OLIGOMERISATION OF METHYLOXIRANE INITIATED BY $(C_6H_5)_3C^+AsF_6^-$, $(C_6H_5)_3C^+SbCl_6^-$ AND $SbCl_5$

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Reactions of methyloxirane with the title compounds lead to the formation of a mixture of cyclic and linear oligomers with average polymerisation degree ranging from 5 to 10. The oligomers are formed by combination of back-bitting reaction with re-initiaiton of the transiently desactivated reaction centers followed by monomer transfer. The important role which these reactions play in the overall oligomerisation of methyloxirane is due to the fact that in addition to active centres with the structure of oxonium ions, also carbenium active centres participate significantly in the reaction. In the systems with stable pair anions AsF_6^-, the irreversible termination of active centres does not take place, in contrast to the latter systems. This termination involves the reaction of the cation of active centre with the pair anion which releases one ligand during this interaction. The results obtained indicate that in the systems initiated by $SbCl_5$ the active centres of amphiion structure can play an important role in initial stages of the reaction.

The results obtained so far show that the mechanism and kinetics of cationic oligomerisation of methyloxirane is more complex than are cationic polymerisations of higher-membered heterocycles[1-7]. The relatively high reactivity of three-membered cyclic oxonium ions with considerable internal strain manifests itself in the increased tendency to form oligomers, similarly as in the case of polymerisations involving carbenium active centres, unless polymerisation is carried out at sufficiently low temperature. This fact is demonstrated also in the present work which concerns with oligomerisations of methyloxirane initiated by the title compounds from the point of view of propagation, transfer and termination. The results obtained in the study of initiation of oligomerisation of methyloxirane by triphenylmethyl salts have been discussed in earlier communication[8].

EXPERIMENTAL

Methods used for purification of the reaction components, techniques of oligomerisations and methods of chemical and spectral analysis of the oligomers and reaction mixtures were reported earlier[8]. Kinetic curves for oligomerisations were obtained from time dependences of the total tension of the reaction mixture with the use of calibration curves constructed on the basis of tensions of mixtures containing 1,2-dichloroethane, methyloxirane and the oligomer. The reactions were carried out in 1,2-dichloroethane at 25°C. The numerical centres of molecular

masses were measured by Knauer vapour osmometer, using solutions of oligomers in 1,2-dichloroethane at 35°C.

Mass spectra of oligomers were recorded with MCH-1303 mass spectrometer. The energy of ionising electrons was 100 eV, temperature of the ionisation chamber was 150 to 170°C and the samples were evaporated from a narrowed capillary tube directly to the ionisation source at 25 to 30°C.

The content of aldehyde end groups in oligomers was determined semiquantitatively from IR spectra of solutions of oligomers in 1,2-dichloroethane, using the calibration curves constructed from data obtained for 1,2-dichloroethane solutions of propanal containing also 1 wt.% of the oligomer. The intensity of bands was evaluated by the baseline method. It was assumed that the absorption coefficients of C=O stretching frequency at 1 730 cm^{-1} are identical for both compounds (propanal and oligomers).

RESULTS

Both triphenylmethyl salts and $SbCl_5$ initiate transformation of methyloxirane to a mixtue of cyclic and linear oligomers having the average polymerisation degree from 5 to 10. As found by organic and spectral analysis, the polymers contain aldehyde, hydroxyl and unsaturated functional groups. In several samples synthesised by means of $(C_6H_5)_3C \pm SbCl_6^-$ we determined semiquantitatively the content of aldehyde groups. From the results shown in Fig. 1 it follows that the amount of CHO groups increased in oligomers monotonously with the concentration of the initiator used to form the oligomer. The contents of further functional groups did not change systematically with the concentration of the initiator (as judged from IR spectra). The oligomers prepared with the use of $(C_6H_5)_3C^+SbCl_6^-$, and $SbCl_5$ contain also bonded chlorine and antimony in oxidation degree III and V (initiators contained only Sb^V). The antimony cannot be removed from the oligomers by re-precipitation.

Formation of cyclic dimers in the course of oligomerisation has been proved in the following way. After three hours, the reaction mixture in which block oligomerisation of methyloxirane was taking place was distilled to remove the unreacted monomer and then the pressure was reduced to remove also the other volatile components which were collected in a flask cooled with dry ice. Their proportion amounted to *v.* 10 per cent of the total amount of oligomers. Mass spectrometric analysis of the volatile components showed that we deal here with the cyclic dimers of methyloxirane, 90% of which were formed by 2,5- and 2,6-dimethyl-1,4-dioxane and the residue (10%) was 2-ethyl-4-methyl-1,3-dioxolane.

All three types of studied oligomerisations proceed typically immediately after mixing the reaction components, *i.e.* without induction period observable by the experimental technique used and their initial fast period is, after 10 to 20 min, followed by the stage which is characterised by the slower reaction rate connected with the change in the reaction order in the monomer. From other aspects the individual reaction systems differ in their kinetic behaviour.

For the systems with $(C_6H_5)_3C^+AsF_6^-$ it is characteristic that at a sufficiently long reaction time one can achieve nearly unit degree of conversion of methyloxirane to oligomers. Even after that, the reaction mixture can be stored *in vacuo* for long time without termination of active centres. If another charge of the monomer is added to such a reaction mixture, its conversion into oligomer takes place essentially quantitatively. As follows from the kinetic analysis performed by the method of initial reaction rates, these oligomerisations are internally the first order in the monomer and in the initiator. The experimental rates were used to estimate the total reaction constant $k_p = 0{\cdot}175 \pm 0{\cdot}030\ s^{-1}\ dm^3\ mol^{-1}$ ($k_p = (-d[M]/dt)_{t=0}[M]_0^{-1}[I]_0^{-1}$) where $[M]$ and $[I]$ are concentrations of monomer and initiator, respectively). In further stage, the reaction order in the initiator remains the same while the order in the monomer changes to one half (Fig. 2). The corresponding rate constant for this stage, as defined by relation (*1*), is $k_{1/2} = 0{\cdot}052 \pm 0{\cdot}013\ s^{-1}\ dm^{3/2}\ mol^{-1/2}$. $[M]_i$ is the values for $[M]$ corresponding to the

$$[M]^{1/2} = [M]_i^{1/2} - \tfrac{1}{2}k_{1/2}[I]_0\, t \qquad (1)$$

intersection between the linear part of the $[M]^{1/2}$ *vs* t dependence and $[M]^{1/2}$ coordinate. In successive runs, the initial stages are less distinct and further stages of the reaction initiated by these systems are qualitatively and quantitatively identical with

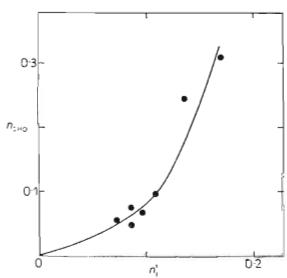


FIG. 1

Dependence of the average number of aldehyde end groups per one molecule of oligomer, n_{DHO}, on the number of molecules of the initiator $(C_6H_5)_3C^+SbCl_6^-$ related to one molecule of the oligomer, n_I

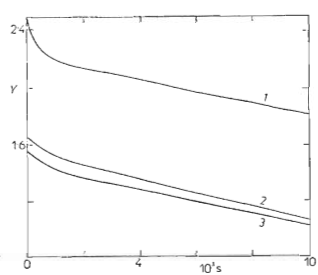


FIG. 2

Kinetic curves for oligomerisation of methyloxirane initiated by $(C_6H_5)_3C^+AsF_6^-$; $[M]_0$ *1* 6·00, *2* 2·69, *3* 2·36 mol dm^{-3}; $[I]_0$: *1* 2·22, *2* 1·96, *3* 1·70 mmol dm^{-3}

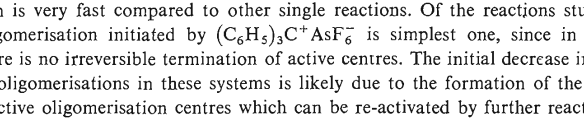
the first oligomerisation (provided that one takes into account the correction for changes in initiator and monomer concentrations caused by the addition of another portion of methyloxirane).

When compared to previous oligomerisations, those initiated by $(C_6H_5)_3C^+SbC_6^-$ differ in that they end generally before unit degree of conversion is achieved. The exception are only reaction mixtures containing relatively high initiator concentrations. In this case methyloxirane is converted into oligomers completely before all the active centres disappear by termination. Subsequent oligomerisations did not take place. According to the analysis performed by the method of initial reaction rates, also these oligomerisations are reactions of the internal first order in the initiator and in the monomer. The corresponding total rate constant $k_p = 0{\cdot}09 \pm 0{\cdot}02\ s^{-1}.\ dm^3\ mol^{-1}$, which is about one half of the value found for the systems with the pair anion AsF_6^-. Kinetic curves of the slower stage of the reaction cannot be treated by a simple kinetic relation.

Oligomerisations initiated by $SbCl_5$ end spontaneously before the unit conversion is achieved, unless higher initial concentration of the initiator is used. Also in these systems, the subsequent oligomeristations do not proceed. The analysis made by the method of initial reaction rates showed that reaction orders in the monomer and initiator are approximately 0·5 and 0·6, respectively. The corresponding total rate constant k_p had a value of $0{\cdot}023\ s^{-1}$. The rate of disappearance of active centres in the initial stage of the reaction is substantially higher compared to previous cases. As a result, the oligomerisation efficiency of the initiator is considerably decreased and the initial fast stage of the reaction determines to a great extent the overall conversion (Fig. 3). Kinetic curves characterizing further stage are in good qualitative agreement with the systems containing $(C_6H_5)_3C^+SbCl_6^-$.

DISCUSSION

In agreement with the assumptions about the initiation of oligomerisations of methyloxirane[8], the above mentioned results can be interpreted on assuming that the initiation is very fast compared to other single reactions. Of the reactions studied, the oligomerisation initiated by $(C_6H_5)_3C^+AsF_6^-$ is simplest one, since in this case there is no irreversible termination of active centres. The initial decrease in the rate of oligomerisations in these systems is likely due to the formation of the transient inactive oligomerisation centres which can be re-activated by further reaction. This dormant active centres can be formed *e.g.* by back-bitting reaction, similarly as in polymerisations of cyclic sulphides[9,10] (equation (*A*)).



(*A*)

In analogy to findings of other authors[7,9–11], macrocyclic oxonium ions can be regarded as little active or inactive in oligomerisation.

Provided that the initiator is completely converted into active centres and that macrocyclic oxonium ions are inactive in oligomerisation, the system under study can be described by relations derived for the desactivation of polymerisation systems by back-bitting reactions[7,9,10],

$$\ln [M]_0/[M]_1 = k_p[I]_0/k_b \qquad (2)$$

(valid for the reactions with specific selection of reactive hetero atom with respect to its position to the active centre),

$$[M]_0 \{\ln ([M]_0/[M]_1) - 1\} + [M]_1 = k_p[I]_0/k_b \qquad (3)$$

(valid for nonspecific selection of reactive hetero atom). $[M]_1$ is the residual concentration of the monomer after the reaction had stopped spontaneously. With regard to possible subsequent activation of dormant centres, the assumption about their inactivity in studied systems is not fully justified. For that reason, the values of $[M]_1$ were taken as the arithmetic means of $[M]_i$ values (Eq. (1)) and $[M]$ values

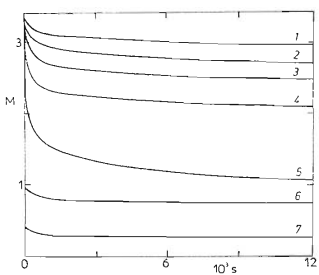


FIG. 3

Kinetic curves for oligomerisations of methyloxirane initiated by $SbCl_5$; $[M]_0$: *1* 3·41, *2* 3·42, *3* 3·43, *4* 3·27, *5* 3·34, *6* 1·00, *7* 0·46 mmol dm^{-3}; $[I]_0$: *1* 1·49, *2* 3·75, *3* 12·5, *4* 25·0, *5* 48·4, *6* 2·78, *7* 3·75 mmol dm^{-3}

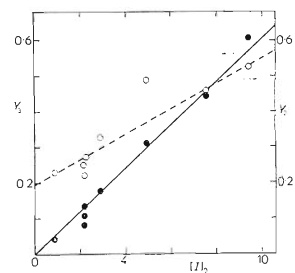
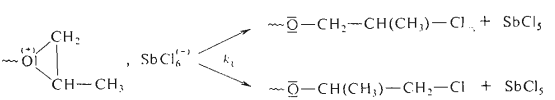


FIG. 4

Analysis of the initial stage of the oligomerisations of methyloxirane initiated by $(C_6H_5)_3C^+AsF_6^-$; ○ according to Eq. (2), ● according to Eq. (3); $Y_2 = \ln ([M]_0/[M]_1)$; $Y_3 = [M]_0 \{\ln [M]_0/[M_1] - 1\} + [M]_1$ (mol dm^{-3}), $[I]_0$ is the initial concentration of the initiator in mmol dm^{-3}

after completion of the initial stages of oligomerisations. From analysis of the results made with the use of Eqs (*2*) and (*3*) it follows that the behaviour of studied systems comports with the model involving nonspecific selection of hetero atom (Fig. 4). This conclusion is in accordance with the composition of reaction products for cationic oligomerisations of methyloxirane[2,3]. Eq. (*3*) was used to calculate the ratio of the rate constants $k_p/k_b = 60$ from the dependence shown in Fig. 4; after substitution for k_p, k_b constant was found to have a value of 0·0029 s^{-1}.

Kinetic data for methyloxirane + $(C_6H_5)_3C^+SbCl_6^-$ systems can be analysed in a similar way. The corresponding kinetic equations have to be modified with respect to the irreversible termination in these systems. The presence of chlorine bound to oligomers speaks for termination of active centres by their reaction with pair anion $SbCl_6^-$ (equation (*B*)).



(*B*)

$SbCl_5$ so formed reacts with the unreacted monomer to form mainly inactive species and to a lesser extent also oligomer active centres (see later).

If one regards termination (*B*) as intramolecular reaction of ion pair and – in agreement with the results obtained with $(C_6H_5)_3C^+AsF_6^-$ – the propagation as one half order in the monomer, the second stage of oligomerisations initiated by $(C_6H_5)_3C^+SbCl_6^-$ can be described by Eq. (*4*), where $[M]_f$ is the concentration of

$$\ln\left([M]^{1/2} - [M]_f^{1/2}\right) = \ln\left\{(k_{1/2}/k_t)\,[P^*]_0\right\} - k_t t \qquad (4)$$

the monomer after spontaneous ending of the oligomerisation in the second stage of the reaction, k_t is the rate constant of termination and $[P^*]_0$ is the initial concentration of active centres. By treatment of kinetic data according to Eq. (*4*) (Fig. 5), it was found that the rate constant of termination $k_t = (2{\cdot}15 \pm 0{\cdot}30) \cdot 10^4\ s^{-1}$. Provided that $[P^*]_0 = [I]_0$: the minimal value of the rate constant $k_{1/2}$ can be estimated as being greater then or equal to 0·03 $s^{-1}\ dm^{3/2}\ mol^{-1/2}$. When considering the inequality $[P^*]_0 < [I]_0$, this result agrees well with data obtained for the systems containing $(C_6H_5)_3C^+AsF_6^-$. By inclusion of the irreversible termination (B) into the reaction scheme depicting the first stage of oligomerisation, the nonspecific selection of hetero atom can be described by relation (*5*).

$$[P^*]_0^{-1}\left\{[M]_0\left(\ln\frac{[M]_0}{[M]_1} - 1\right) + [M]_1\right\} = \frac{k_p}{k_b} - \frac{k_t}{k_b}\,[P^*]_0^{-1}\ln\frac{[M]_0}{[M]_1}. \qquad (5)$$

Using approximation $[P^*]_0 = [I]_0$, experimental data were treated by Eq. (5) and with the use of the value sof k_p and k_t determined for the systems initiated with $(C_6H_5)_3C^+SbCl_6^-$ the following values were obtained: $k_b = 0{\cdot}0024\ s^{-1}$ (from the intercept) and $k_b = 0{\cdot}001\ s^{-1}$ (from the slope). The agreement with the k_b values determined for the pair anion AsF_6^- is quite good, since the approximation used and the greater scatter of experimental data do not allow obviously to get better results (Fig. 6).

On the basis of the above assumptions about the systems with triphenylmethyl salts, the kinetic behaviour of the systems initiated by $SbCl_5$ in the first stage of the oligomerisation cannot be explained either quantitatively or qualitatively. Only the second, slower stage of oligomerisation can be satisfactorily interpreted in terms of termination of active centres, similarly to the systems with $(C_6H_5)_3C^+SbCl_6^-$. From the dependences according to Eq. (4) we determined the value of the rate constant of termination $k_t = (2{\cdot}1 \pm 0{\cdot}4) \cdot 10^4\ s^{-1}$, which is in excellent agreement with the values determined for the preceding system. An attempt to estimate the rate constant $k_{1/2}$ form the intercept by using Eq. (4) and the approximation $[P^*]_0 = [I]_0$ has failed, since the dependence of the intercepts on $[I]_0$ is not linear and does not pass through the origin. This indicates a very complex mechanism of the first stage of the reaction.

From the above mentioned findings it follows that, irrespective of the initiator

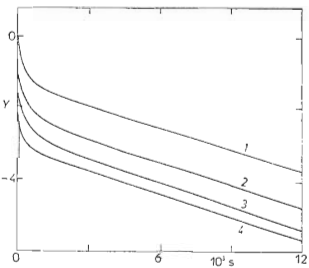


FIG. 5

Kinetic curves for the oligomerisations initiated by $(C_6H_5)_3C^+SbCl_6^-$ plotted according to Eq. (4). $Y = \ln([M]^{1/2} - [M]^{1/2})$ ($mol^{1/2}\ dm^{-3/2}$); $[M]_0$: *1* 2·97, *2* 11·37$_f$, *3* 3·33, *4* 6·65 mol dm^{-3}; $[I]_0$: *1* 2·03, *2* 4·25, *3* 5·62, *4* 9·75 mmol dm^{-3}

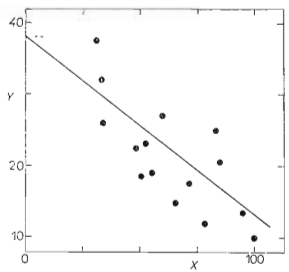
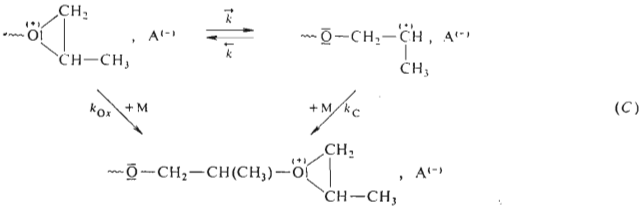


FIG. 6

Analysis of the initial stage of the oligomerisations initiated by $(C_6H_5)_3C^+SbCl_6^-$. $X = [I]_0^{-1} \ln(\{[M]_0/[M]_1\})$; $Y = [I]_0^{-1} \cdot [M]_0 (\ln [M]_0/[M]_1 - 1) + [M]_1\}$ ($mol^{-1}\ dm^3$)

used, the reaction proceeds in the second stage as one half order in the monomer. This fact can be caused by the participation of carbenium ions in oligomerisation and this effect can be eventually strengthened by specific solvation of dormant centres by the monomer, leading to their stabilization. The participation of carbenium ions in oligomerisation of methyloxirane can be depicted by a simplified reaction scheme



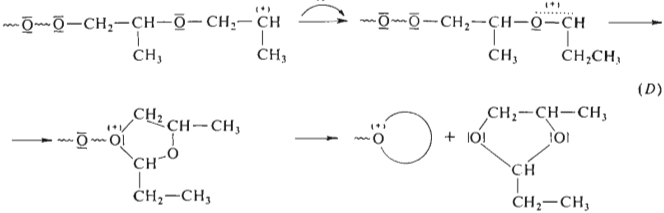
(*C*)

(*C*), where k_{Ox} and k_C are the rate constants of propagation of oxonium and carbenium ions, respectively. With the use of the approximation about steady concentration of carbenium ions, the above scheme can be described by the relation

$$-\mathrm{d}\ln[\mathrm{M}]/\mathrm{d}t = k_C[\mathrm{P}^*]\frac{K + (k_{Ox}/k_C)(1 + k_C[\mathrm{M}]/\vec{k})}{K + 1 + k_C[\mathrm{M}]/\vec{k}}, \qquad (6)$$

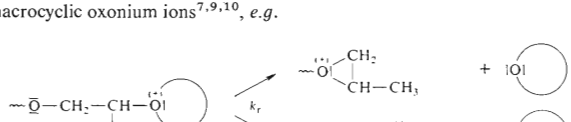
where $[\mathrm{P}^*]$ is the total concentration of active centres of oxonium and carbenium type and $K = \vec{k}/\overleftarrow{k}$. As follows from Eq. (*6*) for $k_{Ox} \ll k_C$ and not too high values of K, the reaction order in the monomer should be less than 1, in extreme case it can be even zero[5]. In such a case, the intramolecular conversion of oxonium to carbenium ions is the rate determining step of the reaction.

The results obtained by the analysis of the reaction products support the idea about the active role of carbenium ions in oligomerisations of methyloxirane, since only their presence can explain satisfactorily the observed formation of 2-ethyl-4-methyl-1,3-dioxolane (equation (*D*)).



(*D*)

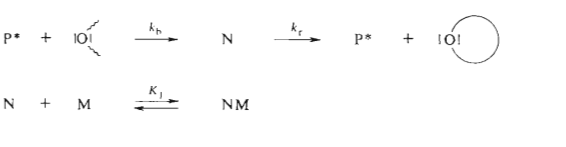
Another explanation of the observed low order of the reaction in the monomer relates closely to the re-initiation which takes place as the intramolecular reaction of macrocyclic oxonium ions[7,9,10], *e.g.*



(*E*)

The re-initiation thus leads to the formation of cyclic oligomers. The intramolecular course of this reaction is evidenced by the observed low order of the reaction in the monomer which indicates formal inhibition effect of the monomer on the formation of active centres (according to the general kinetic equation for propagation it holds that $[P^*] = -\mathrm{d} \ln [M]/k_p \mathrm{d}t$ and after substitution for $[M]$ from Eq. (*1*) it becomes evident that $[P^*]$ is proportional to $[M]^{-1/2}$). Experimental results are thus at variance with the model of re-initiation assuming the reaction of dormant active centre with the monomer.

In accordance with the above mentioned facts, the kinetic dependences can be interpreted in terms of decreasing concentration of active centres with increasing methyloxirane concentration, which can be caused by *e.g.* specific solvation of dormant centres by the monomer (Scheme (*F*)). In the scheme, N is the inactive oxonium ion and NM and NM_2 are the inactive ions stabilised by the monomer. Reaction scheme (*F*) was solved with the use of

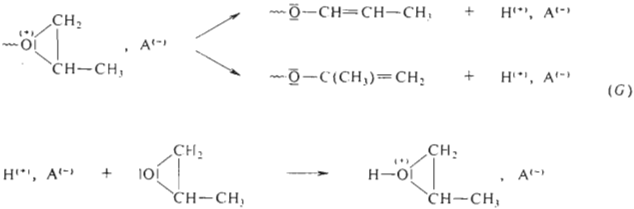


(*F*)

steady state approximation: $k_r[N] = k_b[P^*]([M]_0 - [M])$, and the relation obtained was used to test kinetic curves of oligomerisations initiated by $(C_6H_5)_3C^+AsF_6^-$. Calculated values of the constants showed considerable scatter. This indicates that the above scheme does not depict fully the experimental fact ($k_r = 0{\cdot}01$ to $0{\cdot}10\ s^{-1}$, $K_1 = 4$ to 80, $K_2 = 1-20$).

The presence of hydroxyl, unsaturated and aldehyde end groups (these in greater amounts) can be explained by transfer reactions with participation of the monomer. The unsaturated and hydroxyl end groups are likely formed by proton transfer

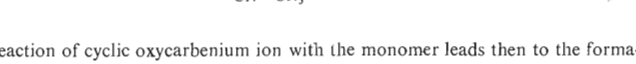
from the active centres to monomer molecules which can take place either directly or with participation of the pair anion (equation (*G*)).



(*G*)

The cleavage of the oxirane ring in the subsequent propagation step results in the formation of hydroxyl end groups. With respect to the low polymerisation degree of products, one cannot exclude that hydroxyl and propenyl ether end groups participate also in the other side reactions which can eventually take place in the reaction mixture.

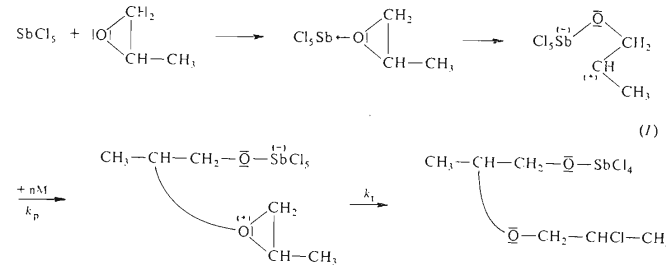
The dependence in Fig. 3 shows that the content of aldehyde end groups in methyloxirane oligomers is higher than the value calculated from $[I]_0$, assuming that initiation proceeds exclusively by the mechanism of hydride ion transfer[8]. It is therefore evident that aldehyde end groups are formed not only by initiation but also by another reaction, most likely by transfer of hydride ion from the monomer to the active centre. The reactivity of oxonium ions is not sufficient to realise this reaction[11], but if also carbenium ions are present in the reaction mixture, the H^- transfer from the monomer to the active centre is possible:



(*H*)

The reaction of cyclic oxycarbenium ion with the monomer leads then to the formation of aldehyde end group. Hence, these results support the idea about participation of carbenium ions in methyloxirane oligomerisation.

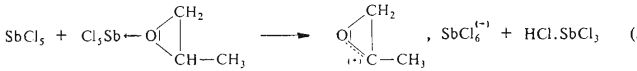
The first stage of oligomerisation of methyloxirane initiated by $SbCl_5$ differs significantly from oligomerisation initiated by triphenylmethyl salts. It seems likely that in these systems, there are active centres of different type which play an important role in the course of this reaction. In analogy to reported data on similar reaction systems[5,12], one can assume that in these cases the active centres have the structure of amphiions:



(*J*)

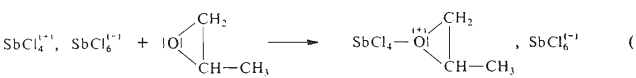
The above scheme explains the presence of chemically bound Sb in oligomers and makes it possible to account for the faster termination of these active centres which is apparently facilitated by the bond of oxygen to antimony, which metal can then release chlorine more easily.

Parallel to the initiation leading to the formation of amphiions, also initiation resulting in the formation of active centres with the structure of oxonium salts can take place, and that both on the expense of the reduction of Sb^{V} to Sb^{III} (refs[13,14]):



(*J*)

or *via* autoionisation of $SbCl_5$:



(*K*)

On the basis of obtained results, the initiation mechanism (*J*) can be preferred, which at the time explains the observed reduction of antimony. The antimony trichloride so formed is inactive in oligomerisation; however, together with the residual $SbCl_5$ it can act also as the initiator (equation (*G*)). While amphiionic centres disappear in initial stages of the oligomerisation, the active centres with the structure of oxonium or carbenium salts with the pair anion $SbCl_6^-$ have longer life time and act the centres for formation of oligomers in the second stage of the reaction.

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