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Mechanism of Polymerization of 1, 3-Dioxolane Initiated by $(C_2H_5)_3$ O $SbCl_6$ and $SbCl_5$

Z. N. Nysenko[a]; E. L. Berman[a]; E. B. Ludvig[a]; V. A. Ponomarenko[a]
[a] Zelinsky Institute of Organic Chemistry U. S. S. R. Academy of Sciences Karpov Scientific Research Physico-Chemical Institute, Moscow, U.S.S.R.

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Mechanism of Polymerization of 1,3-Dioxolane Initiated by $(C_2H_5)_3O^+SbCl_6^-$ and $SbCl_5$

Z. N. NYSENKO, E. L. BERMAN, E. B. LUDVIG, and
V. A. PONOMARENKO

Zelinsky Institute of Organic Chemistry
U.S.S.R. Academy of Sciences
Karpov Scientific Research Physico-Chemical Institute
Moscow, U.S.S.R.

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ABSTRACT

The kinetics of polymerization of 1,3-dioxolane (DiOX) initiated by $(C_2H_5)_3O^+SbCl_6^-$ and $SbCl_5$ has been studied and the elementary stages of the process have been considered. The polymerization of DiOX by $(C_2H_5)_3O^+SbCl_6^-$ is shown to proceed at a steady rate to high conversion. A constant concentration of active centers in the system is maintained due to the equal rates of decomposition of active centers and disproportionation. The nonsteady-state character of DiOX polymerization initiated by $SbCl_5$ is associated with a relatively lower stability of the counter-ion $SbCl_5OR^-$ compared with $SbCl_6^-$. The initiation of DiOX polymerization by $(C_2H_5)_3O^+SbCl_6^-$ proceeds without hydride-transfer reactions, and the concentration of active centers in the system is determined not by processes taking place in the initiation stage, but by the existence of a definite kind of equilibrium with the participation of active centers.

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Many investigations relating to polymerization of cyclic acetals appearing in the past few years have been stimulated by the following facts reported in a number of publications.

There are drastic differences in the rates of polymerization of 1,3-dioxolane (DiOX), depending on the nature of the initiators. The rates of processes initiated by systems containing the anions SbF_6^- or PF_6^- are two to three orders of magnitude higher than those proceeding with initiators systems with anions $SbCl_6^-$ or BF_4^- [1, 2].

There is a considerable increase in the rate of polymerization of DiOX in the presence of initiators with the $SbCl_6^-$ counterion upon introducing α-chloromethyl ether (CMEE) [3].

The absorption at 272 nm in the ultraviolet spectrum, which is characteristic of the counterion $SbCl_6^-$, disappears if polymerization of DiOX is initiated by $(C_2H_5)_3O^+SbCl_6^-$ [4].

Considering the absence of an effect by the counterion on the chain propagation rate constant in the polymerization of tetrahydrofuran [5], all these fact suggest that, in case of unstable counterions, processes leading to a sharp decrease in the number of active centers in the system take place in addition to initiation and chain propagation reactions.

Most recent publications on polymerization of DiOX have dealt mainly with elucidation of those processes which lead to decomposition of the main part of the active centers. These investigations introduced various points of view which failed to elucidate completely the problem in hand.

It should be emphasized that the relative stability of active centers in the polymerization system and the dependence of this stability on the nature of the cation and anion, as well as on the process conditions, is, a problem of general character and deserves special attention.

We have therefore considered it appropriate to investigate in detail the nature and mechanism of the processes taking place in systems in which the concentration of active centers constitutes only a small part of the initiator concentration. The present study is concerned with reactions which take place in polymerization of DiOX initiated by $(C_2H_5)_3O^+SbCl_6^-$ and $SbCl_5$ in CH_2Cl_2.

RESULTS AND DISCUSSION

Polymerization of DiOX Initiated by $(C_2H_5)_3O^+SbCl_6^-$

Conversion curves for the polymerization of DiOX initiated by $(C_2H_5)_3O^+SbCl_6^-$ are shown in Figs. 1 and 2. The process is characterized by an induction period depending on the initiator and

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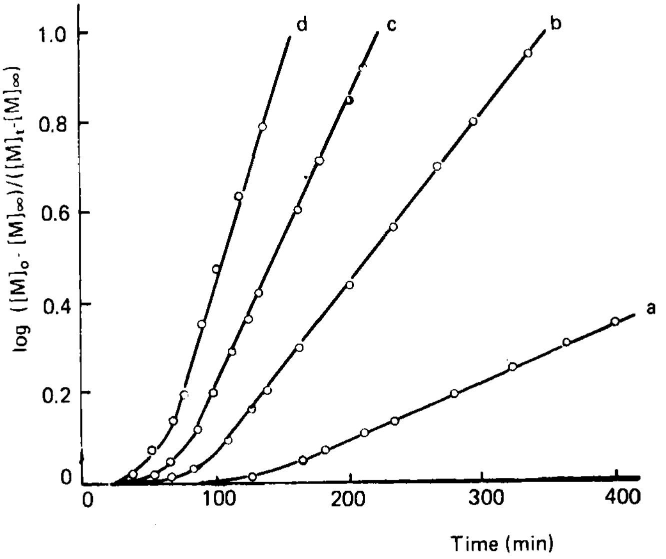

FIG. 1. Kinetic plots for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20° C and $[M]_0 = 2.88$ mole/liter and various $[C]_0$: (a) 1.20×10^{-3}; (b) 2.72×10^{-3}; (c) 4.30×10^{-3}; (d) 6.33×10^{-3} mole/liter.

monomer concentration. After the induction period, the process proceeds at a steady rate to high conversions. The linear dependence of the slope of the straight line parts of the curves in Fig. 1 on the concentration of the initiator (Fig. 3) is indicative of the first-order dependence of the polymerization on the catalyst concentration. The independence of the slope of the curves of the monomer concentration (Fig. 2) shows the first-order character of the polymerization in monomer.

The main kinetic dependences established in the present study are generally in agreement with those found earlier [6]. (The kinetic data presented here differ from those published previously [6] in the presence of an induction period. This was caused by the presence of internal oxonium salt in the trialkyloxonium salt. Special experiments showed that polymerization of DiOX in the presence of the internal oxonium salt proceeds without an induction period.) The fact that the effective rate constant of the second-order reaction does not change with variation in the concentrations of the components

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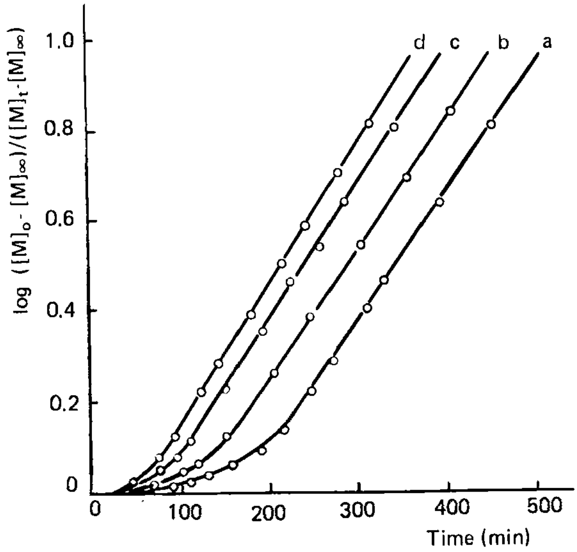

FIG. 2. Kinetic plots for polymerization at DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20°C at $[C]_0 = 1.96 \times 10^{-3}$ mole/liter and various $[M]_0$: (a) 2.30; (b) 3.40; (c) 4.80; (d) 6.40 mole/liter.

is noteworthy and indicative of the steady concentration of active centers in this process.

Data on changes in the ultraviolet spectrum of the system in the course of the process were obtained concurrently with the kinetic results. Some results are presented in Fig. 4. (It should be pointed out that considerable absorption of the solvent CH_2Cl_2 makes investigation of the shortwave region of the spectrum at $\lambda < 230$ nm impossible.) A comparison of the spectral and kinetic data shows that the induction period corresponds to the time at which the maximum at 272 nm responsible for the absorption of the anion $SbCl_6^-$ practically disappears.

Concentration of Active Centers and Rate of the Process

The comparison of the kinetic and spectral data obtained by the authors with the results reported in the studies on polymerization of DiOX initiated by salts with counterions stable under the given conditions confirms the transformation of most of the active centers with the counterion $SbCl_6^-$ into inactive forms.

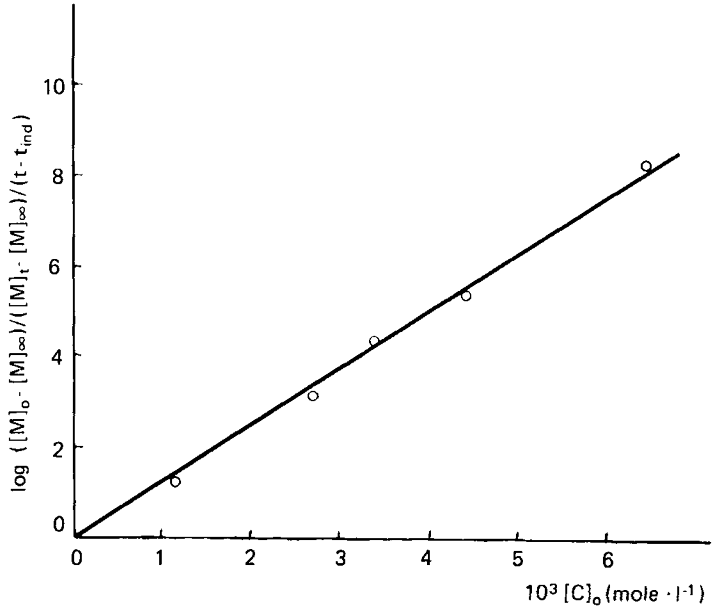

FIG. 3. Plots of log $\{([M]_0 - [M]_\infty)/([M]_t - [M]_\infty)\}/(t - t_{ind})$ vs $[C]_0$ for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20°C.

Approximately equal rates observed when polymerization of DiOX is initiated by various compounds, all having $SbCl_6^-$ as counterion, i.e., $(C_6H_5)_3C^+SbCl_6^-$, $(C_2H_5)_3O^+SbCl_6^-$, $\overline{O{-}H_2C{-}CH_2{-}O{-}C}H^+SbCl_6^-$, $CH_3OCH_2{}^+SbCl_6^-$) [7, 8] are, evidently, associated with the characteristic transformation to inactive forms of active centers by the counterion $SbCl_6^-$.

However the observed steady-state character of the process to high degrees of conversion indicates that the process of decomposition of active centers proceeds concurrently with a reverse process which leads to their regeneration.

Let us consider both processes. The reactions proceeding in the system are presented in scheme 1. The most probable decomposition reaction of the growing active center is reaction (2) at the initial stages of the process (2b). Decomposition of acetal oxonium ions by the counterion BF_4^- was previously shown by a NMR method [9] to occur.

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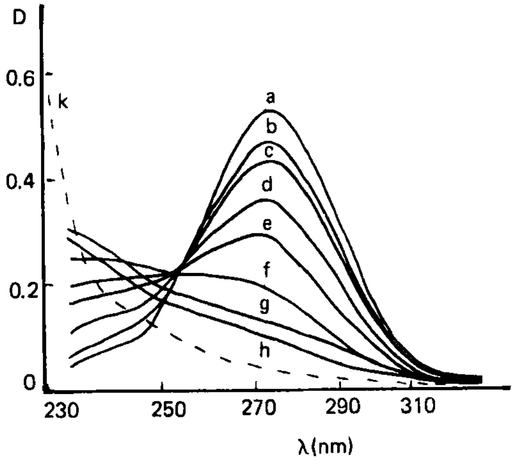
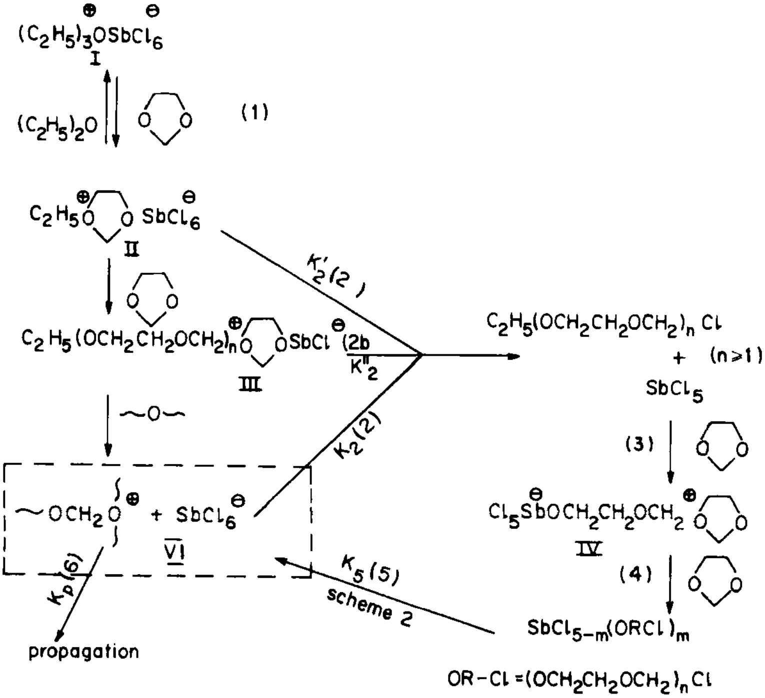


FIG. 4. UV spectra for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20° C: (a) 15 min, (b) 37 min, (c) 45 min, (d) 65 min, (e) 90 min, (f) 120 min, (g) 145 min, and (h) 165 min after the beginning of the experiment. $[M]_0 = 5.65$ mole/liter; $[C]_0 = 0.88 \times 10^{-3}$ mole/liter; (k) $[M]_0 = 5.65$ mole/liter, $[C]_0 = 0$.



SCHEME 1.

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Reactions (2) and (2b) lead to the formation of $SbCl_6$. According to the ultraviolet spectrum, $SbCl_6$–DiOX interaction gives products that absorb in the shortwave region. The following pathways of $SbCl_6$ transformation are possible: hydride-transfer reactions [7, 10] and formation of antimony chloroalkoxychlorides [reaction (4)].

As shown below, hydride-transfer reactions do not contribute significantly to the process. In our opinion, the most probable $SbCl_5$ transformation reaction in the system is reaction (4). The formation of products similar to V for a BCl_3-DiOX-system was demonstrated previously [11].

The formation of antimony chloralkoxychlorides agrees with the data [12-14], according to which chlorine in $SbCl_5$ and $SbCl_6^-$ can be easily replaced by other electronegative groups (OR,OH). This leads to a hypsochromic shift in the ultraviolet spectrum [14].

To verify the above supposition, the monosubstituted compound, $Cl_4SbOC_2H_5$ was synthesized as a model compound for V. (More highly substituted compounds could not be investigated because of difficulties associated with their isolation in pure form.) As expected, the absorption maximum of this compound compared to $SbCl_5$ is shifted towards the shortwave region (Fig. 5). A higher degree of

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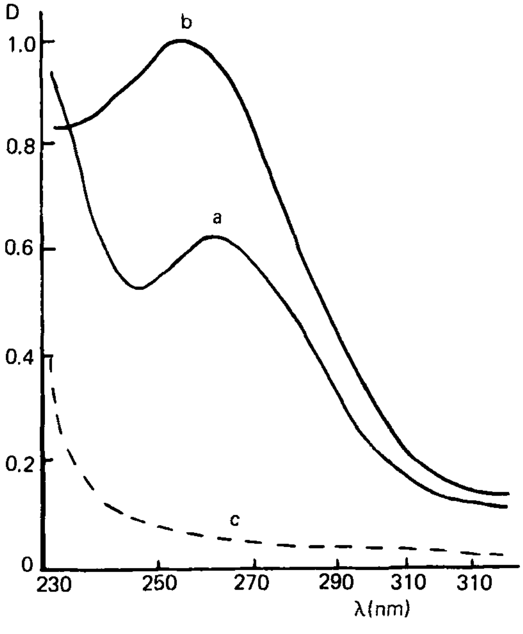
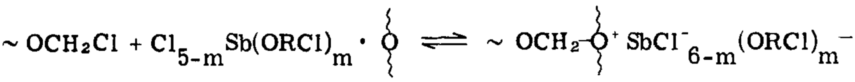


FIG. 5. UV spectra of (a) $SbCl_5$ and (b) $Cl_4SbOC_2H_5$ in CH_2Cl_2 and (c) CH_2Cl_2 alone. $[SbCl_5] = 1.0 \times 10^{-3}$ mole/liter, $[Cl_4SbOC_2H_5] = 1.26 \times 10^{-3}$ mole/liter.

chlorine substitution must shift the absorption maximum still more [14].

The degree of chlorine substitution in $SbCl_5$ in our system is not known, but the ultraviolet spectra show that this substitution is more than one.

Compounds of the type $Cl_{5-m}Sb(OR)_m$ are Lewis acids, their activity decreasing with the substitution of chlorine by an alkoxy radical. Thus, the activity of monosubstituted antimony chloroethoxychloride in polymerization is lower than that of $SbCl_5$. Compounds with high degree of substitution would be practically inactive. Their reaction with CMEE present in the system must lead to a negligible concentration of active centers, insufficient for polymerization:



$$\sim OCH_2Cl + Cl_{5-m}Sb(ORCl)_m \cdot O \rightleftharpoons \sim OCH_2{-}O^+\,SbCl^-_{6-m}(ORCl)_m^- \tag{6}$$

Thus, transformations of $SbCl_5$ decrease the concentration of active centers. The main reaction ensuring their steady concentration must be formation of unsubstituted anions or anions of low substitution degree. This may be the known disproportionation of antimony alkoxychloride [15, 16], shown in Eqs. (7). In view of these reasons, the ionic forms [Eq. (7b)], in this system do not contribute significantly to the process. These processes must be more considerable under special conditions, for instance, a large excess of CMEE. Under the usual conditions the active centers seem to be formed by reaction (7a). The proof for disproportionation is given in a subsequent section.

$$2SbCl_{5-m}(ORCl)_m \overset{k_5}{\rightleftharpoons} [SbCl_{4-2m}(ORCl)_{2m}]^{\oplus}[SbCl_6]^{\ominus} \rightleftharpoons$$

$$\rightleftharpoons [SbCl_{4-2m}(ORCl)_{2m}]^{\oplus} + [SbCl_6]^{\ominus} \tag{7a}$$

$$SbCl_{5-m}(ORCl)_m - [SbCl_{6-m}(ORCl)_m]^{\ominus} \rightleftharpoons$$

$$\rightleftharpoons SbCl_{5-2m}(ORCl)_{2m} + [SbCl_6]^{\ominus} \tag{7b}$$

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Let us consider the kinetics of DiOX polymerization initiated by $(C_2H_5)_3O^+SbCl_6^-$ in its stationary stage, taking into account reaction (2) (Scheme 1) of decomposition of active centers and reaction (5) (Scheme 1) of their formation.

Assuming that the active centers exist as free ions (concentration about 10^{-5} to 10^{-6} mole/liter), the change in their concentration will be described by Eq. (8):

$$-d[X]/dt = k_2\,[X]^2 \tag{8}$$

where k_2 is the rate constant for decomposition of active centers. The rate of formation of active centers according to reaction (5) is:

$$d[X]/dt = k_5\,[C]_0^2 \tag{9}$$

where k_5 is the rate constant of the disproportionation, $[C]_0$ is the concentration of antimony chloralkoxychlorides, which is practically equal to the initial concentration of the initiator.

If the decomposition and disproportionation rates are equal, then:

$$[X] = (k_5^{1/2}/k_2^{1/2})\,[C]_0 \tag{10}$$

The rate of the process will be expressed as:

$$-d[M]/dt = k_p[X]([M] - [M]_\infty)$$

$$= (k_p k_5^{1/2}/k_2^{1/2})\,[C]_0([M] - [M]_\infty) \tag{11}$$

Equation (11) is in agreement with experimental data. The degree of decomposition of active centers to inactive forms is determined by the ratio of the constants $k_5^{1/2}/k_2^{1/2}$, which enters into the effective constant of the chain propagation rate.

Initiation Process and Induction Period

As pointed out above, the induction period corresponds to the time when the concentration of ionic forms diminishes from the concentration of the initiator to that of active centers.

Most probable transformations during the induction period are shown in Scheme 1.

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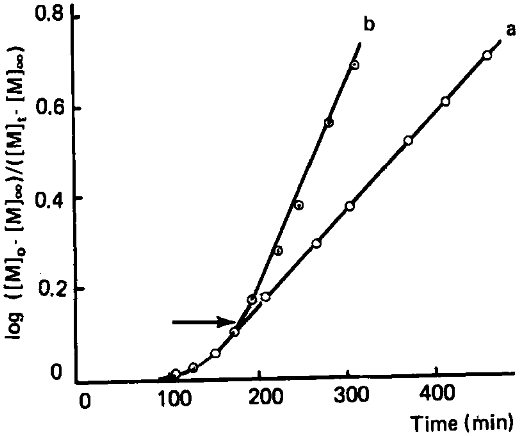

FIG. 6. Kinetic plots for the polymerization of DIOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20°C: (a) $[M]_0 = 5.65$ mole/liter, $[C]_0 = 0.88 \times 10^{-3}$ mole/liter; (b) with the introduction a new portion of $(C_2H_5)_3O^+SbCl_6^-$ (C') into the reaction mixture 170 min after the beginning of the experiment; $[M]_0 = 5.65$ mole/liter, $[C']_0 = [C]_0 = 0.88 \times 10^{-3}$ mole/liter.

The limiting stage of this process, which determines the induction period, may be reaction (1) (Scheme 1). This is in agreement both with the observed dependences of the induction period on the concentration of the reagents and with the literature data on the rates of ether exchange of oxonium salts with tetrahydrofuran [17], 1,3-dioxolane, and 1,3-dioxane [10, 18].

Moreover, the data obtained in the present study show that preliminary introduction of the polymer into the system decreases the induction period. Thus, after formation of a sufficient quantity of polymer, a new portion of the initiator, equal to the initial one was introduced into the reaction mixture. As seen from Fig. 6, the induction period decreased. The ultraviolet spectrum of the system showed an increase in the decomposition rate of the new portion of the salt (Fig. 7). If polymerization does not take place, the decomposition rate noticeably diminishes. All these results may be the consequence of different rates of reaction (1) (Scheme I) for DIOX and its polymer.

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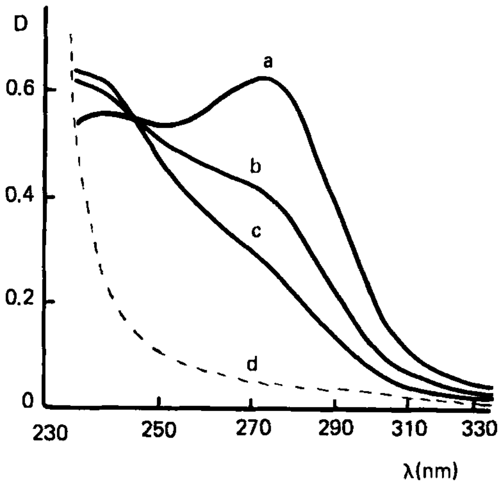

FIG. 7. UV spectra for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+Sb^-Cl_6$ (C) in CH_2Cl_2: (a) 10, (b) 25, and (c) 40 min after introduction of a new portion of $(C_2H_5)_3O^+SbCl_6^-$ (C'). $[M]_0$ = 5.65 mole/liter, $[C]_0 = [C']_0 = 0.88 \times 10^{-3}$ mole/liter (d) $[M]_0$ = 5.65 mole/liter, $[C]_0$ = 0.

Polymerization of DiOX Initiated by $SbCl_5$ and $Cl_4SbOC_2H_5$

According to Scheme 1, $SbCl_5$ and its derivatives play an essential role in the transformation of active centers in DiOX polymerization initiated by $(C_2H_5)_3O^+SbCl_6^-$. For this reason we investigated in detail the kinetics and mechanism of DiOX polymerization with these initiators. Kinetic curves for polymerization of DiOX in the presence of $SbCl_5$ are given in Fig. 8. Unlike the process initiated by the oxonium salt, in this case no induction period occurs. The initial rates depend linearly on the catalyst and monomer concentrations (Fig. 9), and as the process proceeds the decomposition of active centers is observed.

The change in the spectral characteristics of the system is shown in Fig. 10. As compared with the case of oxonium salt, the spectrum of the system changes rapidly and in the same manner: the absorption

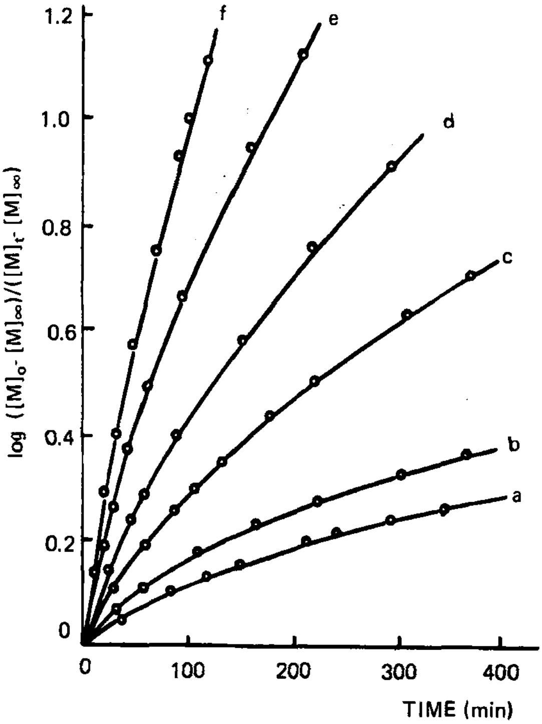

FIG. 8. Kinetic plots for the polymerization of DiOX (M) initiated by $SbCl_5$ (C) in CH_2Cl_2 at 20° C: (a) $[M]_0 = 2.80$, $[C]_0 = 0.65 \times 10^{-3}$ mole/liter; (b) $[M]_0 = 2.54$, $[C]_0 = 0.85 \times 10^{-3}$ mole/liter; (c) $[M]_0 = 4.40$, $[C]_0 = 1.67 \times 10^{-3}$ mole/liter; (d) $[M]_0 = 4.40$, $[C]_0 = 2.54 \times 10^{-3}$ mole/liter; (e) $[M]_0 = 4.40$, $[C]_0 = 3.20 \times 10^{-3}$ mole/liter; (f) $[M]_0 = 4.40$, $[C]_0 = 4.0 \times 10^{-3}$ mole/liter.

of $SbCl_5$ diminishes and the absorption in the region of shorter wavelengths increases. If the concentrations of DiOX is below the equilibrium one the spectrum changes more slowly. These facts indicate that the spectral changes are not related to $SbCl_5$ complexation.

The absence of an induction period and rapid changes in the UV spectrum of the system are associated with the absence, in this case, of the ether exchange stage (1, Scheme I) which limits both the initiation and the salt decomposition. Probably processes taking place in the DiOX polymerization initiated by $SbCl_5$ are given in Eq. (12).

If $k_d \gg k_{in}$, the concentration of active centers would be only a

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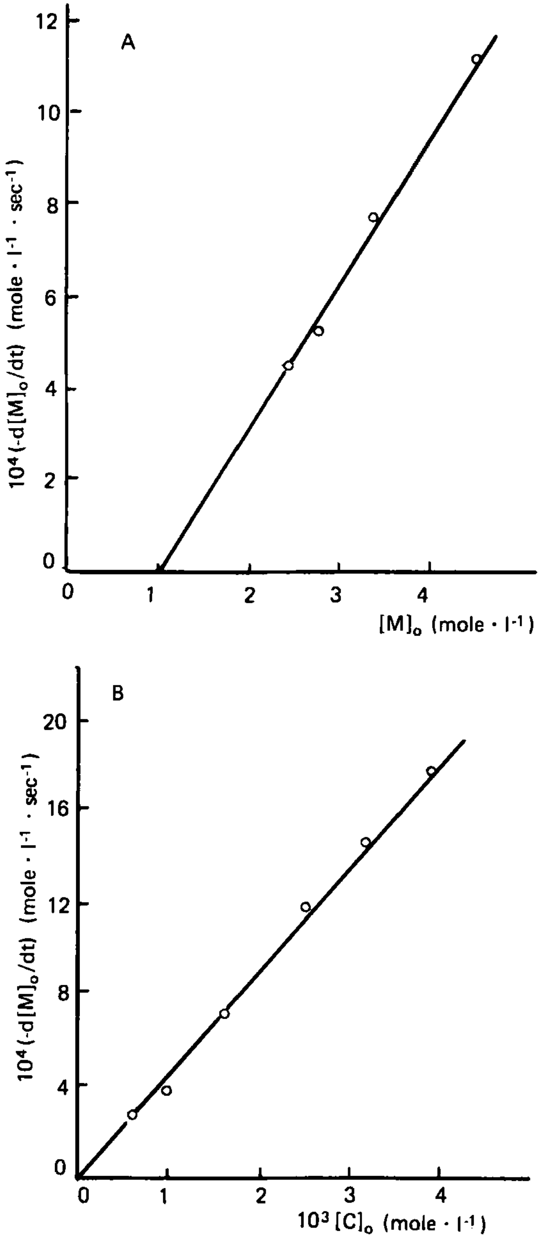

FIG. 9. Plots of (A) - d$[M]_0$/dt vs $[M]$ and (B) - d$[M]_0$/dt vs $[C]_0$ in the polymerization of DIOX initiated by $SbCl_5$ in CH_2Cl_2 at 20° C.

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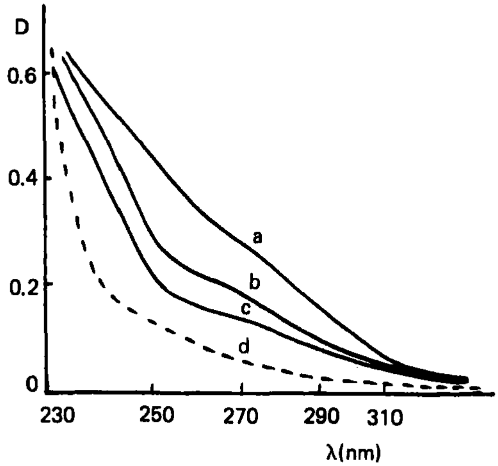
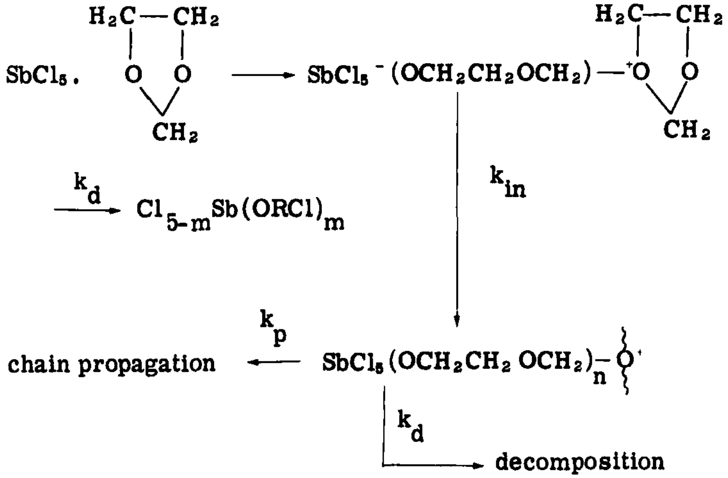


FIG. 10. UV spectra for the polymerization of DIOX (M) initiated by $SbCl_5$ (C) in CH_2Cl_2: (a) 13, (b) 95, and (c) 150 min after the beginning of the experiment. $[M]_0 = 4.7$ mole/liter, $[C]_0 = 1 \times 10^{-3}$ mole/liter. (d) $[M]_0 = 4.7$ mole/liter, $[C]_0 = 0$.



(12)

small part of that of the initiator. Fulfillment of this condition is confirmed by the low polymerization rates in the presence of $SbCl_5$, as in the case $(C_2H_5)_3O^+SbCl_6^-$, and rapid disappearance of the maximum responsible for the $SbCl_5$ absorption in the UV spectrum of the system.

The second way in which the system $SbCl_5$–DiOX differs from the system $(C_2H_5)_3O^+SbCl_6^-$–DiOX, namely, the nonstationary character of the process, associated with the decomposition of active centers during the reaction can be explained by the scheme (12). Indeed, an active center which is formed when polymerization of DiOX is initiated by antimony pentachloride is, evidently; a zwitterion with an asymmetric anion. The stability of such counterion must be lower than that of the symmetrical $SbCl_6^-$. The decomposition of active centers existing as free ions is a bimolecular reaction. In this case, the process can be described by Eq. (13),

$$[M]/V = (k_d/k_p)t + (I/[X]_0 k_p) \qquad (13)$$

where V is the rate of propagation, k_p and k_d are the rate constants of propagation and decomposition, respectively, and $[X]_0$ is the initial concentration of active centers.

Figure 11 shows a plot of the experimental data on polymerization of DiOX initiated by $SbCl_5$ in the coordinates of Eq. (13). The rate of decomposition of active centers in this case cannot be balanced by the too low rate of disproportionation.

To confirm this conclusion, we have carried out the following experiments. On completion of polymerization, the system $SbCl_5$–DiOX in CH_2Cl_2 allowed to stand for 12-16 hr at 20° C, and a new portion of the monomer was introduced. As seen from Fig. 12b, polymerization of the second portion of the monomer proceeds at a steady state. These data indicate that the disproportionation is slow and cannot form sufficient of $SbCl_6^-$ to maintain a steady-state process in the case of $SbCl_5$ (Fig. 12a). Nevertheless, its rate is sufficient for maintaining constant the low concentration of $SbCl_6^-$ in the system $(C_2H_5)_3O^+Sb^-Cl_6$–DiOX.

Since the equilibrium concentration of active centers is low, it is difficult to prove the existence of the disproportionation reaction by a direct physical method. This, however, becomes feasible when an excess of CMEE is introduced into the system. As seen from Fig. 13 if such a system has been allowed to stand for 15-16 hr, the absorption at 272 nm in the UV spectrum noticeably increases. The

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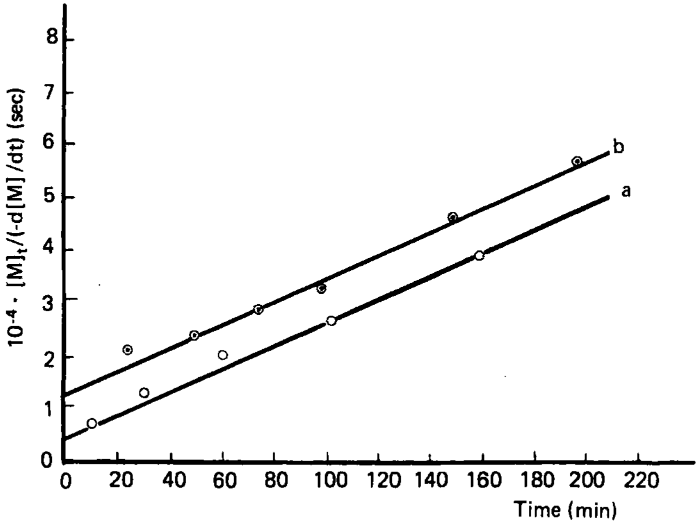

FIG. 11. Plots of $[M]_t/(d[M]t/dt)$ vs t for the polymerization of DiOX (M) initiated by $SbCl_5$ (C) in CH_2Cl_2 at 20°C: (a) $[M]_0 = 4.4$ mole/liter, $[C]_0 = 1.67 \times 10^{-3}$ mole/liter; (b) $[M]_0 = 2.8$ mole/liter, $[C]_0 = 0.65 \times 10^{-3}$ mole/liter.

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presence of CMEE in the system leads to a sharp increase in the concentration of ionic forms through reaction (6), which, in turn, brings about an increase in the rate of disproportionation through reaction (7b).

Polymerization of DiOX initiated by $Cl_4SbOC_2H_5$ (Fig. 14) proceeds at a lower rate than in the case of $SbCl_5$. The shape of the kinetic curve indicates of chain termination. Spectral changes of this system are similar to those of $SbCl_5$–DiOX.

Effect of CMEE on the Process of DiOX Polymerization with $(C_2H_5)_3O^+SbCl_6^-$, $SbCl_5$

CMEE is known to accelerate the DiOX polymerization in the presence of $SbCl_5$ and initiators with the counterion $SbCl_6^-$ [3].

If CMEE is introduced into the $(C_2H_5)_3O^+SbCl_6^-$–DiOX and $SbCl_5$–DiOX systems before the polymerization process, the observed

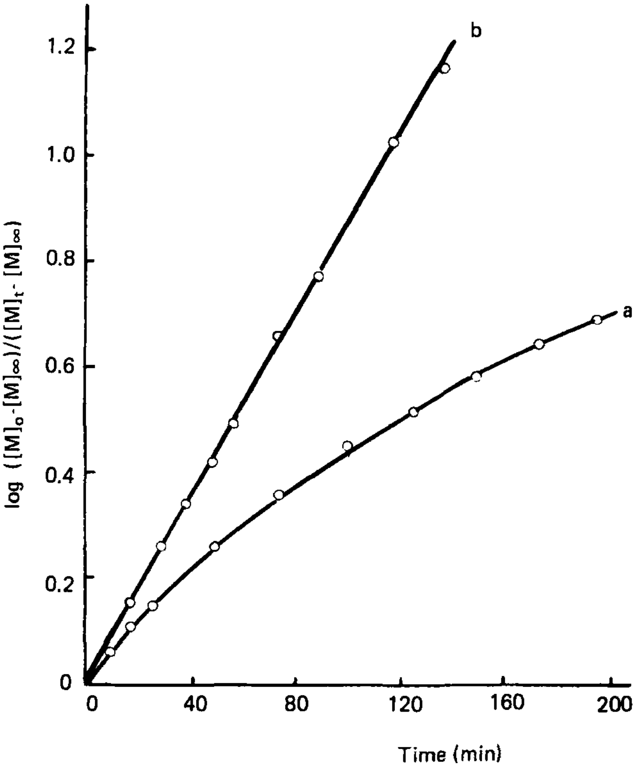

FIG. 12. Kinetic plots for the polymerization of DiOX (M) initiated by $SbCl_5$ (C) in CH_2Cl_2 at 20° C: (a) $[M]_0$ = 4.40 mole/liter, $[C]_0$ = 2.74×10^{3} mole/liter; (b) with the introduction of a new portion of the DiOX 16 hr after the completion of polymerization; $[M]_0$ = 4.40 mole/liter, $[C]_0$ = 2.74×10^{-3} mole/liter.

increase in the process rate is parallel with the increase in the concentration of CMEE (Fig. 15).

Changes in the UV spectra of the two systems show that, in the presence of CMEE, the peak at 272 nm diminishes to a certain residual magnitude and then does not change further in the course of the polymerization. These results indicate that in the presence of CMEE the transformation of $SbCl_5$ to alkoxy derivatives competes with the reaction (14).

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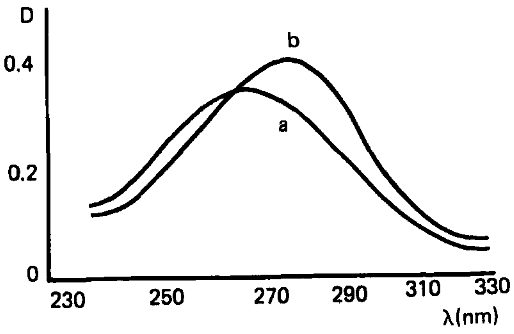

FIG. 13. UV spectra for the system $(C_2H_5)_3O^+Sb^-Cl_6$–DiOX–CMEE relative to the system $(C_2H_5)_3O^+SbCl_6^-$ –DiOX in CH_2Cl_2: (a) after the completion of polymerization; (b) 18 hr after completion of polymerization, $[M]_0 = 6.0$ mole/liter, $[C]_0 = 1.21 \times 10^{-3}$ mole/liter, $[CMEE] = 1.4 \times 10^{-1}$ mole/liter; (c) $[M]_0 = 6.0$ mole/liter, $[C]_0 = 0$.

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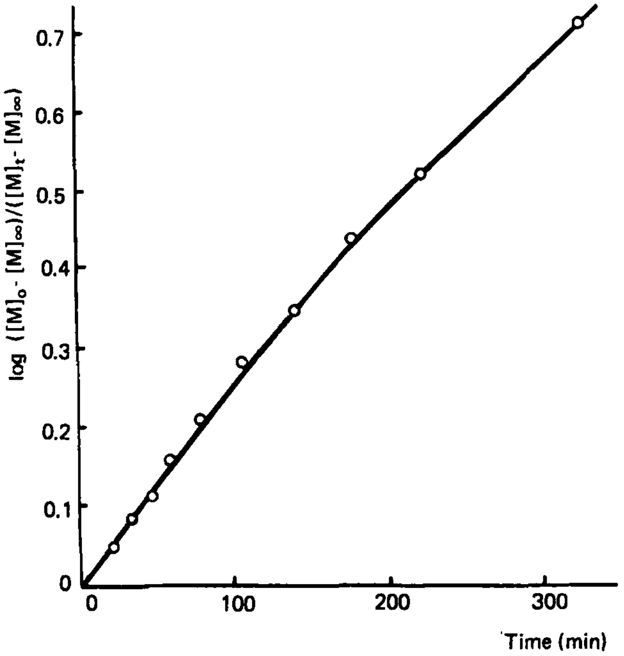


FIG. 14. Kinetic plots for the polymerization of DiOX (M) initiated by $C_2H_5OSbCl_4$ (C) in CH_2Cl_2 at 20° C; $[M]_0 = 5.0$ mole/liter, $[C]_0 = 2.38 \times 10^{-3}$ mole/liter.

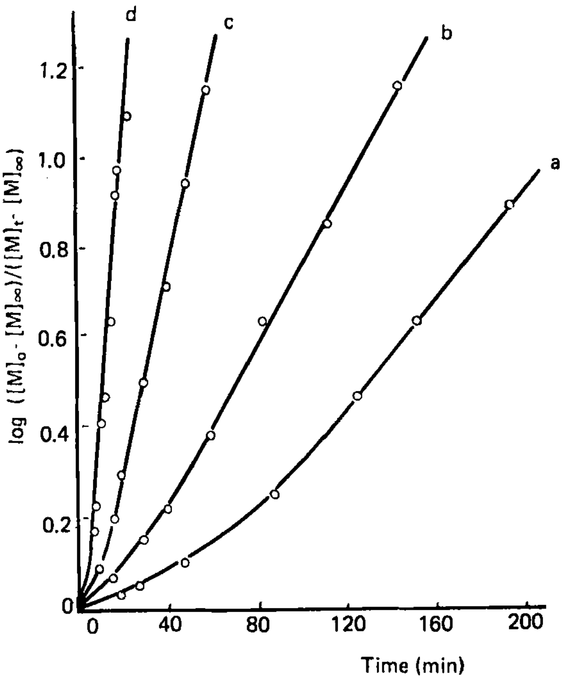
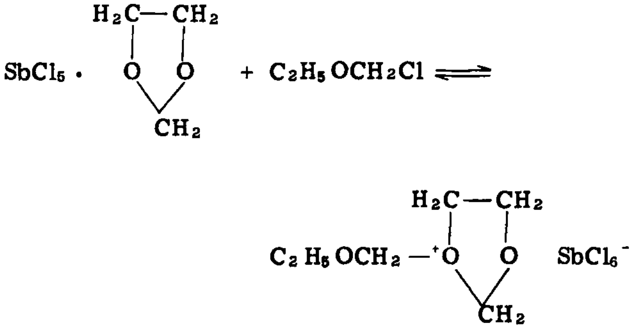


FIG. 15. Kinetic plots for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ (C) in CH_2Cl_2 at 20° C in the presence of CMEE at $[M]_0 = 2.83$ mole/liter, $[C]_0 = 1.1 \times 10^{-3}$ mole/liter: (a) $[CMEE] = 0.9 \times 10^{-2}$ mole/liter; (b) $[CMEE] = 1.97 \times 10^{-2}$ mole/liter; (c) $[CMEE] = 7.8 \times 10^{-2}$ mole/liter; (d) $[CMEE] = 9.65 \times 10^{-2}$ mole/liter.



(14)

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Moreover, an increase in the concentration of CMEE leads to an increase in the rate of reaction (7b). These reactions explain the tendency towards straightening of the polymerization curves in the case of $SbCl_5$ in the presence of CMEE. It is obvious that the introduction of CMEE changes the ratio of the $SbCl_6^-$ and $SbCl_5OR^-$ ions and thus affects the equilibrium of the process.

When DIOX polymerization is initiated by $(C_2H_5)_3O^+SbCl_6^-$, the process remains stationary with varying concentration of CMEE. If the concentration of CMEE is constant, the polymerization proceeds as first order in catalyst (Fig. 16).

Introducing CMEE into the system after the beginning of polymerization causes a smaller increase in the rate than introduction of

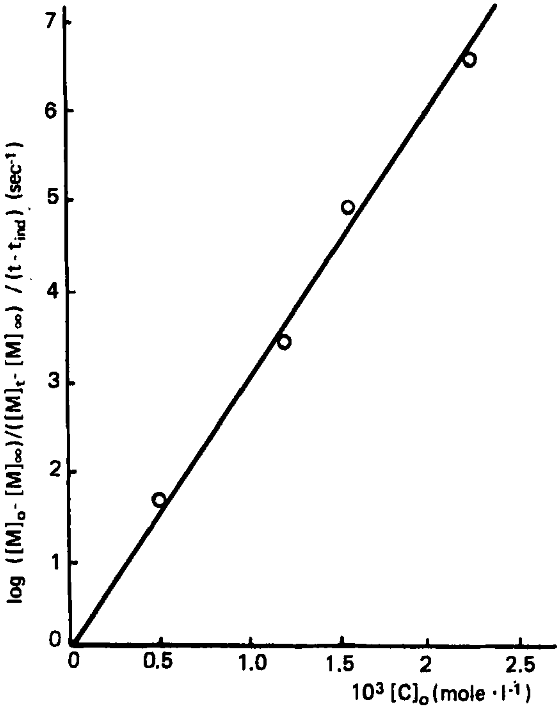

FIG. 16. Plot of log $\{([M]_0 - [M]_\infty)/([M]t - [M]_\infty)\}/(t - t_{ind})$ vs $[C]_0$ for the polymerization of DIOX (M) in the presence of CMEE in CH_2Cl_2 at 20° C; $[M]_0$ = 2.62 mole/liter, [CMEE] = 7.8×10^{-2} mole/liter.

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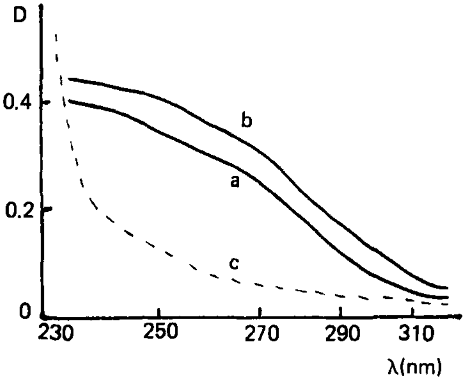

FIG. 17. UV spectra for the polymerization of DiOX (M) initiated by $(C_2H_5)_3O^+SbCl_6^-$ in CH_2Cl_2: (a) before and (b) after introduction of CMEE: (a, b) $[M]_0 = 4.4$ mole/liter, $[C]_0 = 0.94 \times 10^{-3}$ mole/liter, $[CMEE] = 1.98 \times 10^{-2}$ mole/liter; (c) $[M]_0 = 4.4$ mole/liter, $[C]_0 = 0$.

CMEE before the polymerization. In the former case, evidently, most of the $SbCl_5$ has been transformed into chloroalkoxy derivatives, and the increase in the rate is associated mainly with the shift of the equilibrium (6) that is characterized by a smaller constant.

The UV spectrum taken after the introduction of CMEE changes significantly (Fig. 17). As pointed out above, an increase in the absorption at 272 nm resulting from the disproportionation is observed only after the system has been allowed to stand for a long time.

Hydride Transfer in DiOX Polymerization Initiated by $(C_2H_5)_3O^+Sb^-Cl_6$

The authors [7, 10, 11] found that the hydride transfer occurs in DiOX polymerization initiated by trityl salts and came to the conclusion that this reaction is general in character and inherent also to trialkyloxonium salt-DiOX systems.

In our investigation of the DiOX–$(C_2H_5)_3O^+SbCl_6^-$ system we employed the tracer method. Polymerization was initiated by a salt labeled with ^{14}C and then terminated at various stages of conversion. The polymer was reprecipitated and its activity was investigated. The resultant data are presented in Table 1.

TABLE 1

Polymer yield (% of equilibrium yield)	Polymer activity (% of initial activity of catalyst)
13.5	24[a]
51.5	31.6
100	30.3
	36.8
	37.4

[a] With low polymer yield, a too low value of the activity may be obtained due to the loss of the low molecular weight fraction, since the specific radioactivity of the low molecular weight fraction is higher because of increased relative content of labeled endgroups.

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As seen from Table 1, the polymer activity in all the cases was approximately 1/3 the initial activity of the initiator. These data indicate that one ethyl group enters into the polymer chain. If hydride-transfer reactions proceeded [7, 10], active ethyl groups would have entered into the low molecular weight fraction of the reaction products.

Further investigation of the system was carried out by means of GLC techniques. Care has been taken that only the volatile products of the reaction mixture, rather than the reaction mixture itself, should be admitted into the chromatograph (at elevated temperatures the reaction mixture may undergo decomposition).

Analysis of the resultant chromatograms showed that the products originating from hydride-transfer reactions, namely, ethane and β-chloroethyl formate, are absent in the system.

The data obtained in the present study lead to the conclusion that the initiation of DIOX polymerization by trialkyloxonium salts proceeds without hydride-transfer reactions. Analysis of the experimental data published in the literature supports the conclusion that even if such reactions do take place, their contribution to the process is comparatively small and they cannot determine its main direction.

The obtained experimental data are fully in agreement with the scheme suggested in the present paper.

EXPERIMENTAL

1,3-Dioxolane, methylene chloride, ethyl chloride, diethyl ether were prepared, purified, and handled as previously described [6].

$SbCl_5$ was purified by several vacuum distillations. $(C_2H_5)_3O^+SbCl_6^-$ was prepared by direct interaction in vacuo of $(C_2H_5)_2O^+SbCl_5$ and C_2H_5Cl by Meerwein's method [20]. ^{14}C-Labeled $(C_2H_5)_3O^+SbCl_6^-$ was prepared by use of diethyl ether labeled with ^{14}C.

$C_2H_5OCH_2Cl$ was prepared from ethyl alcohol, aqueous CH_2O solution, and gaseous HCl [21]. $Cl_4SbOC_2H_5$ was synthesized by the method of Kolditz and Brink [13]. $ClCH_2CH_2OCHO$ was prepared as described by Palomaa and Herna [22]; its NMR spectra was in agreement with its structure.

The polymerizations were carried out in high vacuum dilatometers.

Differential ultraviolet spectra were recorded on a UV-Vis Specord spectrophotometer; cell thickness 0.1 cm.

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