The Polymerisation of Cyclic Formals by Triethyloxonium Tetrafluoroborate

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Summary In the polymerisation of 1,3-dioxolan by $Et_3O^+BF_4^-$ the formation of active centres (which are *stable* when formed) is slow, and it is accompanied by competitive hydride abstraction from monomer and decomposition of the catalyst.

TRIETHYLOXONIUM TETRAFLUOROBORATE (I) and other triethyloxonium salts have been used extensively for the polymerisation of oxygen compounds, including alkyl vinyl and cyclic ethers, and cyclic formals. We report here preliminary findings concerning the polymerisation of 1,3-dioxolan (II) and 1,3-dioxepan (III), mainly by (I), in methylene dichloride solution under vacuum conditions with apparatus free from greased taps and joints. The monomers were prepared and purified as described;[1,2] (I) was prepared by Meerwein's method[3] on a vacuum line and distributed into phials by standard methods.[4,5] Kinetic measurements were made in a dilatometer, fitted with platinum electrodes for conductivity measurements.[6]

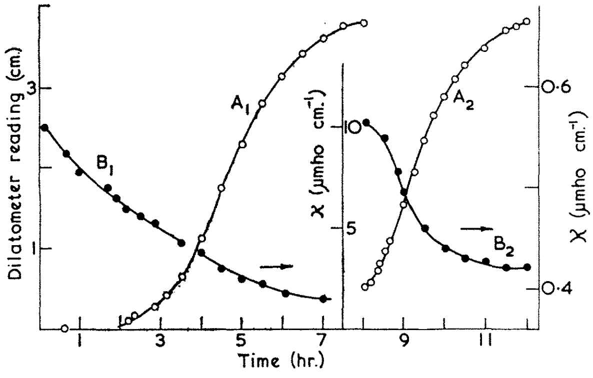


FIGURE. *Polymerisation and re-polymerisation of dioxolan.* [*Dioxolan*] = 3M, [*triethyloxonium tetrafluoroborate*] = 10^{-3}M. A_1, A_2 *Dilatometer readings*; B_1, B_2 *specific conductance. Note different scales for* B_1 *and* B_2.

The reaction pattern is shown in the Figure, in which A_1 is the first conversion curve and B_1 is the corresponding plot of the specific conductivity (κ). As soon as (I) was introduced into the solution of (II), there was a very sharp rise in κ, which then fell steadily. Polymerisation, however, did not start until about 2 hr. later; it accelerated and then became of first order, whilst κ continued to fall; it became constant at a very low value after about 21 hr.

Thereafter the reaction mixture was depolymerised by warming it to 40°, and it was then brought back to 25°. Depolymerisation had raised κ from 0·42 μmho cm.$^{-1}$ at the end of the first polymerisation to 0·57 μmho cm.$^{-1}$ (25°) at the start of the second (curve A_2 and B_2). This started without any induction period, the acceleration phase was much shorter than in the first reaction, and the first-order phase was correspondingly longer; during the second reaction κ fell back to 0·42 μmho cm.$^{-1}$. This cycle of operations could be repeated many times and each time the pattern was the same as that of the second reaction. The first-order rate constant (k_1) was always the same and identical with that for the first reaction. The value of k_1 depends rectilinearly on the concentration, c, of (I), such that $k_1/c = 10$ l.mole^{-1}min.$^{-1}$ at 25°; for catalysis by perchloric acid (no induction period, but acceleration phase followed by a first-order phase[7]) $k_1/c = 1{\cdot}26 \times 10^3$ l.mole^{-1}min.$^{-1}$ at 25°.

With (III) and (I) the behaviour pattern is the same as that of (II), whereas perchloric acid polymerises (III) without an acceleration phase.[2]

When (II) was polymerised by triethyloxonium hexafluoroantimonate (IV), k_1/c was of the same order of magnitude as for perchloric acid.

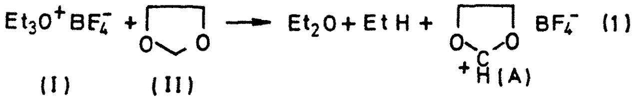
In reaction mixtures of (I) and (II) ethane and ethyl fluoride were identified by g.l.c., the concentration of the former reaching its maximum constant value very rapidly, whereas the concentration of the latter continued to rise as long as κ was falling. In the polymerisation of (II) by (IV) neither ethane nor ethyl fluoride was detectable.

Boron trifluoride etherate polymerised (II) very much more slowly (at the same concentrations) than (I).

The polymers obtained from (II) and (III) by (I) or (IV), like those obtained with perchloric acid, appear to have no end-groups and must therefore be cyclic.[1,2]

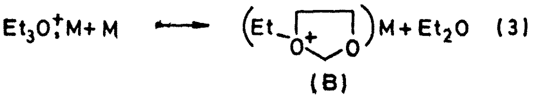
These observations have the following significance: (i) In the polymerisation of (II) by (I) most or all of the ions present initially in the reaction mixture are not concerned in the polymerisation. (ii) These ions decay to nonconducting products. (iii) The initiating species is formed slowly and its concentration reaches a maximum, constant value, which is unaffected through several polymerisation–depolymerisation cycles. (iv) The concentration of propagating ions is much lower than that of the ions present initially. (v) The course of the reactions between (II) and a triethyloxonium salt depends critically upon the nature of the anion [different behaviour of (I) and (IV)]. (vi) Polymerisation appears to occur by the ring-expansion mechanism.

It follows that when (I) is introduced into a solution of (II) there are at least two concurrent reactions. Reaction (1) is a fast hydride abstraction from (II):



Reaction (2) is a slow decomposition of (I) to ethyl fluoride, diethyl ether, and boron trifluoride; our study of this reaction is the subject of the following Communication. However, reaction (2) must be preceded by some process which competes with reaction (1) (which would otherwise go to completion) and which changes the reactivity of the triethyloxonium ion so that it cannot undergo reaction (1), but can take part in (2). The most plausible such reaction is solvation of the triethyloxonium ion by (II), because conductivity studies have given us direct evidence for it; the ion-pairs and triple ions, and probably also the tetrafluoroborate ion, will also be solvated by (II).

Neither reaction (1) nor reaction (2) leads directly to polymerisation, and the nature of the initiation reaction is still obscure. Initiation could be by the ethylation reaction (3), where M represents (II):



The ethylated dioxolan would then react with more monomer to give polymer in the same way as the protonated dioxolan. We also have some evidence that the dioxolenium salt (A) may be able to initiate polymerisation, though very slowly and inefficiently.

The initiation by (I) is certainly not the simple, unambiguous reaction which Yamashita believes it to be;[8] the salt (IV), on the other hand, appears to react rapidly and cleanly to give a high yield of growing centres which we believe to be ethylated dioxolan (B).

Yamashita and co-workers have reported a detailed study of the polymerisation of (II) by (I) in methylene dichloride,[8] and their observations agree well with ours. However, they calculated a second-order rate constant from the maximum rate and identified it with k_{p}, assuming that the concentration of growing chains was equal to c; our work shows clearly that this procedure is invalid and that their k_{p} values are therefore erroneous.

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