SOME ASPECTS OF THE POLYMERISATION
OF 1,3-DIOXACYCLOALKANES

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Abstract—This paper is concerned with the evaluation of old and new evidence concerning the mechanism of polymerisation of 1,3-dioxacycloalkanes (DCA). The most recent evidence on polymerisations initiated by perchloric acid shows that in strictly anhydrous systems the propagating species is a sec. oxonium ion, so that under these conditions the propagation must be by the ring-expansion mechanism. In the presence of water, tert. oxonium ions are formed. A comparison of the polymerisation behaviour of DCA and tetrahydrofuran (THF) leads to the conclusion that the propagation mechanisms must be different. By comparing the activation entropy of DCA polymerisations initiated by organic cations on the one hand with that of DCA polymerisations initiated by perchloric acid, and on the other with that of the polymerisation of THF, it appears that the polymerisations of DCA initiated by organic cations are most probably also propagated by the ring-expansion mechanism.

Some mechanistic suggestions by Penczek and by Okada are scrutinized and the status of the oxy-carbenium ion as a propagating species is analysed.

INTRODUCTION

Our knowledge of the polymerisation of 1,3-dioxacycloalkanes (DCA) is still rather incomplete. In this paper I will point out some of those areas which now appear to be well understood and to discuss others where clarification is required. Since I did something similar in 1969, the present review can be regarded as a sequel and a progress report.[1]† As I had the privilege of revising my paper after the Jablonna Microsymposium at which it was presented, I have taken the opportunity of including some matters which arose during our discussions there.

INITIATION BY PROTONIC ACIDS

The generality of this title is misleading, since a worthwhile amount of information is only available for perchloric acid. The mechanism of the initiation and propagation in the polymerisation of DCA, especially 1,3-dioxolan (DXL), has been discussed many times,[1–7] and the origin and nature of the differences of opinion on these subjects need not be explained here at length. The most important facts can be summarised as follows.

When DCA are polymerised under anhydrous conditions by perchloric acid, no end-groups are detectable by a variety of analytical methods, except traces of OH groups. The more rigorous the drying of monomer, solvent and apparatus, and of the reagent used for neutralising the reaction mixtures, the smaller is the concentration of OH groups and this is always much smaller than the concentration of polymer molecules;[8–10] most workers are therefore agreed that the greater part of these are cyclic.[11] It has also been found that under clean, dry

†Because of their anomalous behaviour 1,3,5-trioxan and higher polymers of formaldehyde are excluded from the present discussion, unless they are mentioned specifically.

conditions the polymerisations are strictly reversible and that even after many polymerisation-depolymerisation cycles the depolymerised reaction mixtures contain no degradation products, but only solvent, monomer, and acid.

The mechanisms which have been proposed for this polymerisation by perchloric acid include the Mainz mechanism due to Jaacks and his school and the Keele mechanism due to Plesch and Westermann. Although both these have been described many times, it is worth restating them here, because even now some experienced workers appear not to understand the essential points of the controversy; this was evident again during the discussions at the Jablonna Microsymposium. The Mainz theory envisages the initiation as a two-step process in which protonation of the monomer (eqn 1) to give the secondary oxonium ion (I) is followed by reaction of the resulting ion with another monomer molecule to give the tert. oxonium ion (II):

$$HClO_4 + \overset{\frown}{OCH_2O} \longrightarrow H\overset{\frown}{O}CH_2\overset{+}{O} \quad ClO_4^- \qquad (1)$$
$$\text{(DCA)} \qquad \text{(I)}$$

$$HO-CH_2-\overset{+}{O} + \overset{\frown}{O}-CH_2-\overset{\frown}{O} \rightleftharpoons HO---OCH_2\overset{+}{O}-CH_2-O$$
$$\text{(II)}$$

$$(2)$$

According to this view the macrocyclic molecules found in the reaction product are formed by a back-biting reaction (3) in which the formal CH_2 group adjacent to the tert. oxonium ion reacts with an oxygen atom along the chain, generating a macrocyclic tert. oxonium ion:

$$HClO_4 + n\,\square + \longrightarrow H[O(CH_2)_2OCH_2]_{n-1} - \square\; ClO_4^-$$

$$H[O(CH_2)_2OCH_2]_{n-2} - O-(CH_2)_2-O-CH_2 \cdots \longrightarrow H[O(CH_2)_2OCH_2]_{n-2} - \overset{+}{O}-(CH_2)_2O\overset{|}{C}H_2 \qquad (3)$$
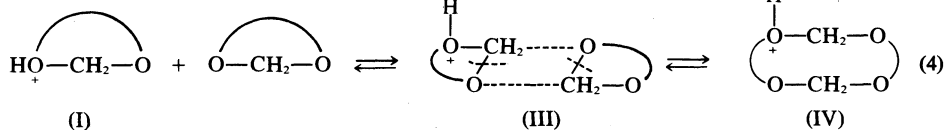
It is not difficult to show by conductance measurements that when the polymerisation of dioxolan becomes of first order, roughly at the first half-life, all the available acid has reacted with monomer or oligomer to produce active centres.[10] Thus on the Mainz theory one would expect to find a number of OH groups of the same order of magnitude as the number of perchloric acid molecules introduced; this is evidently not so, as long as the water concentration in the system is significantly less than that of the acid.[10] For 1,3-dioxepan the protonation is very much faster than for DXL and is complete long before the first half-life of the polymerisation.

According to the Keele theory the primary reaction between the perchloric acid and the monomer is also (1), but thereafter the growth is by a ring-expansion reaction (4) in which no free end is ever formed; this goes by way of a four-centred transition state and gives the cyclic product (IV):

In the standard procedure the neutralised polymer is purified and hydrolysed and the hydrolysate is examined for ethanol. The absence of ethanol indicates that no tert. oxonium ions containing a polymeric moiety and no polymeric oxycarbenium ions could have been present in the reaction mixture.

The presence of the ethanol in the hydrolysate, however, signifies not only the existence of tert. oxonium ions in the reaction mixtures but also the presence of hemiformal groups as will be shown below: The DCA and their oligomers can react with small quantities of water in the presence of acid to give diols (strictly, hemiformal-ω-ols) which react with ethoxide ions as shown in scheme (7):

$$\text{(7)}$$

$$\text{(4)}$$

It is evident that the main difference between the two theories is that according to the Mainz theory the propagating species is a tertiary oxonium ion, whereas according to the Keele theory it is a secondary one. A simple and useful method of distinguishing between secondary and tertiary oxonium ions is due to Jaacks's group and consists of neutralising the reaction mixture with an alkoxide.[12] Details of the method have been described, but it is worthwhile repeating here exactly what it shows. If EtO$^-$ is added to a reaction mixture containing secondary oxonium ions, whatever their structure may be, it abstracts the proton, forms ethanol, and leaves the oxygen compound:

$$\text{EtO}^- + \text{HOR}_2^+ \longrightarrow \text{EtOH} + \text{R}_2\text{O} \qquad (5)$$

Thus, whatever the nature of R$_2$O, it does not contain an ethoxyl group.

If the reaction mixture contains tert. oxonium ions (V) (reactions 6a, b), or oxycarbenium ions (VI) (reaction 6c), or any other oxygen-containing cations which are stoichiometrically equivalent to these (see e.g. (X) and (XI) below), the ethoxide ions combine with them and are thus incorporated in the polymer:

Upon hydrolysis of the product or of the analogous compounds formed from DCA oligomers, only the ethyl group attached to the formal group is released as ethanol. Thus the presence of ethanol in the hydrolysate signals the presence both of tertiary oxonium ions *and* of hemiformal hydroxyls. Evidently the number of tert. oxonium ions cannot exceed the number of anions in the system, i.e. the acid concentration, but there is no obvious limit to the number of hemiformal hydroxyls formed from adventitious or deliberately added water. Thus, if one were to interpret the analytical results by equating the number of mols of ethanol with the number of tert. oxonium ions, one could arrive at the absurd result that this number is greater than the number of anions in the polymerising system.†

The method of Jaacks and his co-workers was used by Firat and Plesch to study the nature of the cations present when DXL, 4-methyl-DXL, and 1,3-dioxepan (DXP) were polymerised by anhydrous perchloric acid in methylene dichloride. They showed that when these polymerisations are done under the most rigorously dry conditions, the concentration of tert. oxonium ions in the polymerising mixtures is at most close to the limit of detection and much less than the original concentration of perchloric

$$\text{R}' = \text{HO(CH}_2)_2[\text{OCH}_2\text{O(CH}_2)_2]_n\text{---}, \quad \text{R}^3 = \text{R}'\text{OCH}_2$$

†This mistake was made in Table 1 of Ref. 10 where the column [tert. ox. ion] should be labelled [tert. ox. ion]+[-COH$_2$OH]; this matter arose during discussion at the Jablonna Microsymposium.

acid and the concentration of ions in the polymerising solution.

Since most types of experimental inadequacy or incompetence produce more ethanol in the hydrolysate than

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.[10] (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.[8] 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.[5]

Table 1. Formation of tert. oxonium ions and hemiformal groups from DXL ($1.9 \, \mathrm{mol \, l^{-1}}$) in CH_2Cl_2 at 0°C in the presence of $HClO_4$ and H_2O (concns. in $\mathrm{mol \, l^{-1}}$)[10]

$10^3[HClO_4]$	4.64	5.12	4.69	4.86
$10^3[H_2O]$	0	1.28	2.40	4.86
10^3([tert. ox. ions] +[-OCH$_2$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,[13] and the very few other strong

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†In Ref. 17 Penczek alleges erroneously that Meerwein et al.[18] 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.)

acids with anions of sufficiently low nucleophilicity (HSO_3F, HSO_3CF_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 Ph_3C^+ or Et_3O^+. 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 intepreted 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.[14] 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 $SbCl_6^-$, 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;[15–17] other groups using similar initiators but having a much more naive approach to these systems, remained completely unaware of these complications.
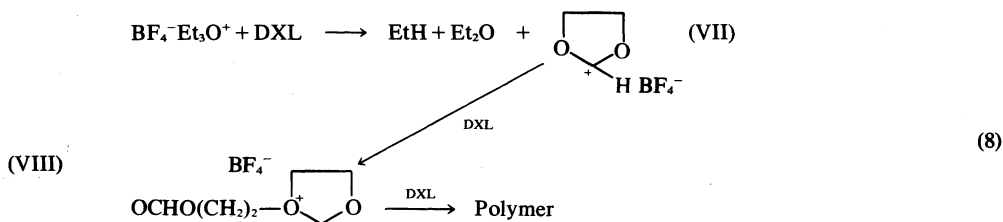
However, even when one simplifies the systems by using initiators with very stable anions, such as SbF_6^- or ClO_4^-, one must take into account the possibility that initiation by Ph_3C^+ or Et^+ (from Et_3O^+) or the "dioxolenium" (1,3-dioxolan-2-ylium) ion (VII) would produce a species whose growth 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).[1] 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[18] report that $Et_3O^+BF_4^-$ reacts with 2-substituted DXL to give ethane† was confirmed by Jones and Plesch for DXL and $Et_3O^+BF_4^-$, but with $Et_3O^+SbF_6^-$ and DXL no ethane was formed; [19] 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).[15]

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

$$BF_4^-Et_3O^+ + DXL \longrightarrow EtH + Et_2O + \quad (VII)$$

(8)

$$(VIII) \quad BF_4^-$$

$$OCHO(CH_2)_2-O^+ \underset{O}{\overset{DXL}{\longrightarrow}} \text{Polymer}$$

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

Since the formation of ethane upon mixing DXL with a solution of $Et_3O^+BF_4^-$ was very rapid and then ceased completely, it was suggested[20] that only the Et_3O^+ 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 $Et_3O^+ \cdot DXL$ 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

$$Et_3O^+ \underset{O}{\overset{O}{\longrightarrow}} Et_2O$$

$$+ \quad Et-O^+ \underset{O}{\overset{DXL}{\longrightarrow}} \text{Polymer} \quad (9)$$

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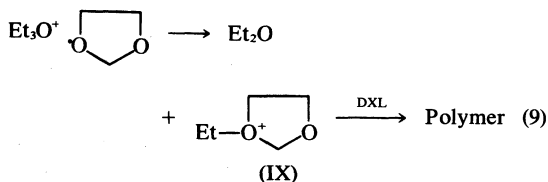
which is less basic than diethyl ether, this reaction is promoted by the relatively high concentration of monomer relative to diethyl ether. During the periods in which a solvated ion is paired, it can decompose slowly to boron trifluoride, ethyl fluoride and diethyl ether:

$$BF_4^- \cdot Et_3O^+ \cdot O \underset{O}{\overset{}{\longrightarrow}} BF_3 + EtF + Et_2O + DXL$$

(10)
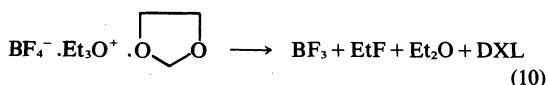
This accounts for the steady formation of ethyl fluoride from triethyl oxonium salts, which is strongly accelerated by DXL.[21]

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[17] has propounded a complicated mechanism

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

$$---CH_2CH_2-O \underset{CH_2}{\overset{CH_2CH_2---}{\underset{O}{\overset{O}{\cdots}}}} \quad (X)$$
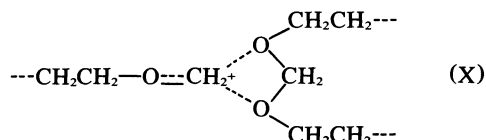
It was difficult to criticise this concept constructively because no spectroscopic or other characterisation was given by means of which the species (X) could have been recognised. Further, there did not appear to the present author to be anything in Penczek's results that could not be explained without 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 alkoxymethylene groups, and which is in an environment of alkoxymethylene groups, so that by the making and breaking of formal CH_2-O bonds the location of the charge can change rapidly.

3. Okada's theory

Okada et al.[22] used the unpolymerisable 1,3-dioxan as a model compound and let it react with $Et_3O^+BF_4^-$ in CH_2Cl_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 Et_3O^+), is the propagating species:

$$Et_3O^+ + \underset{O}{\overset{O}{\longrightarrow}} EtO(CH_2)_3O \overset{+}{=} CH_2 \cdots OEt_2$$

(XI)

(11)
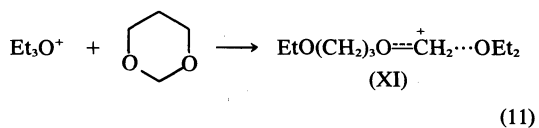
The validity of this conclusion is dubious because the products formed from a DCA in the presence of the very high concentrations of $Et_3O^+BF_4^-$ used in this work during 24 hr probably comprise several compounds in considerable concentrations, which have nothing to do with the polymerisation; the work of Jones and Plesch on the decomposition of $Et_3O^+BF_4^-$ and on the conductance changes in solutions containing DXL and that initiator, provide strong evidence for that.[21] 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 $-(CH_2)_n OCH_2^+ (n \geqslant 2)$ (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):

$$-(CH_2)_n OCH_2 - O - \overset{+}{C}H_2 - O$$
$$XIII$$
$$\rightleftharpoons -(CH_2)_n OCH_2^+ + DCA$$
$$XII$$
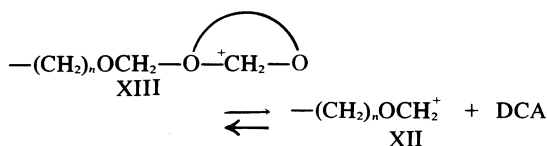
Or one can say that even if the equilibrium constant for the above reaction is negligibly small, the unsolvated oxycarbenium ion (XII) is a part of a relatively unimportant canonical form of the tert. oxonium ion, which implies a certain probability that the oxycarbenium ion may react as such by detaching 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.
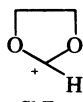
5. The nature of the propagation by tert. oxonium ions

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 (ΔS_{ss}^0) and activation $(\Delta S\dagger)$ for the polymerisations of DXL, DXP, and THF. Four features are immediately evident: (1) The $\Delta S\dagger$ is about the same for DXL and DXP initiated by perchloric acid; (2) the $\Delta S\dagger$ for DXL is about the same for initiation by perchloric acid and by (VII); (3) the $\Delta S\dagger$ for DXL and DXP are much more negative than for THF; and (4) for DXL and DXP the $\Delta S\dagger$ are considerably more negative than the corresponding ΔS_{ss}^0.

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 (ΔS_{ss}^0) and activation $(\Delta S\dagger)$ for polymerisation of DXL, DXP, and THF in cal deg^{-1} mol^{-1} (rounded to nearest whole number)

Monomer	Initiator	HClO$_4$	$\overset{+}{}$H SbF$_6^-$	Et$_3$O$^+$ BF$_4^-$	AlEt$_3$+H$_2$O + epoxide	Various
DXL	$-\Delta S_{ss}^0$	19				
	$-\Delta S\dagger$	34	35			
	Ref	8 32	17			
DXP	$-\Delta S_{ss}^0$	12				
	$-\Delta S\dagger$	30				
	Ref	9 32				
THF	$-\Delta S_{ss}^0$		21			17–19
	$-\Delta S\dagger$		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)   (XV)
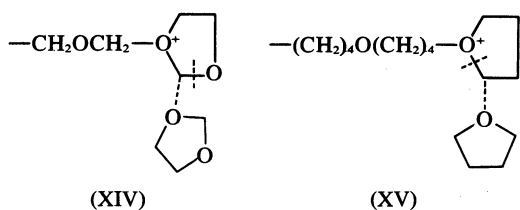
(XIV). It is reasonable to suppose that the $\Delta S\dagger$ corresponding to (XIV) would have a value close to that for (XV); however, the $\Delta S\dagger$ for (XV) shown in Table 2 is much less negative than that for the polymerisation of DXL by (VII). It is evident therefore that whatever may be 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.$\dagger$

As far as the polymerisations of DCA other than DXL by non-protonic initiators are concerned, Kops and Spanggaard[11] 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[23] provide very strong evidence that polyoxymethylene crystals in contact with monomer and BF_3Et_2O also grow by a ring expansion reaction which is completely analogous to that proposed for DXL and 1,3-dioxepan.[8,9] 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

$\dagger$It was pointed out in discussion at Jablonna that our deductions from $\Delta S\dagger$ 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 $\Delta\Delta S\dagger$ for the two mechanisms should be of the order of magnitude of the rotational entropy, but is in fact appreciably greater; (3) The $\Delta S\dagger$ 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 $\Delta S\dagger$ could arise from this source. Nonetheless, it seems to us that the close similarities of the three $\Delta S\dagger$ values for the DCA on the one hand, and of the two $\Delta S\dagger$ values for THF on the other, are unlikely to be coincidences, and that therefore these $\Delta S\dagger$ 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,[24-27] and an acid catalysed insertion of olefins into DCA occurs quite readily whereby the DCA are converted into cyclic ethers.[28]

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 $Et_3O^+PF_6^-$ were such as were to be expected if no copolymerisation occurred, and they concluded that there are two concurrent homopolymerisations.[29]

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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