





could be derived from tert. oxonium ions, one must conclude from this evidence that the propagating species is a secondary oxonium ion. It follows necessarily that the ring-expansion mechanism is the best representation of the propagation reaction, that tert. oxonium ions do not play an essential role in the polymerisation of DCA by perchloric acid, and that therefore this part of the old controversy appears now to be settled.

There remains the interesting question why in the hands of Firat and Plesch the method gave this result, whereas the workers who devised it found that in their reaction mixtures tert. oxonium ions were dominant.

The answer was found when water was added deliberately to the reaction mixtures before the perchloric acid, a procedure which produced relatively large amounts of ethanol in the polymer hydrolysate.<sup>10</sup> (Table 1). Earlier work of the Keele group had already shown that if water was present in the reaction mixtures before the perchloric acid was added, hydroxyl end-groups were found in the polymer, which also implies the existence of tert. oxonium ions.<sup>8</sup> An examination of the works of the Jaacks group showed that in their reaction mixtures apparently the amount of residual water was such that the formation of relatively large amounts of tert. oxonium ions and of hydroxyl groups, including of course hemiformal hydroxyls, would be expected. Moreover, they found that DXL in the presence of water formed 1,3,5-trioxepan in quantities which were approximately equivalent to the amount of water present, and they suggested a mechanism for this reaction.<sup>5</sup>

Table 1. Formation of tert. oxonium ions and hemiformal groups from DXL ( $1.9 \text{ mol l}^{-1}$ ) in  $\text{CH}_2\text{Cl}_2$  at  $0^\circ\text{C}$  in the presence of  $\text{HClO}_4$  and  $\text{H}_2\text{O}$  (concn. in  $\text{mol l}^{-1}$ )<sup>10</sup>

$10^3[\text{HClO}_4]$	4.64	5.12	4.69	4.86
$10^3[\text{H}_2\text{O}]$	0	1.28	2.40	4.86
$10^3$ ([tert. ox. ions] +[-OCH <sub>2</sub> OH])	<0.1	7.8	8.5	9.0

It follows from these observations that when DCA are polymerised by a protonic acid under "ordinary" conditions (not rigorously dry), the polymerising mixtures contain neutral and protonated rings, rings with chains attached at a tert. oxonium ion, tert. oxonium ions consisting of three linear segments (alkoxy-alkylated chains), protonated chains, and neutral chains. Since each of the chains will have at least one hydroxyl end-group from reactions similar to (2), (3) and (7), the concentration of the chains will be of the same order of magnitude as that of the water, and the propagation is then mainly by tert. oxonium ions. Whether these are alkylated monomer (II) growing by a reaction analogous to (2), or whether they are macrocyclic molecules (V) analogous to (IV) with an oxy-alkyl group in place of the proton, and growing by ring-expansion, will be discussed in the next section.

#### INITIATION BY ORGANIC CATIONS

Perchloric acid which gives polymerisations with a relatively simple behaviour pattern, is unfortunately a little troublesome to prepare as an anhydrous solution in e.g. methylene dichloride,<sup>13</sup> and the very few other strong

acids with anions of sufficiently low nucleophilicity ( $\text{HSO}_3\text{F}$ ,  $\text{HSO}_3\text{CF}_3$ ) also present some technical problems. For this reason by far the greatest number of polymerisation studies have been done with initiators which can either be taken from a bottle, such as borontrifluoride etherate, or which can be prepared relatively easily, such as the various salts of  $\text{Ph}_3\text{C}^+$  or  $\text{Et}_3\text{O}^+$ . Unfortunately most investigators have not realised that the saving in effort which they had hoped to make by using such readily available initiators was largely nullified either because they were not aware how complicated the resulting reactions are and thus analysed their systems and interpreted their results in such a very naive manner that their findings are almost useless; or they realised that they were faced with a tangle of competing and successive reactions which they then attempted to disentangle with much persistence and ingenuity; this produced some interesting new chemistry which, however, has little to do with the actual polymerisations.

An extreme example of chemical naiveness in this field is found in Andrews and Semlyen's attempts to apply the Jacobsen-Stockmayer theory to poly-DXL.<sup>14</sup> They assumed that the reaction product contained significant quantities of linear polymers without attempting to prove this, and they did not attempt to identify the end-groups. Thus they were unable to prove the existence and specify the chemistry of the end-to-end ring-closure reaction, the existence of which is one of the fundamental axioms of the theory which they were attempting to apply.

One of the obvious problems that has arisen from the use of a variety of initiators is whether the nature of the initiator has any influence on the nature of the propagation reaction. It is to be expected that initiators which involve, or from which can be generated, reactive anions such as  $\text{SbCl}_6^-$ , would produce a variety of side-reactions and by-products and generally a very complicated reaction pattern; this has been confirmed amply by the findings of Penczek's group,<sup>15-17</sup> other groups using similar initiators but having a much more naive approach to these systems, remained completely unaware of these complications.

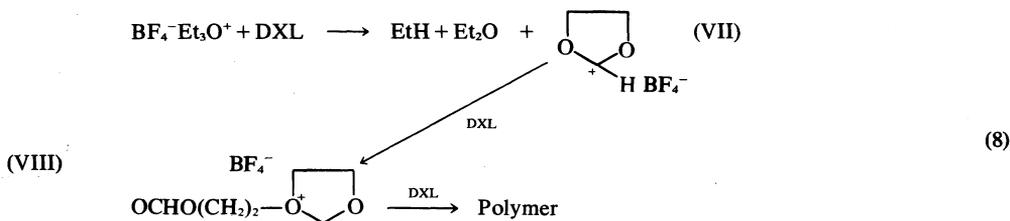
However, even when one simplifies the systems by using initiators with very stable anions, such as  $\text{SbF}_6^-$  or  $\text{ClO}_4^-$ , one must take into account the possibility that initiation by  $\text{Ph}_3\text{C}^+$  or  $\text{Et}^+$  (from  $\text{Et}_3\text{O}^+$ ) or the "dioxolenium" (1,3-dioxolan-2-yl) ion (VII) would produce a species whose growth might proceed by a mechanism different from the ring-expansion of secondary oxonium ions.

It was suggested by Plesch that with organic cations as initiators a tert. oxonium ion would be formed which would grow by ring expansion, just like the ion (I) in reaction (4).<sup>1</sup> What the tert. ion is that is formed from each particular initiator is not always clear, and with some systems at least, more than one type of initiating organic cation may be formed from the ostensible initiator. Meerwein's<sup>18</sup> report that  $\text{Et}_3\text{O}^+\text{BF}_4^-$  reacts with 2-substituted DXL to give ethane<sup>†</sup> was confirmed by Jones and Plesch for DXL and  $\text{Et}_3\text{O}^+\text{BF}_4^-$ , but with  $\text{Et}_3\text{O}^+\text{SbF}_6^-$  and DXL no ethane was formed;<sup>19</sup> the reason for this difference is not known.

This observation implies the formation of the "dioxolenium" ion (VII) which can initiate polymerisation by the intermediacy of the ionic formic ester (VIII). This sequence of reactions is shown in reaction scheme (8).<sup>15</sup>

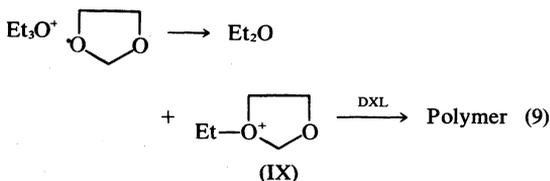
Actually, because of the abnormally low basicity of DXL the second stage of reaction scheme (8), i.e. the

<sup>†</sup>In Ref. 17 Penczek alleges erroneously that Meerwein *et al.*<sup>18</sup> had reported finding no ethane by GLC. On the contrary, Ref. 18 contains the explicit statement that the formation of ethane was confirmed gasometrically. (GLC was not available in 1958.)

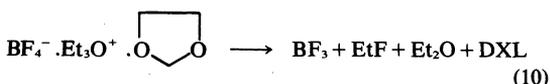


cationation of the DCA to give the ionic formate (VIII), will be slower with DXL than with its oligomers or any other DCA.<sup>17</sup>

Since the formation of ethane upon mixing DXL with a solution of  $\text{Et}_3\text{O}^+\text{BF}_4^-$  was very rapid and then ceased completely, it was suggested<sup>20</sup> that only the  $\text{Et}_3\text{O}^+$  ions which were not paired at the instant of mixing took part in that reaction, and that those which were paired were rendered relatively unreactive by being solvated by the DXL. Subsequently the  $\text{Et}_3\text{O}^+\cdot\text{DXL}$  unit can take part in two reactions, (9) and (10), both of which are probably slow compared to the establishment of the pairing equilibrium. Whilst unpaired, the solvated ion can rearrange itself by transfer of the ethyl cation from ether to DXL, forming the ethylated DXL (IX) which is another type of cationated monomer which can propagate. Even for DXL



which is less basic than diethyl ether, this reaction is promoted by the relatively high concentration of monomer relative to diethyl ether. During the periods in which a solvated ion is paired, it can decompose slowly to boron trifluoride, ethyl fluoride and diethyl ether:



This accounts for the steady formation of ethyl fluoride from triethyl oxonium salts, which is strongly accelerated by DXL.<sup>21</sup>

#### GROWTH MECHANISMS

Irrespective of the nature of the linear fragment which is attached initially to the monomer molecule at the tert. oxonium ion, there are several possibilities for the growth of the polymer.

##### 1. The views of Jaacks and of Plesch

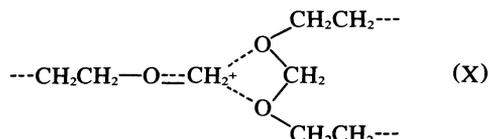
The Jaacks group appears to have held the view that their propagation mechanism (2) is operative, whatever may be the nature of the initiator.

The present author holds the view that since the number of end-groups is always much smaller than the number of polymer molecules, a ring-expansion mechanism, analogous to reaction (4), is the most plausible. This matter will be discussed in section 5 below.

##### 2. Penczek's theory

Penczek<sup>17</sup> has propounded a complicated mechanism

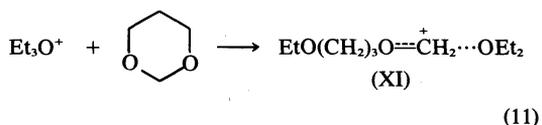
based on a species (X) whose existence depends upon the presence of oligomers or polymers in the reaction mixture:



It was difficult to criticise this concept constructively because no spectroscopic or other characterisation was given by means of which the species (X) could have been recognised. Further, there did not appear to the present author to be anything in Penczek's results that could not be explained without the species (X). However in the course of discussions Penczek explained that the structure (X) represents a tertiary oxonium ion of short lifetime, in which two of the branches consist of alkoxy-methylene groups, and which is in an environment of alkoxy-methylene groups, so that by the making and breaking of formal  $\text{CH}_2\text{---O}$  bonds the location of the charge can change rapidly.

##### 3. Okada's theory

Okada *et al.*<sup>22</sup> used the unpolymerisable 1,3-dioxane as a model compound and let it react with  $\text{Et}_3\text{O}^+\text{BF}_4^-$  in  $\text{CH}_2\text{Cl}_2$  at 21°C for 24 hr. On the basis of the 1 H NMR spectrum of the resulting reaction mixture and its variation with time and temperature, and other evidence, they suggested that the oxycarbenium ion (XI), solvated by diethyl ether (from the  $\text{Et}_3\text{O}^+$ ), is the propagating species:

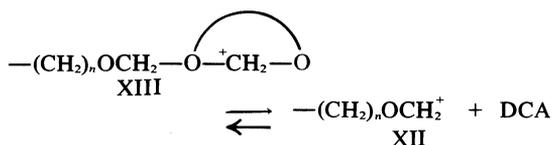


The validity of this conclusion is dubious because the products formed from a DCA in the presence of the very high concentrations of  $\text{Et}_3\text{O}^+\text{BF}_4^-$  used in this work during 24 hr probably comprise several compounds in considerable concentrations, which have nothing to do with the polymerisation; the work of Jones and Plesch on the decomposition of  $\text{Et}_3\text{O}^+\text{BF}_4^-$  and on the conductance changes in solutions containing DXL and that initiator, provide strong evidence for that.<sup>21</sup> Second, there is no explanation of how species (XI) differs from a conventional tert. oxonium ion, but Okada and his co-workers maintain that their 1 H NMR spectra are not compatible with the existence of an appreciable concentration of tert. oxonium ions. For these reasons we conclude that Okada's evidence for the oxycarbenium ion as an essential and principal reagent remains unconvincing.

#### 4. The status of the oxycarbenium ion

The oxy-carbenium ion was the first concept in terms of which the polymerisation of DXL was interpreted by Yamashita and Okada and they quite logically adopted and adapted it from the theories of Kern and Jaacks about the polymerisation of 1,3,5-trioxan. It was subsequently favoured by many other authors in the context of DCA polymerisations. There appears to be no need at present to re-examine the theory of the trioxan polymerisation and it is necessary to mention that the following critique of the oxycarbenium theory as applied to the polymerisation of DCA does not necessarily apply to trioxan, because both the nature of the monomer and the polymerisation conditions are generally very different from those of the DCA.

The bare oxycarbenium ion  $-(CH_2)_nOCH_2^+(n \geq 2)$  (XII) is relatively small and therefore has a high charge-density. It follows that if it is placed in an environment containing basic atoms, such as a solution of a DCA, in a solvent of moderate polarity such as methylene dichloride, it will stabilise itself by reacting with the most basic site available and in the example given it will form a tert. oxonium ion (XIII) with the DCA, in which the charge density is less than in the original ion. One can now adopt a variety of views as to the nature of the resulting species. For instance, one can regard the DCA as being the primary solvator of the oxycarbenium ion and since all such solvations are equilibria, at least in principle, one can conclude that there must be a small but finite concentration of unsolvated oxy-carbenium ions (XII):



Or one can say that even if the equilibrium constant for the above reaction is negligibly small, the unsolvated oxycarbenium ion (XII) is a part of a relatively unimportant canonical form of the tert. oxonium ion, which implies a certain probability that the oxycarbenium ion may react as such by detaching itself from the ether and finding some other basic site. The important point, however, is that under the normal conditions under which DCA are polymerised the attempts to distinguish experimentally between oxycarbenium ions and tert. oxonium

ions as the active species appear at present to be quite pointless.

The situation would be completely different for oxycarbenium ions in a highly polar solvent such as sulphur dioxide which could compete effectively as solvating agent with the DCA and their polymers. In such systems one could envisage that both the solvent-solvated oxycarbenium ions and also the solvent-solvated tert. oxonium ions could co-exist in a true equilibrium, and that each would react according to its own characteristics. This is an area which remains very largely unexplored, although Penczek has made a start in this direction and these considerations arose from discussions with him of his exploratory experiments with sulphur dioxide as solvent.

#### 5. The nature of the propagation by tert. oxonium ions

Thus, when one looks sufficiently critically at the ideas currently under discussion one finds that there appears to be no good reason for discarding the conventional tert. oxonium ion as the propagating species, and that the only clearly identifiable problem is whether propagation through these conventional tert. oxonium ions goes by the Jaacks mechanism or by the ring-expansion mechanism. This is a difficult matter to resolve experimentally because the direct discrimination between the "microcyclic" ions (II), (VIII), and (IX) on the one hand and the macrocyclic ion (V) on the other, requires subtle and sensitive techniques.

Fortunately, there is evidence of a quite different kind available which at least provides a strong indication as to which mechanism is the more probable. In Table 2 are summarised the entropies of reaction ( $\Delta S_{rs}^\circ$ ) and activation ( $\Delta S^\ddagger$ ) for the polymerisations of DXL, DXP, and THF. Four features are immediately evident: (1) The  $\Delta S^\ddagger$  is about the same for DXL and DXP initiated by perchloric acid; (2) the  $\Delta S^\ddagger$  for DXL is about the same for initiation by perchloric acid and by (VII); (3) the  $\Delta S^\ddagger$  for DXL and DXP are much more negative than for THF; and (4) for DXL and DXP the  $\Delta S^\ddagger$  are considerably more negative than the corresponding  $\Delta S_{rs}^\circ$ .

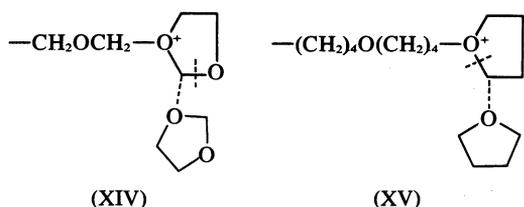
This means (i) that for the DCA the loss of degrees-of-freedom in the transition state is much greater than that due to the incorporation of the monomers into the polymer, and (ii) that the propagation mechanism for reactions started by the two types of initiator are likely to be very similar. It has been shown that in reactions in which perchloric acid is the initiator, the ring-expansion

Table 2. Entropies of reaction ( $\Delta S_{rs}^\circ$ ) and activation ( $\Delta S^\ddagger$ ) for polymerisation of DXL, DXP, and THF in cal deg<sup>-1</sup> mol<sup>-1</sup> (rounded to nearest whole number)

Monomer	Initiator	Initiator				Various
		HClO <sub>4</sub>		Et <sub>3</sub> O <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	AlEt <sub>3</sub> + H <sub>2</sub> O + epoxide	
DXL	$-\Delta S_{rs}^\circ$	19				
	$-\Delta S^\ddagger$	34	35			
	Ref	8 32	17			
DXP	$-\Delta S_{rs}^\circ$	12				
	$-\Delta S^\ddagger$	30				
	Ref	9 32				
THF	$-\Delta S_{rs}^\circ$			21		17-19
	$-\Delta S^\ddagger$			23	25	
	Ref			30	31	Various

mechanism is operative, for which the transition state can probably be represented most realistically as a four-centred structure (III) in which the monomer is tied down very firmly.

In the propagation by the Jaacks mechanism the transition state (XIV) would resemble closely that in the polymerisation of cyclic ethers, such as THF; for this the transition state is (XV) which is evidently very similar to



(XIV). It is reasonable to suppose that the  $\Delta S^\ddagger$  corresponding to (XIV) would have a value close to that for (XV); however, the  $\Delta S^\ddagger$  for (XV) shown in Table 2 is much less negative than that for the polymerisation of DXL by (VII). It is evident therefore that whatever may be the growth mechanism when initiation is by organic cations, it is very unlikely to involve the microcyclic tert. oxonium ion growth centre of Jaacks. Thus all the evidence taken together indicates that in the polymerisation of DXL by organic cations the propagating centre is also a macrocyclic tert. oxonium ion growing by ring expansion, like in the reactions initiated by protons.<sup>†</sup>

As far as the polymerisations of DCA other than DXL by non-protonic initiators are concerned, Kops and Spanggaard<sup>11</sup> favour the ring expansion mechanism for the dimerisation and polymerisation of the *cis*- and *trans*-7,9-dioxabicyclo[4.3.0] nonanes by phosphorus pentafluoride or triethyloxonium hexachloroantimonate, although they have not obtained any definitive evidence for it.

On the other hand, Wegner's studies<sup>23</sup> provide very strong evidence that polyoxymethylene crystals in contact with monomer and  $\text{BF}_3\text{Et}_2\text{O}$  also grow by a ring expansion reaction which is completely analogous to that proposed for DXL and 1,3-dioxepan.<sup>8,9</sup> It is not unlikely that this reaction also occurs in the solution polymerisation of trioxan simultaneously with the oxycarbenium ion propagation of Kern and Jaacks, and that it provides at least some of the cyclic oligomers which are found in these reaction mixtures.

#### DIFFERENCES BETWEEN DCA AND CYCLIC ETHERS

Two further pieces of well-known evidence need to be put into perspective, so that their bearing on the

<sup>†</sup>It was pointed out in discussion at Jablonna that our deductions from  $\Delta S^\ddagger$  values are hazardous for at least three reasons: (1) They require a knowledge of  $k_p$  values for at least two temperatures, and this is not easy to obtain; (2) The  $\Delta\Delta S^\ddagger$  for the two mechanisms should be of the order of magnitude of the rotational entropy, but is in fact appreciably greater; (3) The  $\Delta S^\ddagger$  is strongly affected by the solvation of the initial and transition states, and because of the differences in charge-density between the initial and transition states for the two monomers, considerable differences in  $\Delta S^\ddagger$  could arise from this source. Nonetheless, it seems to us that the close similarities of the three  $\Delta S^\ddagger$  values for the DCA on the one hand, and of the two  $\Delta S^\ddagger$  values for THF on the other, are unlikely to be coincidences, and that therefore these  $\Delta S^\ddagger$  values, if used with adequate circumspection, can provide some pertinent evidence.

mechanistic problem may become clearer. One of these is the fact that under cationic polymerisation conditions cyclic ethers do not copolymerise with olefins, but that at best a mixture of homopolymers may be obtained. On the other hand, copolymerisations between DCA and olefins have been reported,<sup>24-27</sup> and an acid catalysed insertion of olefins into DCA occurs quite readily whereby the DCA are converted into cyclic ethers.<sup>28</sup>

The second concerns the copolymerisation of the two categories of compounds. However, the amount of evidence available is so great and much of it is so conflicting, that it is very difficult to interpret. The main trouble is that many results are of very dubious validity. One of the principal difficulties in this field is that few workers have recorded the DP of the alleged copolymers, but some have shown that in systems of this type the DP may be so low that end-effects (initial or terminal groups) may simulate copolymerisation when in fact only homopolymers, but with ends derived from the co-monomer, were obtained. It will suffice here to say that the evidence for the formation of true random copolymers from DCA and cyclic ethers looks, to say the least, rather unconvincing. This view is strongly supported by the findings of Leonard and his coworkers. They reported that the equilibrium concentrations of DXL and THF in reaction mixtures containing the polymers and initiated by  $\text{Et}_3\text{O}^+\text{PF}_6^-$  were such as were to be expected if no copolymerisation occurred, and they concluded that there are two concurrent homopolymerisations.<sup>29</sup>

All this evidence taken together indicates very strongly that the two types of monomers polymerise by different mechanisms. Whilst this conclusion does not necessarily support the ring-expansion mechanism for the DCA, it makes the propagation via the microcyclic tert. oxonium ion (XIV) appear very unlikely.

#### CONCLUSION

The field which I have surveyed has become obscured by a vast amount of experimental results of very uneven reliability, by excessive concentration on too few monomers and solvents, by a multiplication of interpretative theories lacking in precision and therefore untestable. Although it is impossible to say with confidence that all the phenomena encountered in these polymerisations can be explained in terms of conventional sec. and tert. oxonium ions as propagating species, I hope that I have shown that there does not appear to be a convincing need at present to add to these categories.

What we require now in order to consolidate our understanding is more work with a variety of monomers and solvents, with the simplest possible initiator systems, aimed at obtaining the maximum amount of information on the polymerisations (rates, equilibria, conductivities, constituents of the reaction mixtures before and after neutralisation) and on the polymers (existence, nature and concentration of end-groups, DP distributions). There are unfortunately still too many who think they can base a valid theory on the determination of only one or two features of a polymerisation system.

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