Organic halides as cationic initiators

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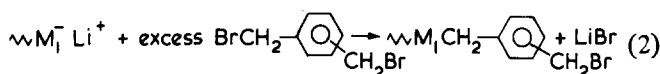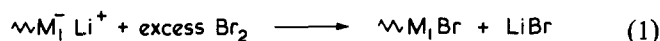*Propellants Explosives and Rocket Motor Establishment, Ministry of Defence, Waltham Abbey,
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The reaction of organohalides with silver hexafluorophosphate or silver perchlorate in THF to gene-
rate cationic initiators has been examined. Reactivities in the order fluoride < chloride < bromide <
iodide and alkyl ≪ allyl ≈ benzyl were found. Selected halides were examined in more detail, and it
was shown that under controlled conditions living polyTHF could be obtained. This was difunctional
if p-xylylene dibromide or 1,4-dibromobut-2-ene was used, or monofunctional with conventional
monohalides. Molecular weight distributions of M_w/M_n ≤ 1.2 were obtained. Experiments demon-
strated that allyl bromide and p-methylbenzyl bromide initiated THF polymerization entirely addi-
tively but, with isopropyl iodide at room temperature, up to 10% proton transfer occurred.

INTRODUCTION

It was shown recently[1-3] that transformation reactions
could be carried out on anionic 'living' polymers to gene-
rate polymeric cations which were then able to propagate
with a second monomer to form block copolymers. These
reactions involved the formation of an intermediate bro-
mide, by reaction either with excess bromine [equation
(1)], or with excess of a xylylene dibromide [equation
(2)].

$$\text{vvM}_1^- \text{ Li}^+ + \text{excess Br}_2 \longrightarrow \text{vvM}_1\text{Br} + \text{LiBr} \qquad (1)$$

$$\text{vvM}_1^- \text{ Li}^+ + \text{excess BrCH}_2\text{-}\langle O \rangle\text{-}\underset{\text{CH}_2\text{Br}}{} \rightarrow \text{vvM}_1\text{CH}_2\text{-}\langle O \rangle\text{-}\underset{\text{CH}_2\text{Br}}{} + \text{LiBr} \qquad (2)$$

It was found in both cases that prior reaction of the living
polymer with magnesium bromide to form the polymeric
Grignard minimized the competing Wurtz coupling reac-
tion and allowed polymeric bromide to be formed with
efficiencies up to 95%[4]. This material was then isolated,
redissolved in an appropriate solvent and second monomer
(usually tetrahydrofuran, THF), and the cationic species
generated by reaction with the silver salt of a strong acid
[equation (3)].

$$\sim\!\!M_1\text{Br} + \text{AgX} \rightarrow \sim\!\!M_1^+X^- + \text{AgBr}\!\downarrow \qquad (3)$$
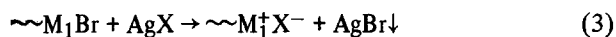
Suitable salts were those of perchloric acid or, preferably,
of hexafluorophosphoric acid. Experiments carried out
with bromine-terminated polystyrene or polybutadiene
gave a rapid precipitation of silver bromide even at low
temperatures, due to the resonance stabilization of the
benzylic or the allylic carbenium ions thus generated. The
efficiency of block copolymer formation was found to be
determined by factors such as the structure of the carbe-
nium ion, the nature of the Gegen ion, the experimental
conditions and, of course, the nature of the second mono-
mer. Under carefully chosen circumstances[5], THF could
be polymerized to form 'living' cationic block copolymers
capable of being functionally terminated or coupled.

The investigation summarized above highlighted the
possibility of using suitably structured small molecule
halides and dihalides directly as cationic initiators. Indeed,
such halides had been used as models for the bromine-
terminated polymers in that work, so that the principle of
their use had been established. This communication des-
cribes a more detailed investigation of the use of these
organic halides as catalysts capable of generating mono-
and difunctional polymers. THF, being the monomer least
susceptible to transfer reactions, was used throughout these
studies.

EXPERIMENTAL

Materials

Silver hexafluorophosphate (Alfa Chemicals) was used
as supplied, and kept stored under nitrogen. Organic ha-
lides were analysed by g.l.c. and, if greater than 99% purity,
were used as supplied. Otherwise, solids were recrystall-
ized and liquids were fractionally distilled.

THF was dried initially by standing over molecular
sieves. It was then titrated with a THF solution of sodium
naphthalene immediately prior to use until a faint residual
green colour was obtained, after which the solvent was frac-
tionally distilled under nitrogen.

Reactions

Preliminary evaluations. Three different experimental
techniques were employed in this study. Firstly, a survey
was made of the ease of precipitation of silver halide at a
specified temperature after mixing THF solutions of silver
hexafluorophosphate and variously structured organic
halides. Next, the kinetics of polymerization of THF in-
duced by this reaction on selected halides were examined.
Finally, the polymerizations of THF by other selected
halides were rapidly terminated by adding methanol and
the oligomeric products thus formed were isolated by g.l.c.
and their structures determined by [1]H n.m.r. Alternatively,
rapid termination was effected by excess lithium chloride,

and any acid generated through proton transfer was evaluated by titration with base.

The survey of alkyl halides was carried out as follows. A stock solution of $AgPF_6$ (5 g, 20 mmol) in THF (100 ml) was prepared under nitrogen and brought to the reaction temperature. The monohalide (1 mmol) or the dihalide (0.5 mmol) was dissolved in a tube sealed with a rubber septum and again cooled to the required temperature before the silver solution (5 ml) was introduced by syringe. The time taken to complete precipitation was recorded and, if this was greater than 10 sec, the solutions after precipitation were placed in a bath at $20°C$ and an assessment was made of the time taken to attain a visually observed standard high viscosity. If the time to complete precipitation was less than 10 sec the experiment was repeated at successively lower temperatures until this time was exceeded, when the procedure described above was then followed.

Kinetic experiments. The kinetic experiments were carried out in a 250 ml three necked flask fitted with a thermometer, a nitrogen bleed and a rubber septum. The flask and glass attachment had previously been cleaned with chromic acid, water and acetone, dried in an oven at $120°C$ for 2 h, assembled hot and allowed to cool under dry nitrogen. Solid $AgPF_6$ (0.28 g, 1.1 mmol) was introduced under nitrogen followed by THF (100 ml), and the flask contents were stored and cooled to the initiation temperature. The monohalide (1 mmol), or the dihalide (0.5 mmol) was then introduced as a solution in THF (5 ml) and the temperature adjusted to $-10° \pm \frac{1}{2}°C$ at which it was maintained for the duration of the polymerization. Samples were removed by syringe, terminated with methanolic KOH and subjected to g.p.c. analysis within 2 h of removal.

G.l.c. analysis. Alkyl halide (1 mmol) and a selected g.l.c. marker (0.1 g) (usually hexadecane) were dissolved in THF (2 ml) and cooled to the required temperature before adding to a solution of $AgPF_6$ (1 mmol) dissolved in THF (10 ml) at the same temperature. Almost immediately, dry methanol (1 ml) was added to terminate polymerization, and the products were extracted with ether and brine and analysed by g.l.c.

Acid–base titration. Alkyl halide (25 mmol) in THF (5 ml) was reacted at room temperature with $AgClO_4$ (27.5 mmol) in THF (10 ml). After precipitation of the silver halide was complete, LiCl (75 mmol) in THF (20 ml) was added to prevent polymerization. The reaction products were then added to water and titrated against phenol phthalein using 0.1 N NaOH.

Gel permeation chromatography. Gel permeation chromatography (g.p.c.) was carried out on a Waters Associates model ALC/GPC 301 chromatograph fitted with differential refractometer (thermostatically controlled at $25°C$) and ultra-violet (254 nm) detectors. Four styragel columns were used in sequence with porosities 10^4, 10^4, 10^3 and 10^3 Å, respectively. Elutions were carried out at ambient temperature with THF as solvent and with a flow rate of 1 cm^3/min. The retention time was compared with those of a series of polystyrene standards under the same conditions to obtain an apparent polystyrene molecular weight. This was converted into the molecular weight of polyTHF by multiplying by a factor of 0.556^3.

Gas liquid chromatography. Gas liquid chromatography (g.l.c.) was carried out on a Pye Unicam Series 104 dual column chromatograph with flame ionization detectors. Preparative separations for n.m.r. analysis were carried out using a 3 ft, 7 mm i.d. column packed with 10% OV1 on 80/100 mesh 'Chromosorb G'. Temperature programmes in the region $100°$ to $300°C$ were used.

1H nuclear magnetic resonance spectroscopy. 1H n.m.r. spectra were recorded on a Jeol PS 100, 100 MHz spectrometer using solutions in deuterochloroform with tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

The experiments carried out may be conveniently divided into two parts. Initially a survey was conducted using a variety of mono- and difunctional halides to form a qualitative assessment of the labilities of differently structured carbon–halogen bonds in order that the generality of this method of creating cationic initiators might be established. Subsequently, a number of halides were selected from those shown to be suitable and examined in more detail in order to assess whether their initiation of THF was additive and whether the polymerization process was without termination or transfer under the specified experimental conditions.
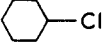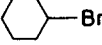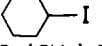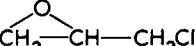
Preliminary Survey.
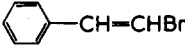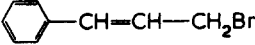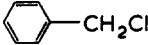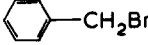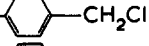
The preliminary survey took the following form. A THF solution of $AgPF_6$ was added to a THF solution of the halide at $-10°C$ and the time for completion of precipitation (i.e. coagulation) noted, after which the solution was brought rapidly to $20°C$, polymerization allowed to ensue, and the time taken to attain some arbitrary high viscosity was estimated. If the time for complete precipitation was less than 10 sec the experiment was repeated at lower temperatures until this value was exceeded, and this time was recorded. With halides which were unreactive at $-10°C$ the mixing procedure was repeated at ambient temperature, and the precipitation time and polymerization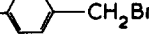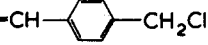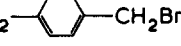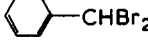 time were taken from the time of mixing; in many of these cases precipitation and polymerization were taking place concurrently throughout the times recorded. Some of the results are listed in *Table 1*. It should be stressed that the times quoted are only broad indications of halide reactivity and are not of quantitative significance. The trends are of interest, however, and will be commented upon.

The organohalides listed in *Table 1* have for convenience been divided into three broad categories, alkyl, allyl and benzyl, and they are considered in this order. The reactivities of the saturated alkyl halides are in the anticipated sequence iodide > bromide > chloride > fluoride. Since it is a requirement for the synthesis of narrow dispersity polymers that the active initiating species be generated quickly and initiate with equal rapidity, it is clear that the iodides are most suitable for this role. They react very quickly even down to $-50°C$ and could certainly be used to generate narrow dispersity living polyTHF at the temperature of $-10°C$ specified by Croucher and Wetton[5]. Short polymerization times indicate that fast initiation by the generated carbenium ions prevails.

1,6-Dibromohexane initiates rapidly at room temperatures but less quickly at $-10°C$ and could therefore be used to prepare difunctionally active polymer, although the molecular weight distributions under these circumstances would be rather broad; more efficient difunctional initiators are found in the allyl and benzyl groups.

Methylene bromide and, more importantly, methylene chloride are virtually inactive toward $AgPF_6$ over long periods. This means that the latter may be conveniently

Table 1 Times of complete precipitation of silver halide in the reaction between organohalides and $AgPF_6$ in THF. Times of subsequent polymerization of THF at 20°C to a visually estimated standard viscosity

	Organohalide	Times of complete precipitation (°C)				Polymerization time
		−70	−50	−10	+20	
Alkyl	$CH_3(CH_2)_5F$				3 days	3 days
	$CH_3(CH_2)_2Cl$				2 days	2 days
	CH_3CH_2Br				15 min	1.2 h
	$(CH_3)_2CHI$	25 min				20 min
	⬡—Cl				2 days	2 days
	⬡—Br		5 min			1.2 h
	⬡—I	20 min				1 h
	$Br(CH_2)_6Br$			20 min		1 h
	CH_2Cl_2				>10 days	20 days
	CH_2Br_2				3 days	3 days
	CH_2—CH—CH_2Cl (epoxide)				3 days	3 days
	CH_2—CH—CH_2Br (epoxide)				30 min	10 h
	CH_2=CHBr				5 days	5 days
	C₆H₅—CH=CHBr				>20 days	>20 days
Allyl	CH_2=CH—CH_2Cl				15 min	1 h
	CH_2=CH—CH_2Br		1 min			20 min
	C₆H₅—CH=CH—CH_2Br	<10 sec				20 min
	$BrCH_2$—CH=CH—CH_2Br	30 sec				20 min
Benzyl	C₆H₅—CH_2Cl				10 min	40 min
	C₆H₅—CH_2Br	12 min				20 min
	CH_3—C₆H₄—CH_2Cl			30 sec		20 min
	CH_3—C₆H₄—CH_2Br	7 min				20 min
	o and p CH_2=CH—C₆H₄—CH_2Cl			10 min		20 min
	$BrCH_2$—C₆H₄—CH_2Br	15 min				20 min
	C₆H₅—$CHBr_2$	15 min				20 min

used as co-solvent for these cationic initiations. Indeed, parallel experiments carried out in the absence of THF with benzene or methylene chloride—benzene as solvent (the silver salts are soluble in benzene but virtually insoluble in pure methylene chloride) showed that precipitation of silver halide occurs with equal facility in these media.

Epichlorhydrin is unreactive at room temperature, but epibromhydrin does yield a silver bromide precipitate much more readily and, although not an ideal initiator, it does introduce the interesting feature that the terminal epoxide group may participate in the subsequent THF polymerization as a co-monomer. Vinyl bromide is virtually inactive toward silver salts, and β-bromostyrene completely so.

As expected, the allyl halides are generally much more reactive than the alkyl species. Even allyl chloride is a moderately efficient initiator, and cinnamyl bromide reacts virtually instantaneously at the lowest temperature studied. The latter compound generates a particularly

strongly resonance stabilized carbenium ion derived from the two canonical forms I and II.
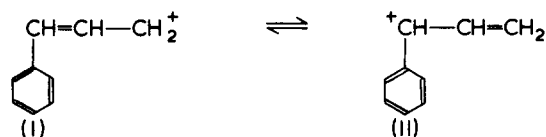
Since II is the more favoured energetically, polymers initiated by the cinnamyl carbenium ion should contain predominantly ethylenic rather than vinylic terminal groups, although this has not yet been confirmed experimentally. 1,4-Dibromobut-2-ene is a fast initiator and was examined to determine its suitability as an initiator for preparing living difunctional polyTHF (see below).

Earlier work[1] had shown that halides such as 1-bromoethylbenzene which possess hydrogens on the β carbon atom do not initiate polymerization entirely by an additive

process. The principal side reaction is one of β hydrogen elimination [equation (4)].

$$CH_3\text{-}CHBr + AgPF_6 \rightarrow AgBr\downarrow + CH_3\text{-}CH^+ {}^-PF_6 \overset{THF}{\rightleftharpoons} CH_2\text{=}CH + HPF_6 \quad (4)$$
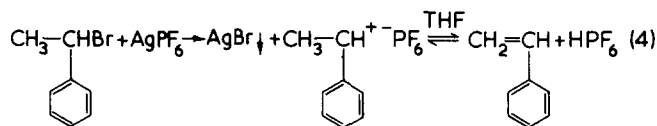
Benzyl bromide, not possessing a β hydrogen is unable to undergo this elimination, and it was shown to carry out additive initiation exclusively[2]. For this reason all the benzylic compounds tested in this series were primary halides so that any undesired elimination reactions should be minimized.

Reactivities of the same general order as the allylic halides were observed in the benzyl series studied. The precipitation process with benzyl chloride took about 10 min to complete at ambient temperature, but it occurred significantly faster with the *para*-methyl derivative where the positive inductive effect weakens the carbon—chlorine bond and increases the stabilization of the resulting carbenium ion. A similar effect was observed with benzyl bromide and *p*-methylbenzyl bromide, although the temperature employed was very much lower.

Chloromethylstyrene (obtained as a mixture of isomers) is an interesting potential cationic initiator as it should be capable of producing polymers which possess terminal styryl units and, if these are terminated after being generated under 'living' conditions by species such as cinnamyl alcohol[6], two terminal styryl units per chain may be introduced. In either event these polymers may be subsequently reacted with alkyllithium compounds to yield terminal styryl anions from which a variety of monomers may be propagated anionically. Thus a cation to anion transformation may be effected which could result in an interesting series of new block copolymers. This area is currently under investigation.

Both *para*-xylylene dibromide and benzal bromide are capable of rapid initiation at low temperature and are consequently likely candidates as difunctional initiators. They are considered in more detail for this role below.

Six aryl halides were introduced separately to AgPF$_6$ in THF at room temperature but none, not even iodobenzene, yielded any precipitate of silver halide over a period of a week. Clearly the carbon—halogen bond strength is too great in this class of compounds for them to have any value as cationic initiators. The chlorosilanes, (CH$_3$)$_3$SiCl, (CH$_3$)$_2$SiCl$_2$ and CH$_3$SiCl$_3$ all gave immediate precipitation of silver chloride even at the lowest temperatures, but no THF polymerization was observed. Subsequent analysis showed that the silane—PF$_6$ salts were not coprecipitated with the silver chloride, and so it must be concluded that the silane cation is not electrophilic enough to initiate THF polymerization.

Kinetic measurements

Kinetic experiments were carried out with selected halides to ensure that THF could be polymerized by these species under living conditions. Isopropyl iodide, allyl bromide and benzyl bromide were chosen as monofunctional initiators best representing the three classes of halides in *Table 1*; all react very rapidly with AgPF$_6$ at $-10°$C. Initiation was carried out at this temperature and polymerization allowed to proceed under isothermal conditions. Samples of the product were removed at hourly intervals, terminated with methanolic potassium hydroxide and the molecular weight of polyTHF determined by g.p.c. Similar

experiments were carried out with the dihalides 1,4-dibromobut-2-ene and *p*-xylylene dibromide but at half the molar concentration used with the monohalides. The plots of molecular weight against time for both sets of halides are shown in *Figure 1*.

As expected, the plots of the three monohalides are very similar, as are those of the two dihalides, and both show a linear relationship between molecular weight and polymerization time. The slopes of the rectilinear curves have values of 3600 h^{-1} for the monohalides and 8500 h^{-1} for the dihalides. The linearity of these curves indicates that living conditions prevail and that little if any chain transfer has occurred. This is reinforced by the observation that, within the rather large experimental error involved in this analysis, the rate of molecular weight increase with the difunctional initiators is approximately double that obtained with the monofunctional variety. Further, the molecular weight distribtuions of both series at the highest molecular weights achieved are relatively narrow ($M_w/M_n =$ 1.15 for monofunctional initiator, and $M_w/M_n =$ 1.20 for difunctional initiator) with no apparent tailing, and these results provide a particularly powerful indication that chain transfer is negligible under these conditions.

Since the polymer chains initiated by the two dibromides grow at about double the rate of those initiated by the monobromides, both of these difunctional species must initiate additively (see below) and they therefore provide a relatively simple means of preparing difunctional living polyTHF. Thus an attractive route is available for the synthesis of new ABA block copolymers by direct reaction of such species with anionic living polymers. Such reactions are currently being successfully exploited in these laboratories[7] and will be reported in a later communication.

Neither of the linear plots in *Figure 1* passes through the origin but they give intercepts of the order of 5—10 min. Although this is longer than the times assessed for the completion of precipitation at $-10°$C, it must be related to the rate of generation of active centres. Whatever the explanation, however, the deviation is small enough not to affect the production of narrow dispersity living polymers.

Benzal bromide was also tested kinetically as a difunctional initiator. Interestingly, a linear relationship was again found between molecular weight and polymerization time, but the slope was 3700 h^{-1}, i.e., the compound be-
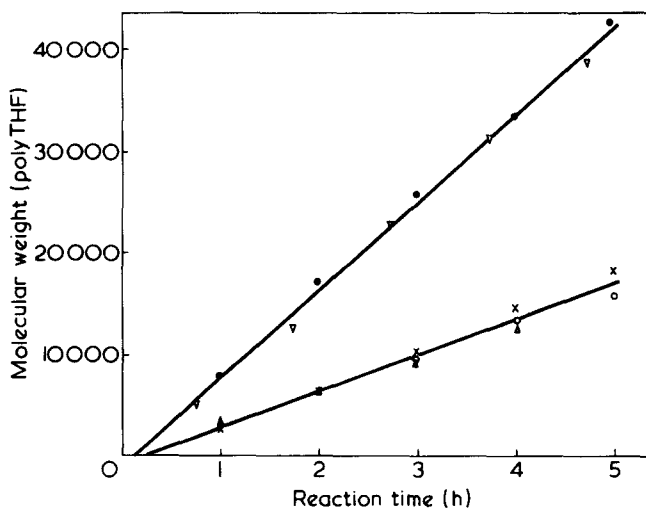

Figure 1 Molecular weight of polyTHF as a function of reaction time at $-10°$C using as catalyst AgPF$_6$ and $\bigcirc$, allyl bromide; X, benzyl bromide; $\triangle$, isopropyl iodide; $\triangledown$, *para*-xylylene dibromide; $\bullet$, 1,4-dibromobut-2-ene

haved as if it were a monofunctional initiator. Gravimetric analysis of the precipitated silver bromide showed that both of the bromines in the molecule had been reacted, and the linearity of the plot and the narrowness of the molecular weight distribtuion $(M_w/M_n \approx 1.1)$ indicated that neither chain transfer nor random chain scission was the cause of this anomalous behaviour. G.l.c. analysis of the product obtained after the reaction had been terminated almost immediately after initiation either by methanol or by lithium chloride showed that at least 80% of the benzal moiety was recovered as benzaldehyde. Thus it seems that some process, which is independent of the termination mode, occurs very soon after initiation and results in the elimination of the central benzal grouping creating two independent propagating monofunctional chains. This may be related to the fact that the central unit is of an acetal structure (structure III) which is unstable and can eliminate benzaldehyde,
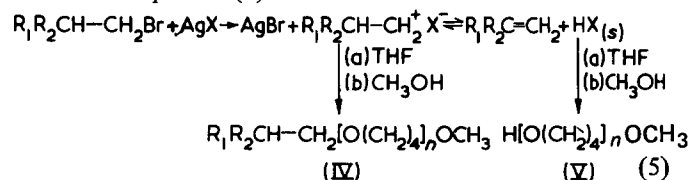
$$\text{\tiny\textbackslash\textbackslash}(CH_2)_4\text{—O—CH—O—}(CH_2)_4\text{\tiny\textbackslash\textbackslash}$$

(III)
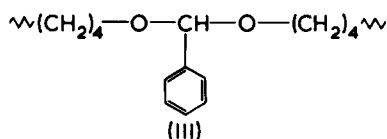
although the nature of the polymer chain ends thus created is open to speculation. Work is continuing on this system.

Additive initiation

The kinetic experiments described in the previous section give positive proof that the difunctional initiators 1,4-dibromobut-2-ene and *p*-xylylene dibromide initiate additively, since only by this mechanism can the chains themselves be difunctional and thus grow at twice the rate observed with the monofunctional species.

The interpretation of the results obtained with the monofunctional halides is less certain because the kinetic measurements may be insensitive to the presence at the initiation stage of a proton elimination reaction analogous to that shown in equation (4). Three cases may be considered depending on the initiating capability of the parent acid generated: where the acid is as active an initiator as the carbenium ion the number of chains initiated and their rate of growth will be the same as in the absence of transfer; where the acid is relatively inert the rate of growth of the chains will again be the same as with no transfer but their number will be correspondingly reduced; finally, where the acid is a slow initiator chains will be initiated throughout the polymerization period and the polymeric product will have a pronounced low molecular weight tail. Examination of the g.p.c. traces excluded this last possibility, but measurement of the rate of molecular weight increase alone cannot distinguish between the absence of transfer and either of the first two cases of transfer. The efficiency of additive initiation was therefore examined by two other complementary methods.

In the first technique employed the selected monohalide was reacted with a solution of the silver salt in THF at room temperature, methanol added immediately after silver halide precipitation was complete, and the oligomers formed isolated by g.l.c. and structurally examined by [1]H n.m.r. The possible reaction pathways are shown for a primary bromide in equation (5).

$$R_1R_2CH\text{—}CH_2Br + AgX \rightarrow AgBr + R_1R_2CH\text{—}CH_2^+ \, X^- \rightleftharpoons R_1R_2C\text{=}CH_2 + HX_{(s)}$$

(a)THF
(b)CH₃OH

(a)THF
(b)CH₃OH

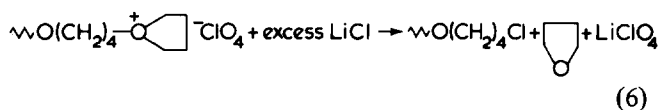$$R_1R_2CH\text{—}CH_2[O(CH_2)_4]_nOCH_3 \qquad H[O(CH_2)_4]_nOCH_3$$

(IV) (V) (5)

Thus g.l.c. measurement of the amount of olefin produced should quantify the degree of additive initiation occurring in the system, and an evaluation of the relative amounts of species IV and V should yield a measure of the initiating power of the parent acid relative to the carbenium ion. This technique was employed previously in a study of the initiation of THF polymerization by the 1-bromoethyl-benzene—AgClO₄ system[1]. G.l.c. analysis showed that, at room temperature, 63% of the initiator was converted into styrene, whereas all the major oligomeric peaks could be ascribed to structure IV; some very small peaks (<10%) were also observed which could be due to oligomers of structure V. These results therefore showed that proton transfer predominated with this reagent, and that the HClO₄ generated was a relatively slow initiator.

It was decided to examine the additive initiating efficiency of isopropyl iodide and allyl bromide as these had been studied kinetically; *p*-methylbenzyl bromide was chosen to represent the benzyl halides rather than benzyl bromide since the latter had been examined in this way previously[2]. For these experiments AgClO₄ was used instead of AgPF₆ so that the results could be compared directly with those obtained previously with 1-bromo-ethylbenzene and with benzyl bromide. It is realized, however, that the values obtained cannot be applied directly to the systems in which AgPF₆ is used since the Gegen ion may play an important role in determining the course of reaction of the carbenium ion. Nevertheless qualitative indications may be obtained.
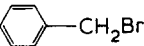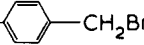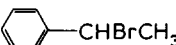
With isopropyl iodide and allyl bromide as initiators, the corresponding olefins, propene and allene, are too volatile to measure directly by g.l.c., although they can be looked for directly in the cooled reaction mixture by [1]H n.m.r. Nevertheless, although indicatiohs of proton transfer may be found by this means or by the presence of very small peaks on the g.l.c. trace at specified retention times, due to species V, an alternative method has to be devised to quantify the process.

One such method relies on the fact that the perchloric acid generated by transfer is a very slow initiator of THF and so under conditions of rapid termination the bulk of the acid produced remains in that form. Thus the introduction of a terminating agent which, unlike methanol, will not generate the acid would allow an acid—base titration to determine the degree of transfer. Excess of a solution of lithium chloride in THF has been shown to be effective in this regard, the propagating end being converted to the covalent chloride [equation (6)].

$$\text{\tiny\textbackslash\textbackslash}O(CH_2)_4\text{—}O^+\text{<} \quad ClO_4^- + \textit{excess } LiCl \rightarrow \text{\tiny\textbackslash\textbackslash}O(CH_2)_4Cl + \square + LiClO_4$$

(6)

This method is susceptible to two major sources of error; one is due to the slow initiation by perchloric acid after its generation which will reduce the titre, and this can be minimized by quenching the reaction in water immediately after addition of the lithium chloride solution, whilst the second is caused by water being present in any of the reagents or solvents employed, and this will increase the titre by regenerating the acid by reaction with the cationic oligomers. Benzyl bromide was used as a blank for the latter reaction, on the assumption that initiation by the carbenium ion of this species was exclusively additive[2] so that any acid generated would reflect contaminating moisture in the other reagents.

Table 2 Titration by 0.1 N NaOH of $HClO_4$ generated from organohalides by reaction in THF with $AgClO_4$ at room temperature (organohalide = 25 mmol)

Organohalide	Titre (ml)	Relative titre (ml)	Transfer (%)
◇—CH₂Br	1.6	–	–
(CH₃)₂CHI	3.4	1.8	7
CH₂=CH—CH₂Br	1.5	0	0
CH₃—◇—CH₂Br	2.7	1.1	4
◇—CHBrCH₃	18.6	17.0	68

The validity of the method was checked by comparing the result obtained for proton transfer by this procedure with 1-bromoethylbenzene with that obtained by g.l.c. measurement of styrene content. The figure of 68% transfer obtained (*Table 2*) compares very well with the 63% calculated from g.l.c. This agreement confirms the view that $HClO_4$ is a slow initiator. It is surprisingly good in view of the fact that the concentration of $AgClO_4$ used in the acid—base experiment is over twenty times that used in the g.l.c. experiments (see Experimental). Pocker et al.[9,10] have demonstrated that perchlorates, and lithium perchlorate in particular, have a profound catalytic effect on the ionization and reactivities of organic halides in ethereal solvents. Evidently in this case the effect is principally kinetic and the course of the reaction is relatively unaffected.

Both the g.l.c. method and the acid—base titration were used to examine the additive initiating efficiency of the three halides previously specified. They will be considered separately.

Isopropyl iodide

The g.l.c. trace of the products from this initiator is shown in *Figure 2a*. The numbered peaks were isolated separately and were identified by [1]H n.m.r. as being of structure IV with sequential values of n. In comparison with the other g.l.c. traces shown in *Figure 3* this trace shows a number of small peaks associated with the main peaks but at shorter retention times, which could well be of structure V and thus indicate a degree of proton transfer. Since propene is too volatile to be observed under these g.l.c. conditions, the unseparated product of reaction was examined by [1]H n.m.r. and small resonances attributable to this olefin could be observed.
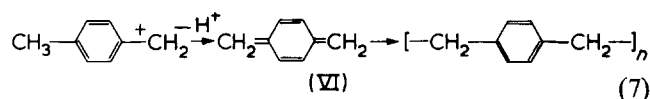
The acid—base titration method gave a titre which was significantly higher than the benzyl bromide blank (*Table 2*) and confirmed that proton transfer took place but that it did not exceed about 10% at room temperature.
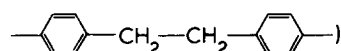
Allyl bromide

The g.l.c. trace of the products obtained from allyl bromide and shown in *Figure 2b* gives peaks which are solely due to structure IV, and therefore this is a strong indication that initiation with this reagent is predominantly additive. Furthermore no allene could be observed by [1]H n.m.r. in the reaction mixture and the acid—base titration (*Table 2*) coincided with that of the blank. Thus this initiator may be assumed to be quantitatively additive.

p-Methylbenzyl bromide

Again the g.l.c. of the products from this initiator (*Figure 2c*) is very clean with all major peaks ascribed to structure IV, and so it may be inferred that initiation is principally by addition. With this reagent the only olefin which can conceivably be formed by proton abstraction from the carbenium ion is p-xylelene (structure VI) which has been shown to polymerize spontaneously even at low temperatures[11] [equation (7)].

$$CH_3—\langle\bigcirc\rangle—\overset{+}{C}H_2 \xrightarrow{-H^+} CH_2=\langle\bigcirc\rangle=CH_2 \longrightarrow [—CH_2—\langle\bigcirc\rangle—CH_2—]_n$$
$$(VI) \tag{7}$$

No olefin could be observed by g.l.c. in this case, and [1]H n.m.r. examination of the reaction mixture to identify poly (p-xylelene) (observed by the characteristic single at 7.2 τ due to the methylene units in the grouping

$$—\langle\bigcirc\rangle—CH_2—CH_2—\langle\bigcirc\rangle—)$$

was also unsuccessful. Although the acid—base titre obtained was greater than that of benzyl bromide (*Table 2*),
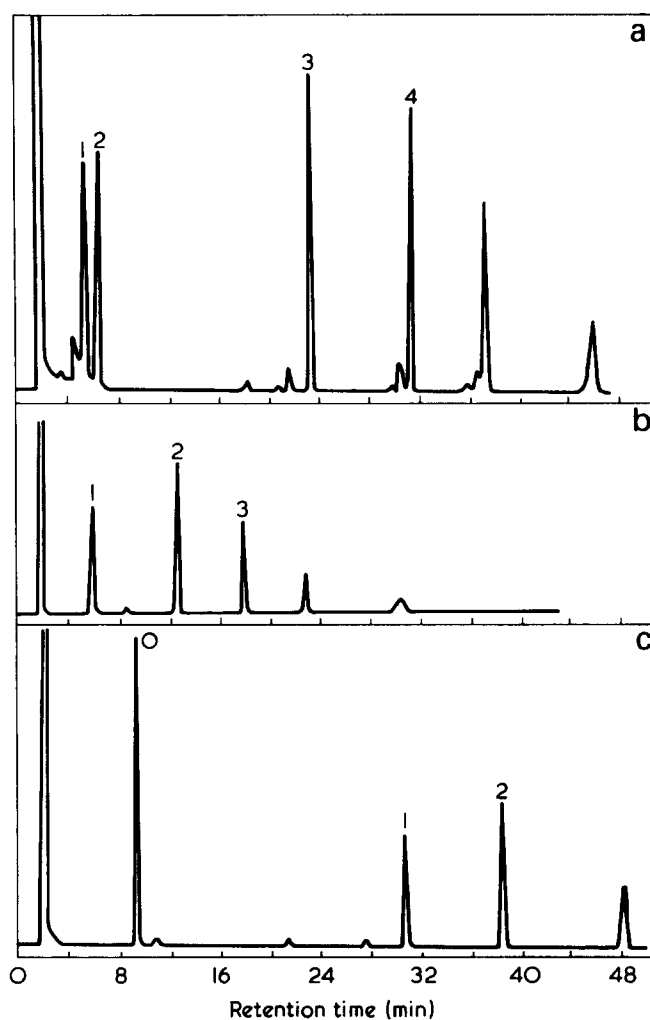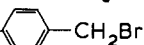

Figure 2 G.l.c. traces of products of general formula $R(O(CH_2)_4)_nOCH_3$ obtained by the methanol termination of the reaction of an organohalide (RX) with $AgPF_6$ in THF. Identification of labelled peaks by [1]H n.m.r. spectroscopy. (a) RX = $(CH_3)_2CHI$, $n = 1, 2,$ 3 and 4. (b) RX = $CH_2=CH—CH_2Br$, $n = 1, 2$ and 3. (c)

$$RX = CH_3—\langle\bigcirc\rangle—CH_2Br \quad n = 0, 1 \text{ and } 2.$$ G.l.c. temperature programmes: (a) 100°C for 10 min followed by 8°C/min to 300°C; (b) 100° to 300°C at 12°C/min; (c) 100° to 300°C at 6°C/min

the authors feel that this represents a small amount of water in the former halide rather than evidence of significant proton transfer.

It should finally be stressed that although proton transfer may occur to a significant extent at room temperature with certain organic halides, it may be very much reduced by lowering the initiation temperature. Experiments with 1-bromoethylbenzene have shown that 63% β proton elimination at room temperature is reduced to 33% at $0°C$ and to $<5\%$ at $-78°C^1$ and it is expected that similar reductions would occur with other organic halides.

CONCLUSIONS

(a) The reactivities of alkyl halides toward silver salts in THF to generate cationic initiators increase in the order fluoride $<$ chloride $<$ bromide $<$ iodide. The rates of reaction at $-10°C$ are such that fast initiation occurs with alkyl iodides and in certain cases with alkyl bromides.

(b) The reactivities of allyl and benzyl halides toward $AgPF_6$ are much greater than the alkyl halides. The bromides react very rapidly even at very low temperature, and selected dibromides were shown to produce living difunctional polyTHF under specified conditions.

(c) Allyl bromide, benzyl bromide[2] and p-methylbenzyl bromide on reaction with $AgClO_4$ initiate THF polymerization uniquely additively, but there is evidence that about 10% proton transfer occurs at room temperature when isopropyl iodide is used as initiator.

ACKNOWLEDGEMENT

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