLENE DICHLORIDE AT 23°C

| $[I]_0$ x 10$_4$, mol.dm$^{-3}$ | $[M]_0$, mol.dm$^{-3}$ | $k_i$ x 10$^3$, dm$^3$. mol$^{-1}$ sec$^{-1}$ |
|---|---|---|
| 7.6 | 0.66 | 1.3 |
| 5.6 | 0.66 | 1.5 |
| 4.0 | 0.66 | 1.7 |
| 3.9 | 0.50 | 2.0 |
| 3.8 | 0.31 | 1.4 |

DISCUSSION

The chromatographic and nmr analyses establish that initiation in the DPB
-Ph$_3$CSbCl$_6$ system occurs through addition of the trityl group to the
monomer double bond, since trityl groups were shown to be incorporated in
the higher molecular weight reaction products.  The ratio of trityl-
containing products to dimer increased as the monomer to initiator ratio
decreased.  Furthermore the obvious alternative initiation mechanism would

involve hydride abstraction from the  -methyl substituent on the DPB double bond

$$Ph_3C^\oplus + CH_3-CH = CH\text{-Ar} \longrightarrow Ph_3CH + CH_2 = CH-\overset{\oplus}{C}H\text{-Ar}$$

(Ar = 3,4-dimethoxyphenyl, $OCH_3$, $OCH_3$)

with consequent formation of a eugenyl double bond. This type of double bond was not observed in the reaction products by either NMR(no peak at $\delta=5.0$ppm) or IR (no peak at 1650 cm$^{-1}$) spectroscopy.  Similar evidence was reported earlier concerning the anethole-$Ph_3CSbF_6$ system (ROONEY, 1978).

Another striking feature of the HPLC analyses is the observation that prop-agation in the DPB-$Ph_3CSbCl_6$ system does not occur to any appreciable extent beyond the dimerization stage. The presence of large amounts of cyclic dimer in the reaction mixture (without attached trityl groups) together with the presence of smaller amounts of higher molecular weight material containing trityl groups suggests that chain initiation is follow-ed by the addition of one monomer unit, rapid cyclization and expulsion of a proton to initiate another chain:

$$R-\overset{CH_3}{\underset{}{C}H} - CH^\oplus\ A^\ominus \quad \xrightarrow{\ DPB\ } \quad R-\overset{CH_3}{\underset{}{C}H} - CH-\overset{CH_3}{\underset{}{C}H}-CH^\oplus\ A^\ominus$$

$$\downarrow$$

$$R-CH-\overset{CH_3}{\underset{}{C}H}-\overset{CH_3}{\underset{}{C}H}\ \cdots \quad +\ H^\oplus\ A^\ominus$$
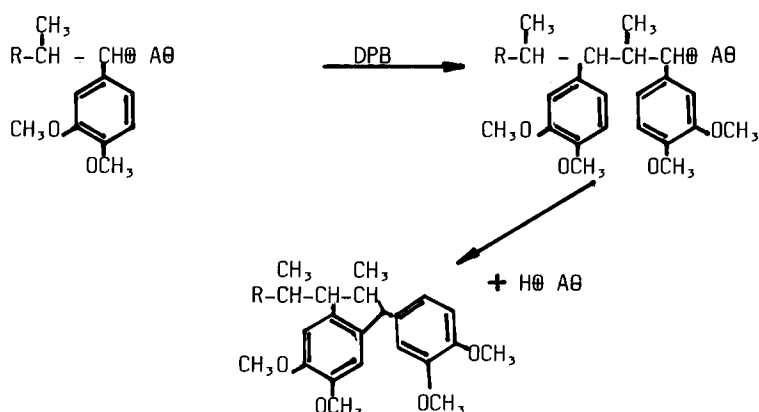
$(R = H, Ph_3C; A = SbCl_6)$

Cylizations of this type have been reported for anethole under certain conditions(HIGASHIMURA, 1981) but the structure of DPB results in an incre-ased freqeuncy of these reactions relative to monomer addition.  With ane-thole, ring attack can occur only at a position meta to the ring-activating methoxy substituent.   DPB contains a second methoxy group and ring attack can occur in the favoured ortho and para positions with respect to this group.   Exclusive formation of cyclic dimers at -12°C has been observed for the structurally similar monomer isosafrole (ALEXANDER, 1981).

The fact that monomer conversion is very low at reduced [I]$_0$ levels (with no increase in conversion after 24 hours beyond the initial 1.5 - hour reaction time) suggests that at least one major termination step occurs in the DPB-$Ph_3CSbCl_6$ system.   At similar initiator concentrations the poly-

merization of anethole was found to proceed to at least 80 percent monomer conversion, although kinetic analyses showed that a significant termination process reduced the concentration of active centres as polymerization progressed. In the anethole-$Ph_3CSbF_6$ system a peak at 501 nm in the visible spectrum appeared after an induction period. The development of this peak appeared to coincide with the calculated decrease in the concentration of active centres in the polymerization solution. Under similar conditions in the DPB-$Ph_3CSbCl_6$ system a peak at 545 nm appears immediately upon mixing the reagents, an observation consistent with the fact that kinetic termination is much more rapid in this system. The graph of simultaneous decrease in initiator absorbance and increase in the absorbance at 545 nm shown in Figure 1 might lead to the conclusion that the peak at 545 nm could be ascribed to propagating centres such as the DPB cation. However previous studies have shown that visible bands of this type are more probably associated with side reactions of the propagating cations (HIGASHIMURA 1967) and even occur in non-polymerizing systems where methoxylated aromatic structures interact with Lewis acids (KINSTLE, 1981). In the present work the cessation of monomer consumption at low conversions in the presence of this chromophore is strong evidence that the 545 nm peak does not correspond to a propagating cation. The fact that this peak appears in DPB systems in the presence of Bronsted acids precludes the possibility that it corresponds to a side reaction of the trityl ion.

The low DPB conversions encountered in the present work simplify the kinetic analysis of the initiation step. Since this reaction has been shown to involve simple addition of the trityl cation to the DPB, the rate expression should be first order in monomer and initiator. At low monomer conversions the DPB concentration remains virtually constant and semilogarithmic plots of initiator absorbance as a function of time should be linear. In Figure 5 such linearity is demonstrated for the DPB-$Ph_3CSbCl_6$ system. In the case of anethole polymerizations initiated by $Ph_3CSbF_6$, the relatively rapid consumption of monomer invalidated the first-order correlation and initial rates of trityl consumption were using in determining the value of $k_i$, the rate constant of initiation. Given the difference in methods of analysis, the similarity in the values of the rate constants for the trityl-induced initiation of anethole and DPB is noteworthy. This similarity suggests that the presence of the second methoxy substituent on the DPB ring does not appreciably affect the reactivity of the double bond.

## LIST OF REFERENCES

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