Reactions of Alkyl Vinyl Ethers catalysed by Triethyloxonium Hexachloroantimonate and its Decomposition Products, in particular Antimony Pentachloride

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I.r. spectroscopy has been used to study the rates of disappearance of vinyl double bonds from systems containing isobutyl, phenyl, or 2-chloroethyl vinyl ethers and triethyloxonium hexachloroantimonate in dichloromethane. A fast primary reaction giving limited conversion of the alkyl vinyl ethers to oligomeric products was ascribed to catalysis by antimony pentachloride formed by the spontaneous decomposition of triethyloxonium hexachloroantimonate. Fast but limited conversion also occurred when antimony pentachloride was added to solutions containing alkyl vinyl ethers. Electronic spectra and conductivities of reacting systems and i.r., ^{1}H n.m.r., and mass spectra of reaction products were recorded. The implications of the results with respect to the initiation, propagation, transfer, and termination steps of the overall reaction are discussed. A slow secondary reaction of alkyl vinyl ethers initiated by triethyloxonium hexachloroantimonate was in part due to the continued generation of antimony pentachloride by decomposition of catalyst but also contained a contribution arising from catalysis by triethyloxonium ions.

SALTS containing carbocations have been used as catalysts for the polymerization of alkyl vinyl ethers.[1,2] Anilinium hexafluoroantimonate acts as an initiator for the polymerization of ethyl vinyl ether.[3] Triethyloxonium salts can also initiate polymerization reactions.[4,5] The object of the work described in this paper was to investigate the use of triethyloxonium hexachloroantimonate as a catalyst for the polymerization of alkyl vinyl ethers. In the early stages of the work it was apparent that this salt, in accord with the behaviour of related salts,[6] undergoes spontaneous decomposition in dichloromethane solvent to give ethyl chloride, diethyl ether, and antimony pentachloride. Details of the decomposition reaction have been published elsewhere.[7]

EXPERIMENTAL

Commercial samples of isobutyl vinyl ether, 2-chloroethyl vinyl ether, and phenyl vinyl ether were purified by the method of Schildknecht *et al.*[8] The b.p. of the purified liquids were 83.2 (101.3), 107.8 (99.3), and 155.4 °C (99.0 kN m^{-2}) respectively. No impurities in the liquids could be detected by g.l.c. analysis. The purification of dichloromethane and antimony pentachloride and the preparation of triethyloxonium hexachloroantimonate were as before.[7]

I.r. spectra were recorded using a Perkin-Elmer 625 spectrometer in conjunction with conventional liquid cells of 0.2 mm path length and with potassium bromide optical windows. A typical experiment first involved the preparation of a solution of triethyloxonium hexachloroantimonate in dichloromethane under nitrogen [7] and subsequent transfer of an aliquot portion of the catalyst solution to a graduated flask containing an alkyl vinyl ether and solvent. The resulting mixture was made to the mark and shaken and a small volume was transferred in a syringe to the i.r. sample cell, all as quickly as possible. A similar cell containing solvent alone had already been placed in the reference beam of the spectrometer. The rates of reaction were measured with the spectrometer in its fixed wavenumber mode. I.r. bands associated with vibrations of the vinyl group in the monomer molecules completely disappeared during the course of reaction. The intense band due to the $-CH{=}CH_2$ stretching vibration of each monomer was chosen for study and a trace of percentage transmission against time was automatically recorded. Percentage transmission values ($100\ I/I_0$) were converted to absorbances [$\log_{10}(I_0/I)$] referred to a baseline corresponding to pure solvent in both spectrometer beams. Triethyloxonium hexachloroantimonate did not have a detectable i.r. spectrum under the experimental conditions which were used. The recorded rates of loss of absorbance referred to reaction solutions at their ambient temperature, estimated to be 28 ± 3 °C, in the optical beam of the spectrometer. The results were reproducible (absorbances to ±0.02). An identical procedure has previously been used in related studies of the iodine-catalysed polymerization of vinyl ethers for which kinetic data deduced from the i.r. results were in good agreement with corresponding data deduced from dilatometric results for the systems prepared and studied completely under vacuum conditions.[9]

Electronic spectra and conductivities of reaction solutions at 298 K were measured as before.[7] Samples of the oligomeric and polymeric involatile products of the reactions of isobutyl and 2-chloroethyl vinyl ethers were obtained by allowing reactions to proceed to completion and subsequently evacuating at *ca.* 293 K to remove solvent. The initial concentrations of the monomers were *ca.* 200—4 000 times greater than the initial concentrations of catalyst in the solutions from which the products were obtained. The present work has shown that the entire catalyst is either incorporated during initiation or termination reactions into the oligomer or polymer product molecules or reacts to give volatile products, for example ethyl chloride and diethyl ether,[7] which would have been removed during the evacuation procedure. Other possible volatile products such as t-butyl chloride and t-butyl alcohol or the corresponding 2-chloroethyl derivatives would also have been removed by evacuation. The resulting involatile viscous liquids were

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[1] C. E. H. Bawn, C. Fitzsimmons, A. Ledwith, J. Penfold, D. C. Sherrington, and J. A. Weightman, *Polymer*, 1971, **12**, 119.

[2] A. Ledwith, *Makromol. Chem.*, 1974, **175**, 1117.

[3] J. J. Harris and S. C. Temin, *J. Polymer Sci., Part A.*, 1972, **10**, 1165.

[4] J. D. Coombes and D. D. Eley, *J. Chem. Soc.*, 1957, 3700.

[5] 'The Chemistry of Cationic Polymerization,' ed. P. H. Plesch, Pergamon, Oxford, 1963 (*a*) ch. 9; (*b*) ch. 10.

[6] F. R. Jones and P. H. Plesch, *Chem. Comm.*, 1969, 1231.

[7] D. D. Eley, D. F. Monk, and C. H. Rochester, *J.C.S. Faraday I*, 1976, 1584

[8] C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. and Eng. Chem.*, 1947, **39**, 180.

[9] D. D. Eley, F. L. Isack, and C. H. Rochester, *J. Chem. Soc.*, (*A*), 1968, 872.

subjected to conventional microanalysis, n.m.r. analysis in carbon tetrachloride solution using a Varian HA100 spectrometer, mass spectrographic analysis using an Atlas MS9 mass spectrometer, and their number average molecular weights (in chloroform solution) were determined using a thermistor drop technique.

RESULTS

I.r. Spectroscopic Measurements.—The spectroscopic effects associated with the loss of vinyl groups from reacting monomer molecules were identical to those which have previously been observed to accompany the iodine-catalysed polymerization reactions of n-butyl vinyl ether in three aprotic solvents.[9] The variations with time of absorbance at 1 614 for isobutyl vinyl ether, 1 620 for phenyl vinyl ether, and 1 644 cm^{-1} for 2-chloroethyl vinyl ether gave, in the same way as before,[9] a measure of the rates of loss of vinyl double bonds in reacting mixtures. For all three monomers the Beer–Lambert Law was applicable.

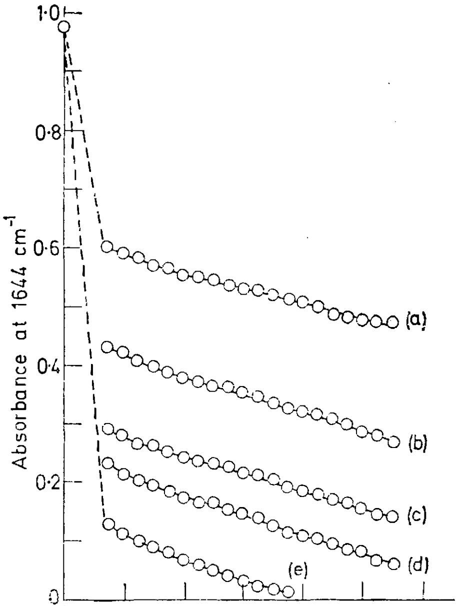

FIGURE 1 The rates of loss of 2-chloroethyl vinyl ether (initial concentration 0.084 mol dm^{-3}) as a function of the age of the solution of triethyloxonium hexachloroantimonate used to initiate the reaction. The initial concentration of catalyst was 3.09×10^{-3} mol dm^{-3} and the times after preparation at which it was added to monomer solution were (a) 2; (b) 14; (c) 33.5; (d) 48.5; and (e) 77 min

Because of the instability of solutions of triethyloxonium hexachloroantimonate in dichloromethane [7] it was necessary to establish the effect of the catalyst decomposition reaction on the catalyst-induced reaction of alkyl vinyl ethers. A series of solutions were prepared containing the same concentrations of alkyl vinyl ether but to which were added a particular volume of catalyst solution at various times after the catalyst solution had been freshly prepared. Typical plots of absorbance against time are exemplified by the results for 2-chloroethyl vinyl ether shown in Figure 1. Similar results were obtained for isobutyl and phenyl vinyl ether. For all three monomers two distinct stages of reaction could be distinguished. The initial fast disappearance of a proportion of the total concentration of vinyl double bonds usually occurred during the time between mixing and transfer of reaction solutions to the i.r. cell. The rates of this first stage of the reaction could not therefore be deduced from the present experimental results. However the proportion of the added monomer which

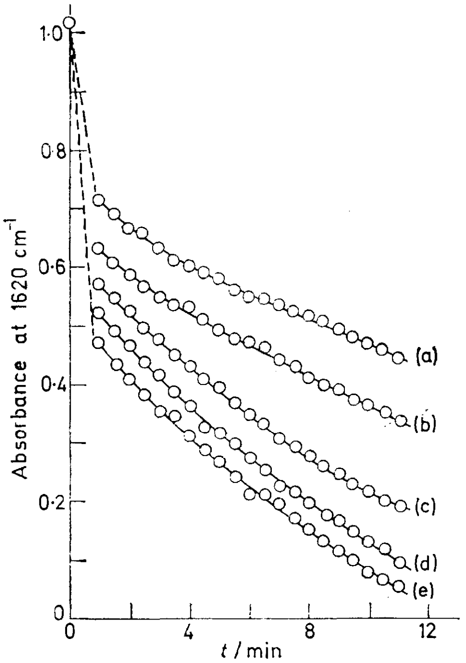

FIGURE 2 The rates of loss of phenyl vinyl ether (initial concentration 0.141 mol dm^{-3}) as a function of the concentrations of triethyloxonium hexachloroantimonate. Initial concentrations (in units of 10^{-3} mol dm^{-3}) of catalyst were (a) 0.67; (b) 0.79; (c) 1.24; (d) 1.57; and (e) 1.97

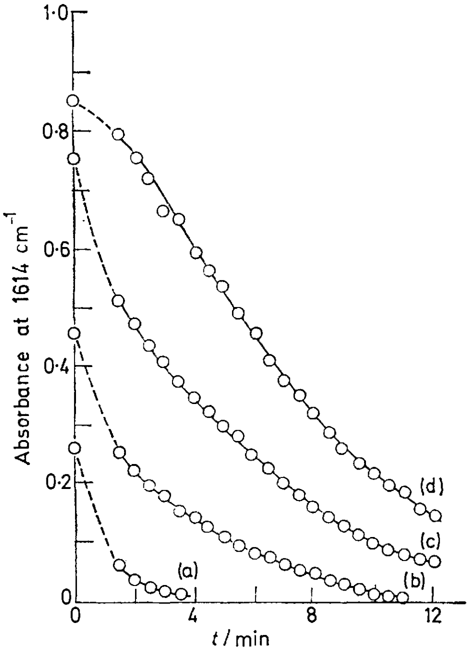

FIGURE 3 The rates of loss of isobutyl vinyl ether catalysed by triethyloxonium hexachloroantimonate (initial concentration 3.54×10^{-4} mol dm^{-3}). Initial monomer concentrations were (a) 0.065; (b) 0.129; (c) 0.202; and (d) 0.220 mol dm^{-3}

reacted during the first stage was greater the longer was the time which had elapsed between preparation of the catalyst solution and mixing of the monomer and catalyst solutions. This result suggests that the first stage in the removal of vinyl double bonds from reacting systems involved catalysis by a product of the decomposition reaction of triethyloxonium hexachloroantimonate. The second stage in the overall reaction was slower than the first and the corresponding rate of removal of vinyl groups from the solutions could be followed using the spectroscopic technique.

The effects of catalyst and monomer concentrations on the rates of disappearance of vinyl double bonds from reacting systems were investigated. The results for all three vinyl ethers were similar and are exemplified by the data for the effects of catalyst concentration on the reaction of phenyl vinyl ether in Figure 2 and of monomer concentration on the reaction of isobutyl vinyl ether in Figure 3. In these experiments all catalyst solutions were prepared 2 min before the reactions with monomer were commenced. The ranges of initial monomer concentrations which were studied were 0.065—0.220, 0.027—0.085, and 0.058—0.235 mol dm^{-3} for isobutyl, 2-chloroethyl, and phenyl vinyl ether, respectively. The ranges of catalyst concentrations studied for the three ethers respectively were 0.000 20—0.000 67, 0.001 10—0.006 55, and 0.000 67—0.001 97 mol dm^{-3}.

The fast primary reaction of vinyl ethers in the presence of triethyloxonium hexachloroantimonate is probably due to the formation of antimony pentachloride in decomposing [7] catalyst solutions. The effect of antimony pentachloride on the reactions of isobutyl and 2-chloroethyl vinyl ether was investigated as a function of the concentrations of both monomer and antimony pentachloride. The ranges of initial concentration of monomer studied were 0.045—0.268 (catalyst range 0.012—0.62 mmol dm^{-3}) and 0.041—0.092 mol dm^{-3} (catalyst range 0.097—0.97 mmol dm^{-3}) for isobutyl and 2-chloroethyl vinyl ether, respectively. As with triethyloxonium hexachloroantimonate as catalyst the completion of a fast but limited primary reaction was followed by a slower second reaction. Typical results are shown in Figure 4. The rate of loss of vinyl double bonds during the second stage was independent of both monomer and antimony pentachloride concentrations and was apparently slower with antimony pentachloride than with triethyloxonium hexachloroantimonate as catalyst. For example, comparison of the results shown in Figures 3d and 4d which are for similar initial isobutyl vinyl ether concentrations show that after 4 min the slopes of the curves are 0.08 and 0.008 absorbance units min^{-1} respectively. Thus there was a ten-fold difference between the rates of loss of vinyl groups. The difference between the catalyst concentrations for the two curves being compared is not significant because it was shown for antimony pentachloride as catalyst that the slopes of the curves were independent of catalyst concentration over a range which extended up to 0.62 mmol dm^{-3}. The difference between the rates of reactions with antimony pentachloride and with triethyloxonium hexachloroantimonate as catalysts may at least in part have been due to the continuous generation of antimony pentachloride in solutions containing triethyloxonium hexachloroantimonate.[7] Thus with the latter catalyst a reaction equivalent to the fast primary reaction between monomer and antimony pentachloride would have been expected to occur throughout the time during which measurements were being made.

The effects of monomer and antimony pentachloride concentrations on the magnitude of the loss of vinyl double bonds during the fast primary reaction were such that at similar catalyst and similar monomer concentrations fewer vinyl double bonds were lost in the fast reaction of 2-chloroethyl than of isobutyl vinyl ether. This result is consistent with the corresponding comparison for the fast reactions of the two monomers catalysed by partially decomposed triethyloxonium hexachloroantimonate.

Spectrophotometric Measurements.—U.v. spectra of solutions containing a vinyl ether and triethyloxonium hexachloroantimonate were similar for all three monomers studied and showed certain features which contribute information concerning reaction mechanism. In the early stages of reaction, spectra were characterized by absorption maxima at 36 500 and 44 200 cm^{-1} (274 and 226 nm) which may be assigned to the hexachloroantimonate ion [7,10] and the π–π^* transition of monomer molecules respectively. Even after *ca.* 3 min the band at 36 500 cm^{-1} was considerably less intense than would be expected [7,10] for a solution containing catalyst alone. Thus some of the hexachloroantimonate ions added to monomer solution are either rapidly decomposed by reaction with the alkyl vinyl ether or become complexed with monomer or cations in solution such that their characteristic spectrum is lost. The spectroscopic results also failed to exhibit the expected [7] slow appearance of antimony pentachloride in the solutions. Thus the presence of a comparatively high concentration of an alkyl vinyl ether apparently caused the immediate reaction of any antimony pentachloride generated in the solution to give products which do not absorb in the region examined. The alternative possibility that the decomposition of triethyloxonium hexafluoroantimonate to antimony pentachloride is impeded by alkyl vinyl ethers is less likely because Jones and Plesch [6] showed that the decomposition reactions of triethyloxonium salts were accelerated, at least

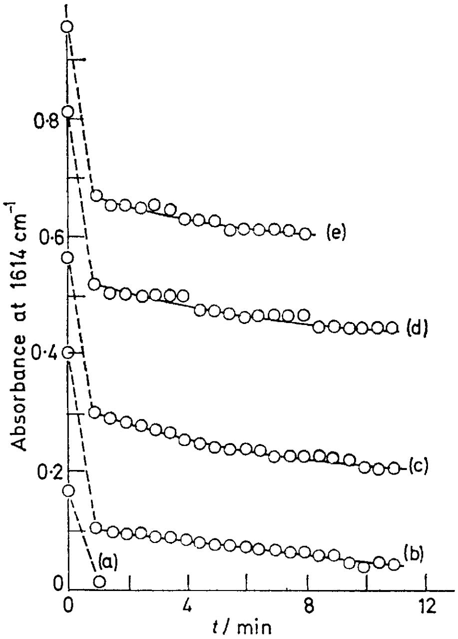

FIGURE 4 The rates of loss of isobutyl vinyl ether catalysed by antimony pentachloride (initial concentration 0.62 × 10^{-4} mol dm^{-3}). Initial monomer concentrations were (a) 0.045; (b) 0.107; (c) 0.156; (d) 0.221; and (e) 0.268 mol dm^{-3}

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[10] A. P. Kubisa and S. Penczek, *Makromol. Chem.*, 1971, **144**, 169.

in the presence of simple ethers. The band at 44 200 cm^{-1} due to isobutyl vinyl ether molecules decreased with time at a rate which was compatible with the slow loss of vinyl double bonds observed using i.r. spectroscopy. The intensity of the band at 36 500 cm^{-1} due to hexachloroantimonate ions was hardly changed during this stage of the overall reaction. The final effects which were observed involved the growth of intense broad absorption maxima at 36 900 and 43 400 cm^{-1} (271 and 230 nm). Reaction solutions became brown at this stage but in accord with related reports [1,11] passed through vivid but transitory coloured states in doing so. The band at 36 900 cm^{-1} may possibly be due to carbonyl species formed during termination reactions.

Conductimetric Measurements.—Conductivities of solutions containing a vinyl ether and triethyloxonium hexachloroantimonate decreased with time. The conductivity changes for one reaction are compared in Figure 5 with the corresponding results for the same concentration of catalyst in the absence of vinyl ether. In the presence of monomer the conductivities decreased rapidly during the first 2—3 min of reaction but subsequently decreased at a rate comparable with that observed for catalyst alone. This supports the conclusion that triethyloxonium hexachloroantimonate continues to decompose to antimony pentachloride in the presence of monomer. Both the i.r. and u.v. spectroscopic data show that the antimony pentachloride formed rapidly reacts with alkyl vinyl ether and catalyses the loss of vinyl double bonds from the reacting system. The rapid reaction between antimony pentachloride and alkyl vinyl ethers is also illustrated by the observation that conductivities of solutions containing both species were appreciably smaller than the conductivities of solutions only containing antimony pentachloride.

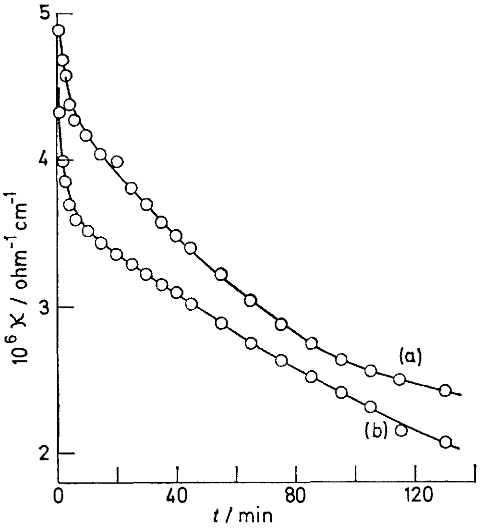

FIGURE 5 Conductivities at 298 K of solutions containing triethyloxonium hexachloroantimonate (0.52 × 10^{-4} mol dm^{-3}). (a) Catalyst solution alone; (b) catalyst plus isobutyl vinyl ether (0.154 mol dm^{-3})

Thus the specific conductivity of a solution containing isobutyl vinyl ether (0.15 mol dm^{-3}) and antimony pentachloride (5.2 × 10^{-5} mol dm^{-3}) slowly decreased from 1.86 × 10^{-7} ohm^{-1} cm^{-1} after 3 min to 1.64 × 10^{-7} ohm^{-1} cm^{-1} after 115 min. These values compare with the specific conductivity of 6.9 × 10^{-7} ohm^{-1} cm^{-1} for a solution (4.6 × 10^{-5} mol dm^{-3}) containing antimony pentachloride alone.[7] These results might be explicable in terms of the equilibrium formation of a Lewis acid–base adduct between antimony pentachloride and vinyl ether. However the i.r. data has shown that a fast irreversible reaction involving a proportion of the ether molecules present must have already reached completion before the first (after *ca.* 1 min) conductivity measurement could be made.

Identification of Reaction Products.—The degrees of polymerization (d.p.) of polyisobutyl vinyl ether or poly-2-chloroethyl vinyl ether formed in the reactions catalysed by triethyloxonium hexachloroantimonate were within the ranges 2.8—6.9 and 2.5—4.4, respectively. The values are listed in Table 1 and show that for polyisobutyl vinyl ether the d.p. value was greater the higher the initial monomer concentration but was decreased by raising the catalyst concentration. These effects were reversed for poly-2-chloroethyl vinyl ether.

TABLE 1

Degrees of polymerization of isobutyl (IBVE) and 2-chloroethyl vinyl ether (CEVE) by triethyloxonium hexachloroantimonate in dichloromethane at 298 K

10^4[Catalyst] mol dm^{-3}	[IBVE] mol dm^{-3}	d.p.	10^3[Catalyst] mol dm^{-3}	[CEVE] mol dm^{-3}	d.p.
1.88	0.042	3.2	1.26	0.060	3.4
1.88	0.084	2.8	1.26	0.075	2.9
1.88	0.126	3.6	1.26	0.090	2.9
1.88	0.168	4.2	0.31	0.060	2.5
1.88	0.210	6.0	0.63	0.060	2.6
1.88	0.252	6.9	0.94	0.060	2.8
0.47	0.168	4.6	1.57	0.060	4.4
0.94	0.168	4.8			
1.41	0.168	4.7			
2.35	0.168	4.3			
2.82	0.168	4.1			
3.76	0.168	3.6			

I.r. spectra of reacting systems contained bands which could be assigned to end groups in oligomer molecules. Similar results were obtained for all three monomers. Two bands which were, for isobutyl vinyl ether, at 3 580 and 1 724 cm^{-1} may be assigned to the stretching vibrations of hydroxy and carbonyl groups respectively. A weak band at 2 720 cm^{-1} is ascribed to the CH stretching vibration of aldehyde groups. Four bands appeared in the range 1 000—1 200 cm^{-1} and may be assigned to vibrations of possibly several types of ether linkage C–O–C involving two saturated carbon atoms. A concomitant decrease in the intensity of a strong band at *ca.* 1 200 cm^{-1} due to $=CH-O-CH_2-$ groups occurred. It is relevant to note that the acetal group C–O–C–O–C, which may be formed as an end group in the polymerization reactions of vinyl ethers,[1] gives four i.r. bands in the 1 000—1 200 cm^{-1} region of the spectrum.[12,13] The i.r. results suggest that hydroxy, ether, formyl, and acetal groups were formed as end groups during the oligomerization reactions. The appearance of carbonyl groups occurred at the same time as the loss of vinyl groups during both the rapid first stage and the second slower stage of the reactions.

Mass spectra of the products of reaction of isobutyl vinyl ether catalysed by triethyloxonium hexachloroantimonate were too complex for complete analysis. The low molecular

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[11] G. A. Latremouille, C. T. Merrall, and A. M. Eastham, *J. Amer. Chem. Soc.*, 1960, **82**, 120.

[12] E. D. Bergman and S. Pinchas, *Rec. Trav. chim.*, 1952, **71**, 161.

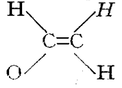
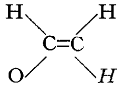
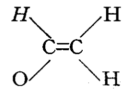
[13] H. Tschamler and R. Leutner, *Monatsh.*, 1952, **83**, 1502.

weights of the products were in accord with the highest detectable peak in the spectrum at an *m/e* value of 446. This result could also be taken as supporting the i.r. results in the sense that it could be due to an ion built up from four isobutyl vinyl ether molecules together with one aldehyde and one hydroxy group. Other predominant peaks occurred at *m/e* values of 45, 57, 73, 87, 89, 129, 203, 229, and 261. Tentative assignments of these maxima may be made by assuming that the parent molecules or the molecular fragments are composed of combinations of one or more of butyl, butoxy, hydroxy, methyl, and formyl groups and individual segments of polyvinyl isobutyl ether chains.

Microanalyses of the products formed by reaction of isobutyl vinyl ether gave carbon and hydrogen contents within the ranges 66—69 and 10.4—12.7% respectively (compared with C 72 and H 12% for unchanged monomer). No chlorine, which might have been derived from the catalyst, could be detected. Unfortunately the microanalyses are of little help towards the identification of the precise nature of the reaction products. However the low % carbon value compared with that for monomer supports the conclusion (Table 1) that only low molecular weight oligomer and not polymer was being formed.

TABLE 2

Data from the ^{1}H n.m.r. spectra of isobutyl vinyl ether and the oligomeric product formed by the triethyloxonium hexachloroantimonate catalysed reaction of the ether. Chemical shifts are with respect to Me_4Si internal standard

δ (monomer)	δ (oligomer)	Relative intensities for oligomer	Assignments
9.11	9.11	18	$CH(C\mathit{H}_3)_2$
	8.83	6	$CHC\mathit{H}_2CH$
8.10	8.25	6	$(CH_3)_2C\mathit{H}$ and $CH_2C\mathit{H}CH_2$
	7.50	2	$C\mathit{H}_2CHO$
6.62	6.82	8	$CHC\mathit{H}_2O$
6.15			
5.81			
	5.33	1	$O\mathit{H}$
3.58			
	0.18	1	$CH_2C\mathit{H}O$

The main features of the ^{1}H n.m.r. spectra of the reaction products formed from isobutyl vinyl ether in the presence of triethyloxonium hexachloroantimonate could be assigned to Me_2CHCH_2O–, –$CHCH_2CH$–, –CH_2CHO, and –OH groups. The band positions with assignments are given in Table 2.

DISCUSSION

Fast Reaction between Alkyl Vinyl Ethers and Antimony Pentachloride.—Decomposition of triethyloxonium hexachloroantimonate in dichloromethane solution leads to the formation of antimony pentachloride.[7] The initial rapid loss of monomer which occurs when a solution of triethyloxonium hexachloroantimonate is added to a vinyl ether may be ascribed to initiation by antimony pentachloride formed by decomposition of the oxonium salt. The primary reaction of monomer in solutions containing the oxonium salt and a vinyl ether (Figures 1—3) is therefore best understood by consideration of the results for the reactions of vinyl ethers catalysed by antimony pentachloride alone.

(a) *Initiation reactions.* The initiation of the cationic oligomerization or polymerization of alkyl vinyl ethers by antimony pentachloride cannot involve α-hydride abstraction from the alkyl group because phenyl vinyl ether is also activated by this catalyst. The generation of active monomer by the addition of catalyst or its ionization products [7,10,14] to the alkene may occur according to reaction (1) or (2) in which $[ROCH{=}CH_2,SbCl_5]$ is a

$$ROCH{=}CH_2 + SbCl_4^+ \longrightarrow R\overset{+}{O}{=}CHCH_2SbCl_4 \quad (1)$$

$$[ROCH{=}CH_2,SbCl_5] + SbCl_5 \longrightarrow R\overset{+}{O}{=}CHCH_2SbCl_4 + SbCl_6^- \quad (2)$$

1 : 1 addition complex of monomer and catalyst. The present systems are also favourable [15-17] to the formation of a cation-radical, which could be the active species in the oligomerization reactions [18-20] by transfer of a π-electron from the ether to the Lewis acidic pentahalide. An initiation mechanism involving the formation of an active species ClM^+ by transfer of the ion Cl^+ from $SbCl_5$ to monomer M is also possible [21] but is not proven for the present systems.

Co-catalysis by traces of dissolved water cannot be completely discounted for the systems studied here since distillation of solvent and monomer over sodium films [22] was not carried out. Induction periods [22] were not detected in the present work because the fast primary reactions were complete before the first experimental observation was made.

(b) *Propagation reactions.* The growth of oligomer or polymer chains occurs by the propagation reaction (3) which accounts for the disappearance of vinyl double bonds. The primary reaction was too fast for kinetic study but estimates showed that the propagation rate constants must have been of a similar order of magnitude to those for systems in which free cations rather than ion-pairs constitute the propagating species.[1,23]

(c) *Transfer reactions.* Monomer transfer reactions are probably the main cause of the low molecular weights of the products of the reactions of alkyl vinyl ethers catalysed by antimony pentachloride. Dunn and

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[14] P. H. Plesch, *Makromol. Chem.*, 1974, **175**, 1065.

[15] I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 1965, **43**, 2712.

[16] M. P. Dreyfuss and P. Dreyfuss, *Polymer*, 1965, **6**, 93; *J. Polymer Sci.*, 1966, **A4**, 2179.

[17] O. N. Howarth and G. K. Fraenkel, *J. Amer. Chem. Soc.*, 1966, **88**, 4514.

[18] C. E. H. Bawn, C. Fitzsimmons, and A. Ledwith, *Chem. Comm.*, 1965, 522.

[19] H. Gilbert, *J. Amer. Chem. Soc.*, 1956, **78**, 1669.

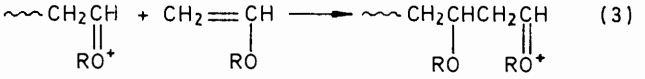
[20] N. Gaylord and M. Svestka, *J. Makromol. Sci. Chem.*, 1969, **3**, 897.

[21] W. Bracke, W. J. Cheng, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, 1969, **91**, 203.

[22] D. D. Eley and A. Seabrooke, *J. Chem. Soc.*, 1964, 2231.

[23] F. Williams, K. Hayashi, K. Ueno, K. Hayashi, and S. Okamura, *Trans. Faraday Soc.*, 1967, **63**, 1501.

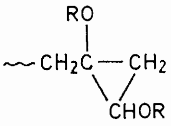
Plesch[24] reached a similar conclusion *via* the use of Mayo plots for related systems. Mayo plots are not applicable for the products (high conversion, low d.p.) obtained in the present work. The simplest possible monomer transfer reaction is (4).[5a] However the low d.p. values and the absence of bands due to C=C stretching vibrations from i.r. spectra of products suggests that reaction (4) was not significant in relation to other transfer or termination reactions.



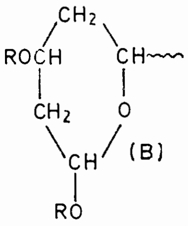
$$\sim\sim CH_2\underset{\underset{RO^+}{\|}}{CH} + CH_2{=}\underset{\underset{RO}{|}}{CH} \longrightarrow \sim\sim CH_2\underset{\underset{RO}{|}}{CH}CH_2\underset{\underset{RO^+}{\|}}{CH} \quad (3)$$

$$\sim\sim CH_2CH{=}\overset{+}{O}R + CH_2{=}CHOR \longrightarrow \sim\sim CH{=}CHOR + CH_3CH{=}\overset{+}{O}R \quad (4)$$

Alternative transfer reactions involving a protonated cyclopropyl derivative or a cyclic oxonium ion as intermediate have been proposed by Bawn *et al.*[1] in connection with the polymerization of isobutyl vinyl ether catalysed by some salts containing carbonium ions. Dead polymer with end groups of structure (A) or (B) may be formed although it was acknowledged that subsequent decomposition of the end groups might occur through reaction with electrophilic species present in the solutions. The formation of species (A) or (B) would be compatible with the present spectroscopic results. In particular i.r. spectra of products support the suggestion that the latter contain ether linkages which differ from those present in the growing polymer chain [equation (3)]. The spectroscopic evidence for acetal groups in reaction products is also consistent with the formation of a cyclic oxonium ion as an intermediate since terminal acetal groups can be formed by reaction of the ion with a further alkyl vinyl ether molecule.[1]



(A)



(B)

Both the ^1H n.m.r. and i.r. spectra of products contain unequivocal evidence for terminal formyl groups in dead oligomer. Equation (5) represents a transfer reaction which would account for the formation of formyl groups. The existence of peaks at *m/e* values of 129 and 229 in mass spectra of reaction products is also consistent with the formation of species (B) and species with terminal formyl groups. Thus *m/e* 229 would correspond to the cyclic fragment (minus the $\sim\sim\sim$ chain) of (B). Also *m/e* 229 and 129 would correspond to fragments $[CH(OR)CH_2]_nCHO$ of the dead product of reaction (5) with *n* 2 and 1 respectively.

$$\sim\sim CH_2CH{=}\overset{+}{O}R + CH_2{=}CHOR \longrightarrow \sim\sim CH_2CHO + RCH_2CH{=}\overset{+}{O}R \quad (5)$$

(d) *Termination reactions*. The majority of product molecules which result from the interactions between alkyl vinyl ethers and antimony pentachloride must have been formed during transfer rather than true termination reactions. Thus typically *ca.* 50—1 000 product molecules were produced for every catalyst molecule present in the systems. The apparent absence of chlorine from the products is not significant because with the relative monomer and catalyst concentrations used the maximum possible level of chlorine present would be on the limit of detection by the standard microanalytical method. Thus chlorine may have been incorporated into the products either during initiation or termination reactions. In fact the fast but limited conversion of alkyl vinyl ether to products shows that there is a net loss of catalyst during the course of reaction either at initiation or termination or at both stages. The loss of catalyst is also evidenced by the absence of bands due to antimony pentachloride in u.v. spectra of systems containing an alkyl vinyl ether and triethyloxonium hexachloroantimonate after the completion of the rapid initial reaction. The importance of true termination reactions is shown by the observed limited conversion of monomer molecules to product species. A likely termination reaction is represented by (6)[1] which leads to the regeneration of a catalyst molecule. However the generation of active species requires two catalyst molecules [for example reaction (1) requires $2SbCl_5 \rightleftharpoons SbCl_4^+ + SbCl_6^-$] and therefore the net effect of reaction (6) is to decrease the total number of active plus potentially active species present in the solutions. Termination reactions leading to $SbCl_3$, HCl, and ROH may also occur[1] although it is impossible to assess their relative importance in the present systems. It is relevant however to compare the transient colours of reaction solutions with the colours attributed by Bawn *et al.*[1] to the formation of conjugated cationic species in the polymerization of isobutyl vinyl ether initiated by triphenylmethyl or tropylium hexachloroantimonates. The concomitant ejection of alcohol molecules[1] may account for the presence of a band at *ca.* 3 580 cm^{-1} in the i.r. spectra of products. Alternatively the alcohol molecules (or phenol molecules in the case of phenyl vinyl ether) may have been formed by the decomposition of acetal end-groups according to reaction (7). In either case the absence of i.r. bands due to –CH=CH groups in reaction products shows that the alkene groups formed by ejection of alcohol molecules must be liable to further reaction which produces saturation. The very low conductivities

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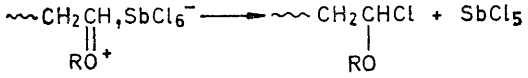
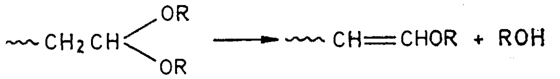
[24] D. J. Dunn and P. H. Plesch, *Makromol. Chem.*, 1974, **175**, 2821.

of solutions containing monomer and antimony pentachloride after the fast primary loss of monomer was completed (*ca.* 1 min after mixing) show that the products of the termination reactions were considerably less ionized than antimony pentachloride itself. This result would be consistent with the proposal that the initiation step (1) in which $SbCl_4$ is lost on the generation of active species and the termination step (6) in which a chlorine



$$\sim\!\sim CH_2\underset{RO^+}{\underset{\|}{C}}H,SbCl_6^- \longrightarrow \sim\!\sim CH_2\underset{RO}{\underset{|}{C}}HCl + SbCl_5 \qquad (6)$$



(7)

atom is lost in the formation of a non-ionic product constitute the overall mechanism for the loss of antimony pentachloride from reacting systems.

(e) *Kinetic analysis.* The limited yields observed for the fast reactions between isobutyl vinyl ether or 2-chloroethyl vinyl ether and antimony pentachloride have previously been reported for the polymerization of isobutyl vinyl ether initiated by boron trifluoride–ether complex.[25] In the latter case slow propagation followed rapid initiation and the initial rates of polymerization were first order in both monomer and catalyst concentrations. Spontaneous termination of active species occurred and led to equation (8) for the rate of loss of

$$-d[M]/dt = k_p[M][C]_0 \exp(-k_t t) \qquad (8)$$

monomer M after time t for an initial catalyst concentration $[C]_0$ and propagation and termination rate constants k_p and k_t, respectively. Integration of equation (8) led to relationship (9) for the ratio $[M]_0/[M]_f$ of initial

$$\ln([M]_0/[M]_f) = (k_p/k_t)[C]_0 \qquad (9)$$

monomer concentration $[M]_0$ to the final concentration $[M]_f$. In the present study this ratio was found to be given by the empirical equation (10) in which k is a constant. The appropriate plots for a range of concentrations of both catalyst and monomer are shown in

$$\ln([M]_0/[M]_f) = k[C]_0^{\frac{1}{2}}/[M]_0 \qquad (10)$$

Figure 6. Consideration of possible mechanisms in terms of the initiation, propagation, transfer, and termination steps discussed above has shown that the form of equation (10) has two possible implications with respect to the mechanism of individual steps in the overall reactions.

If as before [25] initiation is fast compared with propagation then the $[C]_0^{\frac{1}{2}}$ term in equation (10) suggests that the concentration of growing polymer in reaction solutions is itself proportional to $[C]_0^{\frac{1}{2}}$. The initiation step [*e.g.* reactions (1) or (2)] involves the formation of cationic species and a hexachloroantimonate anion the two ions possibly being involved in ion-pairing in accord with equilibrium (11). If the association constant K_A for the

$$RO^+{=}CHCH_2SbCl_4 + SbCl_6^- \rightleftharpoons RO^+{=}CHCH_2SbCl_4,SbCl_6^- \qquad (11)$$

formation of ion-pairs is sufficiently large then the concentration of cations in solution will be approximately equal to $([C]_0/K_A)^{\frac{1}{2}}$. Thus the present result implies that free cations $RO^+{=}CHCH_2SbCl_4$ rather than their ion pairs with hexachloroantimonate anions constitute the most active species in the subsequent transfer and propagation reactions with further monomer molecules. Similar conclusions have been reached for related systems involving catalysis by triethyloxonium salts [26,27] and for the polymerization of alkyl vinyl ethers catalysed by triphenylmethyl hexachloroantimonate.[28]

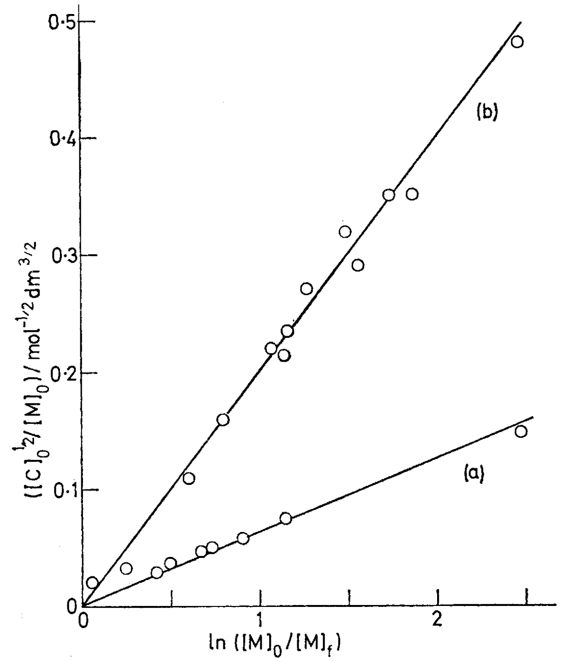


FIGURE 6 Test of equation (10) for (a) isobutyl vinyl ether ($0.107 \leqslant [M]_0 \leqslant 0.268$; $0.12 \leqslant 10^4[C]_0 \leqslant 6.19$) and (b) 2-chloroethyl vinyl ether ($0.041 \leqslant [M]_0 \leqslant 0.092$; $0.97 \leqslant 10^4[C]_0 \leqslant 9.67$). Concentration ranges are in mol dm^{-3}

The reciprocal relationship between $\ln([M]_0/[M]_f)$ and monomer concentration would result if the rate dependence of the termination step was first order in monomer concentration and first order in the concentration of active species. A termination process which would fulfil this requirement is one in which an active cation $SbCl_6^-$ ion-pair reacts with a monomer molecule to give inactive products. Possible reactions are represented by equations (12) and (13). The former would account, at least in part [see also reaction (5)], for the existence of formyl end-groups in products. Reaction (13) would be expected to pass through a transition state or possibly an intermediate state which would resemble an ion-pair of

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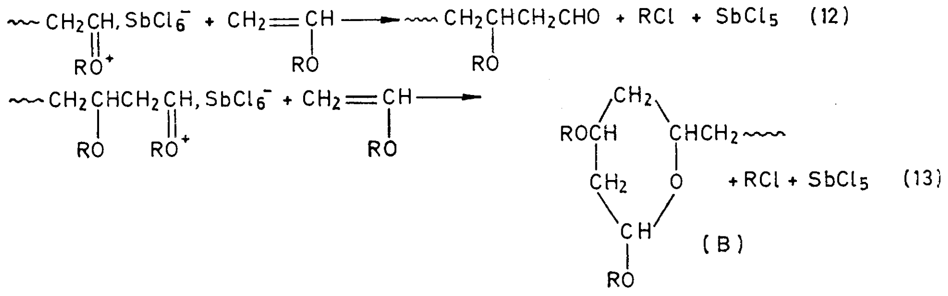
[25] G. J. Blake and D. D. Eley, *J. Chem. Soc.*, 1965, 7412.

[26] J. Sangster and D. Worsfold, *Macromolecules*, 1972, **5**, 229.

[27] E. J. Goethals, *Makromol. Chem.*, 1974, **175**, 1309.

[28] Y. J. Chung, J. M. Rooney, D. R. Squire, and V. Stannett, *Polymer*, 1975, **16**, 527.

the hexachloroantimonate anion and the cyclic oxonium ion[1] which is a precursor of the cyclic ether (B). The decomposition of such an ion-pair to an ether, an alkyl halide, and antimony pentachloride would be entirely consistent with the established decomposition reactions of other oxonium ion salts including hexachloroantimonates.[6,7,29] Analogous termination reactions involving monomer molecules and free active cations may also occur. The R^+ cations formed would be expected to react further with free hexachloroantimonate ions to give RCl and $SbCl_5$.



$$\sim CH_2\underset{RO^+}{\underset{\|}{C}}H,SbCl_6^- + CH_2{=}\underset{RO}{\underset{|}{C}}H \longrightarrow \sim CH_2\underset{RO}{\underset{|}{C}}HCH_2CHO + RCl + SbCl_5 \quad (12)$$

(13)

(B)

Slow Secondary Reaction between Alkyl Vinyl Ethers and Triethyloxonium Hexachloroantimonate.—Consideration of Figure 1a shows that the total loss of vinyl double bonds after *ca.* 12 min reaction time was approximately the same as the fast initial loss for a catalyst solution which had been allowed to undergo spontaneous decomposition for a further 12 min (Figure 1b) before being added to monomer. The rate of loss of vinyl double bonds in the slow reaction between 2-chloroethyl vinyl ether and triethyloxonium hexachloroantimonate was apparently governed by the rate of the spontaneous decomposition reaction of catalyst to antimony pentachloride. The latter undergoes comparatively rapid reaction with the vinyl ether. Despite this conclusion for 2-chloroethyl vinyl ether the results for phenyl vinyl ether and more particularly for isobutyl vinyl ether show that catalysis by triethyloxonium hexachloroantimonate itself must also have contributed to the overall rate of loss of vinyl double bonds in the reacting systems. Thus a set of comparable results for isobutyl vinyl ether to those in Figure 1 showed, for example, that 92% of added monomer had reacted in 12 min following activation 2.5 min after preparation of the catalyst solution. Activation 22.5 min after preparation of the catalyst followed by 2 min reaction with monomer caused the disappearance of only 54% of the added isobutyl vinyl ether. The antimony pentachloride resulting from the decomposition of catalyst was therefore, apparently much less efficient than triethyloxonium hexachloroantimonate in catalysing the reaction of isobutyl vinyl ether. An alternative explanation would be that the ether has a promoting effect on the rates of decomposition of triethyloxonium salts similar to that of diethyl ether.[6] However, isobutyl vinyl ether would have to be considerably more active than diethyl ether in this context if this were to be the correct explanation of the present results.

The initiation reaction involving triethyloxonium ions may be represented by equation (14) which in the

$$Et_3O^+ + CH_2{=}CHOR \longrightarrow EtCH_2CH{=}\overset{+}{O}R + Et_2O \quad (14)$$

presence of hexachloroantimonate anions will be followed by propagation, transfer, and termination reactions analogous to those discussed above in relation to the reactions initiated by antimony pentachloride. There is no obvious reason why the rates of the propagation, transfer, and termination reactions should be significantly altered by the change from one catalyst to the other. However, the rates of the slow secondary reaction involving in part activation by triethyloxonium hexachloroantimonate were considerably less than the rates observed for the fast primary reactions initiated by antimony pentachloride alone. It must be concluded that triethyloxonium hexachloroantimonate is a much less efficient initiator than antimony pentachloride for the generation of the active species in the oligomerization or polymerization reactions of alkyl vinyl ethers.

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[5/1657 *Received, 27th August,* 1975]

[29] H. Meerwein, G. Hinz, P. Hofmann, E. Kroning, and E. P. Pfeil, *J. prakt. Chem.*, 1937, **147**, 257.