

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Polymerization of 1,3-Dioxolane Initiated with 1,3-Dioxolenium Salts: Dual Role of the Ambident Initiator

Andrzej Stolarczyk<sup>a</sup>; Przemyslaw Kubisa<sup>a</sup>; Stanislaw Penczek<sup>a</sup>

<sup>a</sup> Center of Molecular and Macromolecular Studies Polish Academy of Sciences, Lodz, Poland

**To cite this Article** Stolarczyk, Andrzej , Kubisa, Przemyslaw and Penczek, Stanislaw(1977) 'Polymerization of 1,3-Dioxolane Initiated with 1,3-Dioxolenium Salts: Dual Role of the Ambident Initiator', *Journal of Macromolecular Science, Part A*, 11: 11, 2047 – 2064

**To link to this Article:** DOI: 10.1080/00222337708061349

**URL:** <http://dx.doi.org/10.1080/00222337708061349>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **Polymerization of 1,3-Dioxolane Initiated with 1,3-Dioxolenium Salts: Dual Role of the Ambident Initiator\***

ANDRZEJ STOLARCZYK, PRZEMYSŁAW KUBISA, and  
STANISŁAW PENCZEK

Center of Molecular and Macromolecular Studies  
Polish Academy of Sciences  
90-362 Łódź, Poland

### ABSTRACT

1,3-Dioxolenium salts (1,3-dioxolane-2-ylum cations) with stable anions (e.g.,  $\text{AsF}_6^-$ ,  $\text{PF}_6^-$ , or  $\text{SbF}_6^-$ ) are quantitatively formed in the reaction of 1,3-dioxolane with triphenylmethyl cations bearing corresponding anions. This reaction precedes the actual initiation process, involving simultaneous reaction of dioxolenium salts with dioxolane and with already formed polydioxolane. The first product of the former reaction could not directly be observed, and only its product of  $\text{H}^-$  transfer was isolated and characterized. Reaction of the 1,3-dioxolenium salt with polymer segments is very much faster and, because of the ambident reactivity of this salt, proceeds, at the different position than its reaction with monomer. As a model of polymer segment diethoxymethane was used. A reversible process, leading to diethoxymethyl cation is, according to the GLC studies, accompanied by another reaction in which the

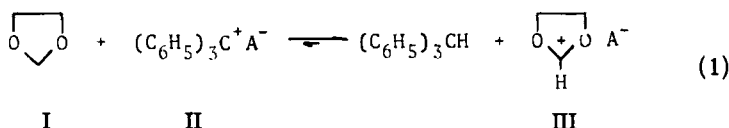
---

\*Presented in part at the 23rd IUPAC Macromolecular Congress, Boston 1971, and at the 3rd International Symposium on Cationic Polymerization, Rouen, 1973.

$C_2H_5O^{\cdots+}CH_2$  cation is formed. This cation is eventually responsible for a fast initiation on a polymer segment.

### INTRODUCTION

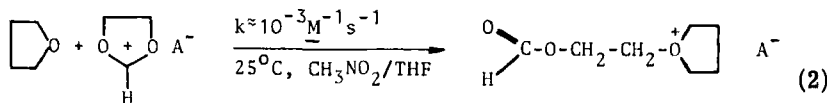
In the polymerization of 1,3-dioxolane (I) initiated by triphenylmethyl salts bearing various anions  $A^-$  (II) the 1,3-dioxolane-2-ylidium (1,3-dioxolenium) salts (III) are formed in the initiation step as intermediates [1, 2].



Preliminary results and tentative explanations concerning the polymerization of I initiated by II and III were given in a review paper published by one of us in 1974 [3].

Hydride-ion transfer reactions, studied by Meerwein et al. [4] and described in recently published reviews [5, 6] also precede the true initiation in polymerizations of tetrahydrofuran [7] and  $\beta$ -propiolactone [8] initiated by II.

We have recently used 1,3-dioxolane-2-ylidium salts ( $III A^-$ ) with different anions ( $A^- = AsF_6^-, PF_6^-,$  and  $SbF_6^-$ ) as convenient initiators for the polymerization of tetrahydrofuran [9] and cyclic esters of phosphoric acid [10]. In both systems initiation proceeds quantitatively by simple nucleophilic attack of monomer on  $C^4$  (or  $C^5$ ) in III with simultaneous ring-opening between  $O^1-C^5$  (or  $O^3-C^4$ ). Thus, for THF:



Reaction (2) was the only process observed in the initiation of THF and the ambident properties of III (reaction at  $C^2$  and at  $C^4$ ) were not revealed in this particular system.

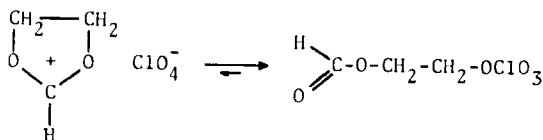
In the present work we describe kinetics and mechanism of initiation of the polymerization of I with  $III A^-$  ( $A^- = AsF_6^-$  and  $SbF_6^-$ ), where the ambident properties of III are responsible for an unusual

reaction path, including a slow reaction of III with I and fast reaction of III with poly-I.

## RESULTS AND DISCUSSION

III  $\text{AsF}_6^-$  and III  $\text{SbF}_6^-$ , prepared as described above, were stable in the solid state for months. Solutions of these salts in  $\text{CH}_3\text{NO}_2$  solvent were also stable, as evidenced from  $^1\text{H-NMR}$  spectra; no new peaks appeared during a prolonged storage of the freshly prepared solutions.

The perchlorate of III, III  $\text{ClO}_4^-$  decomposes in solution to the corresponding ester: ethyleneglycol-1-formate-2-perchlorate. The latter compound was identified by its  $^1\text{H-NMR}$  spectrum, consisting of a



typical AA'BB' pattern for two methylene groups (a multiplet, including four distorted triplets  $\delta$  from 4.2 to 5.0 ppm) and a singlet of a formate proton at  $\delta$  8.1 ppm.

Thus, for a study of reactions between III and I stable III  $\text{SbF}_6^-$  was selected.

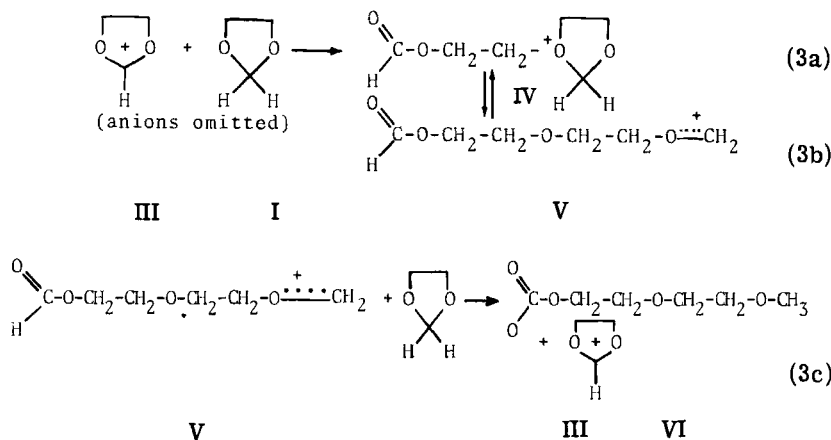
### Cationation of 1,3-Dioxolane with 1,3-Dioxolenium Hexafluoroantimonate

#### Reaction Products

In a typical experiment, 0.5 mole/liter solution of III  $\text{SbF}_6^-$  was mixed with 1.5 mole/liter solution of I in  $\text{CD}_3\text{NO}_2$  solvent at  $25^\circ\text{C}$ . At these conditions no high polymer of I can be formed (ceiling concentration of I at  $25^\circ\text{C}$  is equal to 2.0 mole/liter [11]). Surprisingly, 0.5 mole/liter of the  $>\text{C}^+-\text{H}$  protons, absorbing at  $\delta$  9.25 ppm was converted into more than 1.0 mole/liter of formate protons

$$\begin{array}{c} \text{O} \\ || \\ \text{H-C-O-} \end{array}$$
 , absorbing at  $\delta$  8.1 ppm), and indicating, that simple stoichiometry, as described, e.g., for cationation of THF by Eq. (2), is not obeyed for cationation of I. Thus, every mole of III  $\text{SbF}_6^-$  originally used produces one formate group and gives back one mole of III  $\text{SbF}_6^-$  under the conditions specified above.

This is possible, provided that the first reaction product abstracts  $H^-$  anion from I [Eqs. (3)].



Scheme (3a)-(3c) requires that methoxydiethyleneglycolformate VI is formed.

This last conclusion is in agreement with  $^1H$ -NMR spectrum of the reaction mixture of III  $SbF_6^-$  and I, when the reaction goes nearly to completion. This is shown in Fig. 1 and compared with the NMR spectrum of the original sample of IV prepared from diethylene-glycol monomethyl ether and formic acid. The main assignments are given in Fig. 1.

Although the spectra of the original sample of VI and of the reaction product of III  $SbF_6^-$  with I are not identical, the ratio of formate protons to methoxy protons is very close to the expected value of 1:3. In Fig. 1b two kinds (at least) of  $-O-CH_3$  groups are clearly observed. This can be due to the presence of higher oligomer analogs of VI. The last "generation" of III  $SbF_6^-$  formed, having no more I available to cationate, cationates the linear molecules like VI; protons involved in these oxonium ions can absorb in the region covered by  $CD_nH_{3-n}NO_2$  present in  $CD_3NO_2$ , used as a solvent.

The mass spectrum of the original sample and the mass spectrum of the product with the same GLC retention time, and formed in the reaction between III  $SbF_6^-$  and I ( $[III\ SbF_6^-] = 1.6$  mole/liter,  $[I] = 1.7$  mole/liter) are shown together in Fig. 2. These spectra are compared with a spectrum of the compound producing a GLC peak with the same retention time and separated from the polymerization mixture (polymerization conditions  $[I] = 3.0$  mole/liter,  $[III\ SbF_6^-] = 10^{-3}$  mole/liter,  $25^\circ C$ ,  $CH_2Cl_2$  solvent), this is given in Fig. 2c. The fragmentation

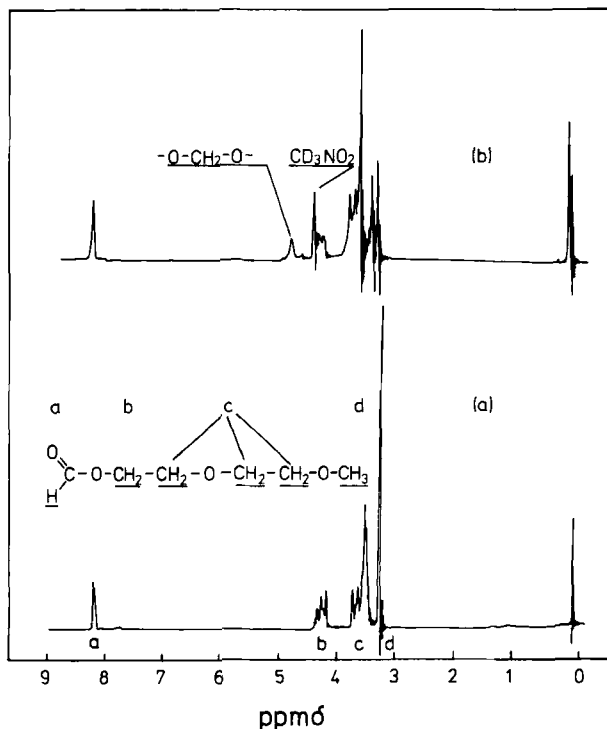
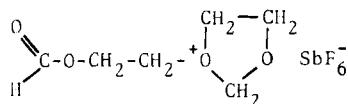


FIG. 1. <sup>1</sup>H-NMR spectrum of (a) O=CHOCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub> (VI) neat compared with (b) spectrum of the reaction product of 2.0 mole/liter of I with 0.5 mole/liter of III SbF<sub>6</sub><sup>-</sup> in CD<sub>3</sub>NO<sub>2</sub> solvent, 25° C.

pattern, explaining the origin of the major sets of peaks in the mass spectrum shown in Fig. 2 is given in Fig. 3. Thus, combined <sup>1</sup>H-NMR and GLC-MS data indicate that the reaction between III SbF<sub>6</sub><sup>-</sup> and I proceeds [e. g., Eq. (3)] through the first cationation product, IV,



IV

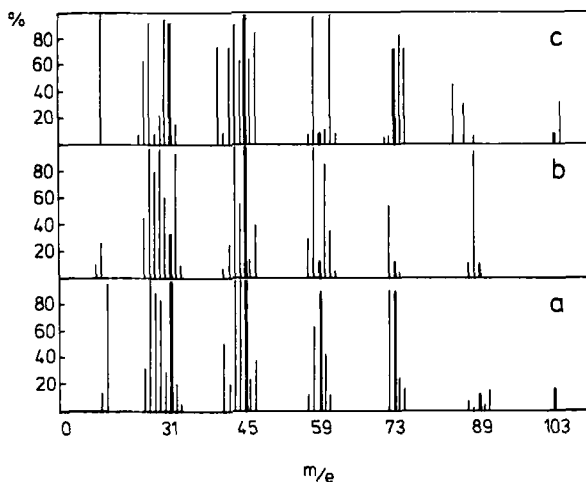


FIG. 2. Mass spectrum of (a)  $\text{O}=\text{CHOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3$  (VI) compared with (b) mass spectra of VI found by GLC in the reaction product of I with III  $\text{SbF}_6^-$  and (c) VI isolated by GLC from the polymerization mixture.

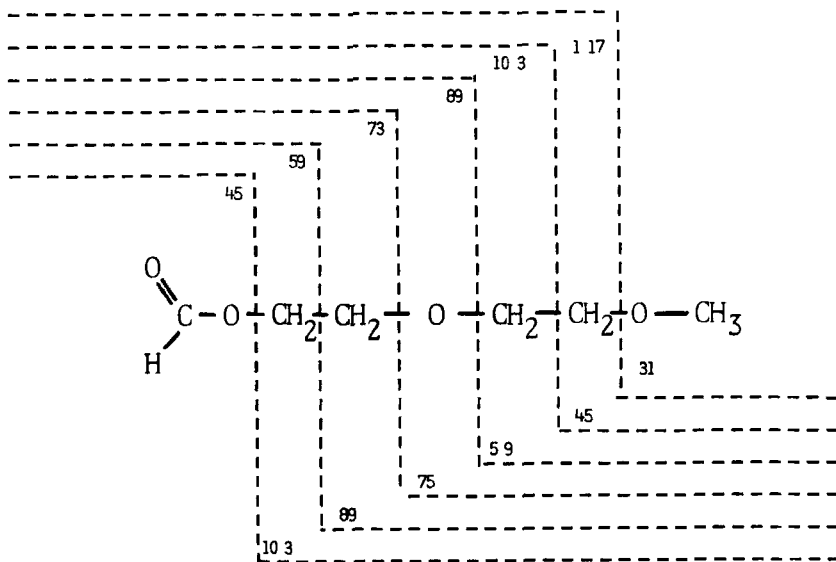
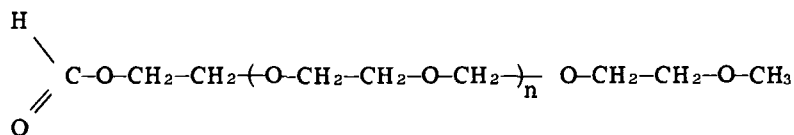


FIG. 3. Fragmentation pattern explaining the origin of the major sets of peaks in the mass spectrum shown in Fig. 2.

identical to that observed in the cationation of THF [ Eq. (2)]. This first cationation product, the tertiary oxonium ion (IV), cannot directly be observed because it rearranges rapidly into the corresponding alkoxycarbenium ion [ Eq. (3b)]. This one abstracts  $H^-$  anion from I or converts into the tertiary oxonium ion, linear or cyclic, depending on the polymer/monomer ratio. Apparently, both rearrangement and  $H^-$  transfer reactions are faster than the cationation processes. Above the ceiling conditions, when the living polymer  $\rightleftharpoons$  monomer equilibrium is shifted to the monomer side, the  $H^-$  transfer would dominate, resulting in short-chain oligomers of the general structure:

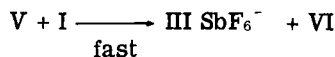
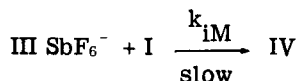


The average value of "n" can be judged on the basis of the ratio of two integrated peak areas: the  $\delta$  4.85 ppm (s) band, characteristic of polymeric  $-\text{O-CH}_2\text{-O-}$ , and  $\delta$  8.1 ppm, giving the concentration of the end groups (Fig. 1).

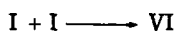
#### Kinetics of Cationation of I with III $\text{SbF}_6^-$

As shown in the previous section, in the cationation of I every cationated molecule of I re-forms one molecule of III  $\text{SbF}_6^-$ , apparently with the rate exceeding the rate of cationation.

Thus the scheme (3a)-(3c) can be rewritten in the following way:



Summing up the left-hand side parts of equations in scheme (4) and the right-hand sides one gets the following formal equation:





Thus scheme (4) is kinetically equivalent to the following equalities:  $[III\ SbF_6^-] = [III\ SbF_6^-]_0 = \text{constant}$ , and  $[I] = [I]_0 - 2[VI]$ . On the basis of the scheme (4) and the equalities formulated above, the kinetic scheme reads:

$$d[VI]/dt = k_{iM}[III\ SbF_6^-][I] \quad (5a)$$

$$= k_{iM}[III\ SbF_6^-]([I]_0 - 2[VI]) \quad (5b)$$

and, eventually for the rate constant of cationation  $k_{iM}$  we have:

$$k_{iM} = \ln \{ [I]_0 / ([I]_0 - 2[VI]) \} / 2[III\ SbF_6^-]_0 \cdot t \quad (6)$$

where  $k_{iM}$  is the rate constant of initiation on monomer. In order to ensure that both scheme (4) and Eq. (6) would be valid for the treatment of kinetic data, low concentration of I (much below its ceiling value) and concentration of  $III\ SbF_6^-$  exceeding that of I were used.

The data of one typical kinetic run are given in Table 1. According to Eq. (6), to calculate  $k_{iM}$  the concentration of a product (VI) for given times  $t$  should be measured. This is proportional to the integral of the singlet at  $\delta\ 8.1$  ppm ( $\begin{matrix} O \\ \parallel \\ H-C- \end{matrix}$ ) while at  $\delta\ 5.5$  ppm we observe the four protons of the methylene groups of  $III\ SbF_6^-$ . The starting concentration of  $III\ SbF_6^-$  ( $[III\ SbF_6^-]_0$ ) is known and does not change within a kinetic run, according to the constancy of integration at  $\delta\ 5.5$  ppm (Table 1). To determine the actual concentration of VI, the integration at  $\delta\ 5.5$  ppm (proportional to  $[I\ SbF_6^-]$ ) was used as an internal standard. The rate constant  $k_{iM}$  was calculated according to Eq. (6) for several experimental points and the average value is given in Table 1, containing in addition the original integration peak areas, expressed in mm of the integration line heights.

In a similar way rate constants  $k_{iM}$  at 35, 10 and 0°C were determined and from these results, plotted in Fig. 4 as a function of  $1/T$ , the corresponding activation parameters were calculated:  $\Delta H_{iM}^\ddagger = 23.3 \pm 3.0$  kcal/mole,  $\Delta S_{iM}^\ddagger = 9.5 \pm 7.0$  cal/deg-mole. These values can be compared with the corresponding activation parameters of cationation of acetonitrile with  $III\ SbF_6^-$  (giving  $O=CHO-CH_2-CH_2-\dot{N}\equiv C-CH_3\ SbF_6^-$ )  $\Delta H^\ddagger \simeq 20$  kcal/mole,  $\Delta S^\ddagger \simeq 0$  [12]. Thus, cationation of I with  $III\ SbF_6^-$ , being a first step in the

TABLE 1. Kinetics of Cationation of 1,3-Dioxolan (I) with 1,3-Dioxolan-2-ylum Salt (III SbF<sub>6</sub><sup>-</sup>) Studied by the <sup>1</sup>H-NMR Method<sup>a</sup>

Time × 10 <sup>-3</sup> (sec)	Area under peak (arbitrary units)		Concentration (mole/liter)		k <sub>iM</sub> × 10 <sup>4</sup> (mole/liter- sec)
	8.1 ppm	5.5 ppm	[VI]	[I]	
1.50	2.5	118	0.07	0.52	1.90
4.05	6.5	124	0.17	0.32	2.05
5.55	8.5	124	0.22	0.22	2.60
7.03	9.5	122	0.26	0.14	2.05
11.59	12.0	124	0.32	0.02	2.85
	(1H)	(4H)		Avg.	2.3 × 10 <sup>-4</sup>

<sup>a</sup>CD<sub>3</sub>NO<sub>2</sub> solvent; 25°C; [I]<sub>0</sub> = 0.66 mole/liter; [III SbF<sub>6</sub><sup>-</sup>] = 0.83 mole/liter.

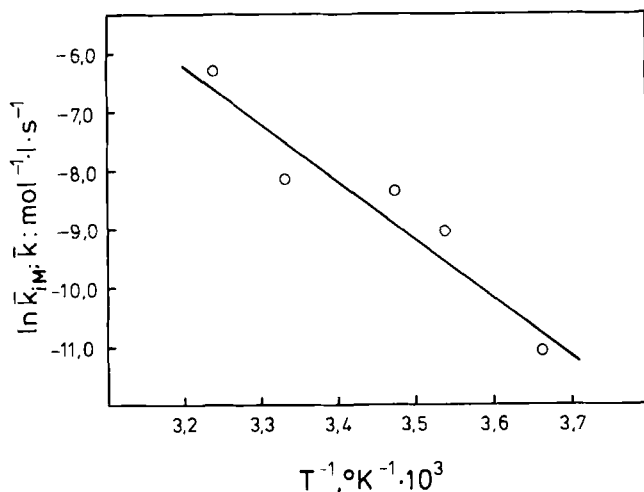


FIG. 4. Dependence of the average rate constant of cationation of 1,3-dioxolane (I) with 1,3-dioxolane-2-ylum hexafluoroantimonate (and/or hexafluoroarsenate) (III SbF<sub>6</sub><sup>-</sup> and III AsF<sub>6</sub><sup>-</sup>) on reciprocal of absolute temperature.

real initiation process, is a slow reaction. Its rate constant  $k_{iM} \approx 10^{-4}$  mole/liter-sec at 25°C is approximately  $10^6$  times lower than the rate constant of propagation of I [3].

Before the present measurements gave the value of the rate constant of cationation and revealed that this is a slow reaction in comparison with a chain propagation, the rate of this process was estimated on the basis of non-direct observations by Plesch [13] and Enikolopian [14]. The former assumed cationation by dioxolenium salt to be a very slow reaction, while the latter author had expected that the rate of cationation could be comparable to that of propagation.

### Reaction of Dioxolenium salt with Diethoxymethane as a Model for Polydioxolane (Poly-I)

#### Reaction Products

For a low ratio of  $k_i/k_p$ , some initiator is left when more or less of polymer is already formed. The proportion of initiator used, before an appreciable amount of monomer becomes converted into a polymer, depends on the starting concentration of initiator and on the above ratio of rate constants [15]. Thus, we report in this section on the reaction between III  $\text{SbF}_6^-$  and diethoxymethane VII as a model for a mer of poly-I:



VII



poly-I

Reaction between III  $\text{SbF}_6^-$  and VII was studied in  $^1\text{H-NMR}$ . In a typical experiment, III  $\text{SbF}_6^-$  (2.0 mole/liter) was mixed with VII (2.1 mole/liter) in liquid  $\text{SO}_2$  solvent at  $-20^\circ\text{C}$  and the  $^1\text{H-NMR}$  spectra were monitored.

In Fig. 5 the final spectrum of the mixture of III  $\text{SbF}_6^-$  and VII is shown. By final we mean a spectrum which does not change with time at given temperature. It was shown, however, that by changing temperature the proportion of substrates and products also changes, indicating an equilibrium process. Interpretation of the spectra is given directly in the corresponding figure.

#### Kinetics of reaction of III $\text{SbF}_6^-$ with VII

Formally, this reaction (7) is a direct  $\text{H}^-$  transfer; however, it is too fast to proceed this simple way. As outlined in Eq. (8), we prepared methoxycarbenium hexafluoroantimonate ( $\text{CH}_3\text{OCH}_2^+\text{SbF}_6^-$ ), a powerful  $\text{H}^-$  abstracting agent which below  $-30^\circ\text{C}$  does not abstract  $\text{H}^-$  from diethoxymethane at a measurable rate [16].

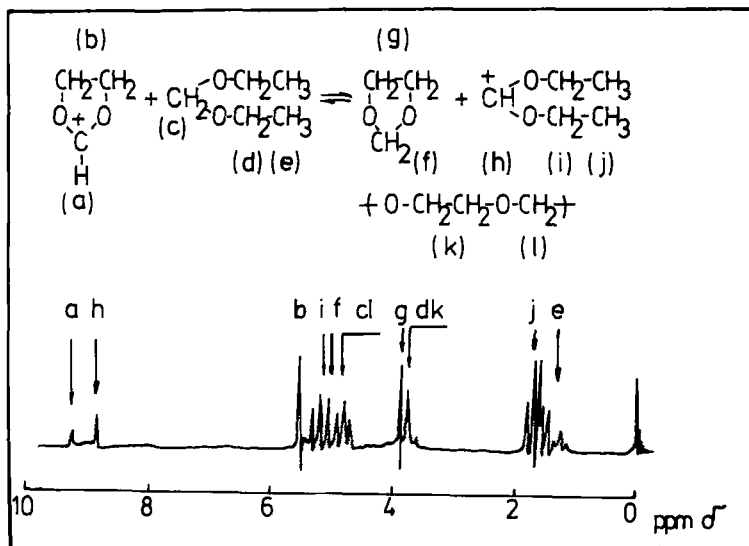
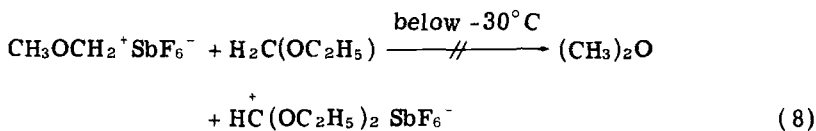
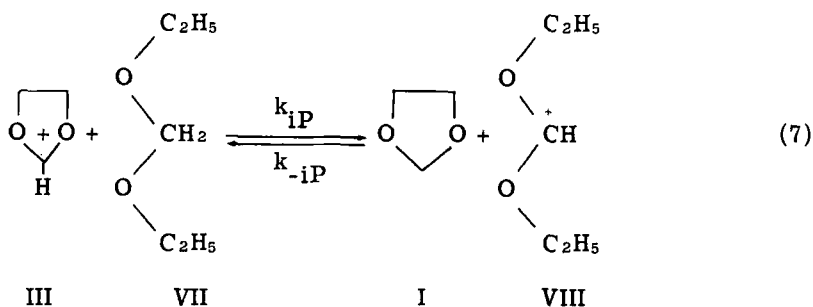


FIG. 5.  $^1\text{H-NMR}$  spectrum of the reaction mixture of 2.0 mole/liter of III  $\text{SbF}_6^-$  with 2.1 mole/liter of VII at equilibrium in liquid  $\text{SO}_2$  solvent,  $-20^\circ\text{C}$ .



Thus, reaction between III  $\text{SbF}_6^-$  and VII obviously proceeds by a multistep mechanism, and rate constants  $k_{iP}$  and  $k_{-iP}$  are not related

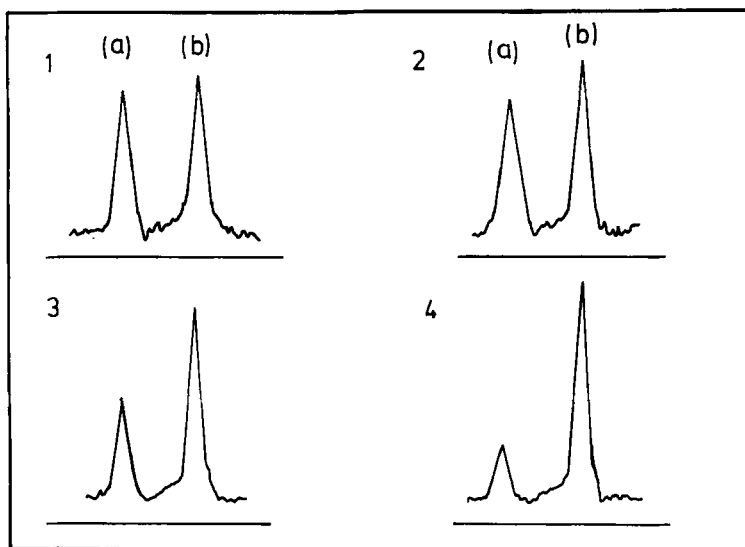


FIG. 6.  $^1\text{H-NMR}$  spectra of the reaction mixture of III  $\text{SbF}_6^-$  and VII (8.5-9.5 ppm region) at different reaction times: (1) 29 min; (2) 40 min; (3) 100 min; (4) 155 min. Peak (a) is  $\delta$  9.25 ppm; peak (b) is  $\delta$  8.85 ppm; liquid  $\text{SO}_2$ ,  $-70^\circ\text{C}$ .

to any individual reaction, being only the effective rate constants of III + VII  $\rightleftharpoons$  I + VIII interconversion.

The kinetics of reaction (8) was followed by observation of the disappearance of a singlet at  $\delta$  9.25 ppm (proton at  $\text{C}^2$  in III  $\text{SbF}_6^-$ ) and appearance of a singlet at  $\delta$  8.85 ppm (proton  $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}$  in VIII).

A sum of integrals at  $\delta$  9.25 ppm and  $\delta$  8.85 ppm was used as an internal standard for calculations.

Figure 6 shows a typical change of the  $^1\text{H-NMR}$  spectrum during the kinetic run.

The rate constant of the forward reaction was calculated from the equation of reversible reactions:

$$\ln \frac{([\text{III SbF}_6^-]_0 - [\text{III SbF}_6^-]_e) ([\text{III SbF}_6^-]_t - [\text{III SbF}_6^-]_e + Q)}{([\text{III SbF}_6^-]_t - [\text{III SbF}_6^-]_e) ([\text{III SbF}_6^-]_0 - [\text{III SbF}_6^-]_e + Q)} = (k_{iP} - k_{-iP}) \cdot Q \cdot t$$

where

$$Q = 1/(K - 1) \sqrt{K^2 ([VII]_0 - [III SbF_6^-]_0)^2 + 4[III SbF_6^-]_0 [VII]_0 K}$$

$$K = k_{iP}/k_{-iP} \quad (9)$$

$[III SbF_6^-]_e$  and  $[XII]_e$  for a given temperature were determined directly from the integrated peak areas after equilibrium had been established. In equilibrium  $[VII]_e = [VII]_0 - [VIII]_e$  and  $[I]_e = [VIII]_e$ ; thus,  $K = k_{iP}/k_{-iP}$  can simply be calculated as:

$$K = \frac{[III SbF_6^-]_e ([VII]_0 - [VIII]_e)}{[VIII]_e^2}$$

A plot of the left-hand side of Eq. (9) against  $Q t$  gives a straight line with a slope equal to  $k_{iP} - k_{-iP}$  (Fig. 7). Thus, both rate constants can be calculated from  $k_{iP} - k_{-iP}$  and  $k_{iP}/k_{-iP}$ . These values are equal to:

$$k_{iP} = 4.7 \times 10^{-4} \text{ liter/mole-sec}$$

and

$$k_{-iP} = 1.0 \times 10^{-5} \text{ liter/mole-sec } (-50^\circ \text{C, SO}_2)$$

From the dependence of  $\ln k_{iP}$  on reciprocal temperature (Fig. 8), the value of  $k_{iP}$  at room temperature was determined as  $k_{iP} = 3.10^{-1}$  liter/mole-sec ( $25^\circ \text{C, SO}_2$ ).

#### Mechanism of Reaction of $III SbF_6^-$ with VII

Reaction of  $III SbF_6^-$  with VII proceeds with a rate constant higher by a factor of  $10^3$  than the rate constant of reaction of  $III SbF_6^-$  with I. This is in agreement with conclusions coming from the studies of kinetics of polymerization of I initiated by  $III SbF_6^-$ , where the kinetic

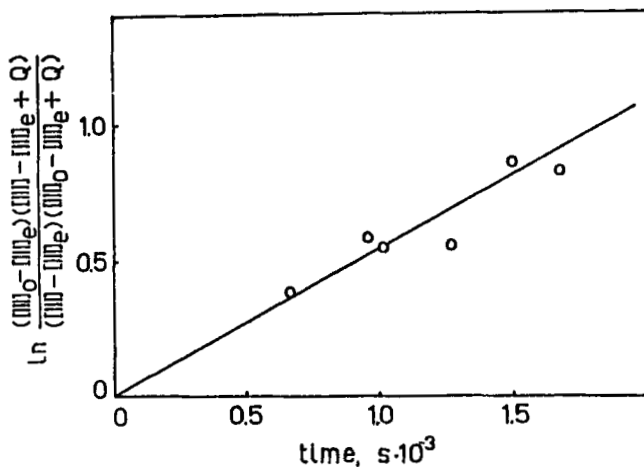


FIG. 7. Plot of equation describing the second-order reversible reaction of III  $\text{SbF}_6^-$  with VII; liquid  $\text{SO}_2$ ,  $-50^\circ\text{C}$ .

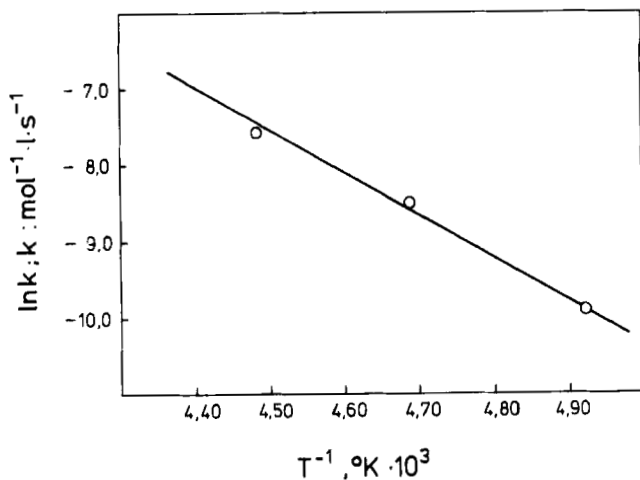
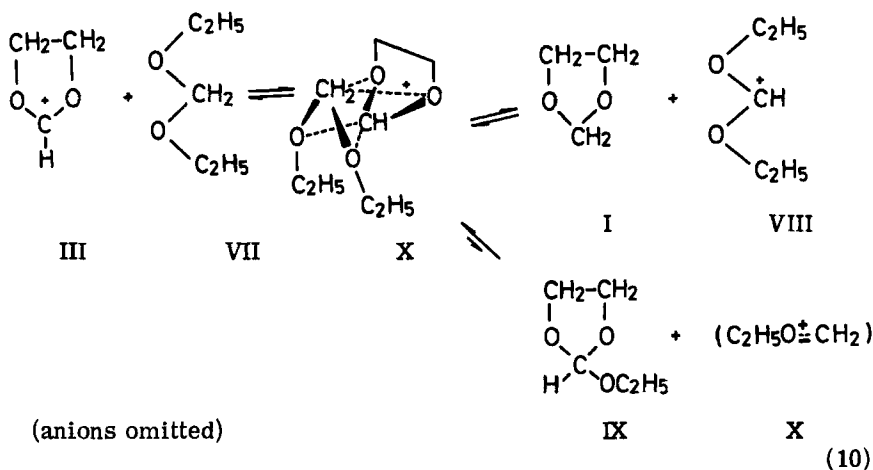


FIG. 8. Dependence of the logarithm of the rate constant  $k_{1P}$  for reaction of III  $\text{SbF}_6^-$  with VII, on reciprocal of the absolute temperature.

curves may be described quantitatively by a formal kinetic scheme involving slow initiation on I and the fast initiation on poly-I [ 3 ].

On the basis of model studies of the reaction between III  $\text{SbF}_6^-$  and VII it is difficult to propose the detailed chemical path of initiation involving poly-I, because the only products which have been directly identified at model conditions on the basis of their NMR spectra, are I and VIII. On the other hand GLC analysis of the products of reaction of III  $\text{SbF}_6^-$  with VII, which was stopped at its early stage by addition of sodium phenoxide, shows the presence of a compound with the same retention time as independently prepared 2-ethoxy-1,3-dioxolane IX.

Thus, we propose the following tentative explanation of the observed phenomena. Reaction of III  $\text{SbF}_6^-$  with VII proceeds through an intermediate solvation product, which, at model conditions, when  $[\text{VII}] \approx [\text{III SbF}_6^-]$  rearranged reversibly to I and XII but at the polymerization conditions may form active species as a result of trapping of very reactive intermediate  $-\text{O}-\text{CH}_2^+$  ions by a large excess of I.



Reaction of X with I is expected to be very fast; thus the rate-determining step in the initiation on poly-I should be that of formation of X. If both VIII and X are indeed formed by rearrangement of the same transient product, then the rate constant of initiation on poly-I should be at least as high as  $k_{iP}$ . This is in good agreement with results derived from studies of polymerization kinetics, showing that the rate constant of initiation is much higher than the rate constant of cationation of I with III  $\text{SbF}_6^-$  ( $k_{iM}$ ).



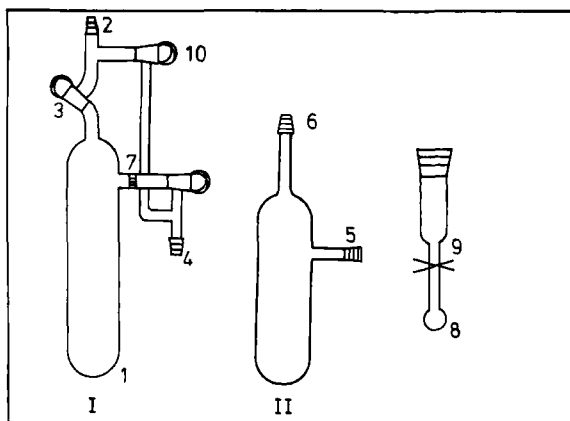


FIG. 9. Reaction apparatus used for synthesis, purification and distribution into vials of 1,3-dioxolane-2-ylum salts. Explanations for numbers given in Experimental Section.

### EXPERIMENTAL

Purification of I, II, and  $\text{CH}_2\text{Cl}_2$  has been described earlier [2].

$\text{CH}_3\text{NO}_2$  and  $\text{CD}_3\text{NO}_2$  (VEB-Berlin Chemie) were fractionally distilled several times under vacuum in the presence of  $\text{CaH}_2$ .

III  $\text{A}^-$  (where  $\text{A}^- = \text{AsF}_6^-$  or  $\text{SbF}_6^-$ ) were prepared by a slight modification of the method described for III  $\text{SbCl}_6^-$  [2]. A 3-g portion ( $6 \times 10^{-3}$  mole) of purified II  $\text{SbF}_6^-$  (commercial product from Ozark-Mahoning, Tulsa, Oklahoma) was dissolved in  $\text{CH}_2\text{Cl}_2$  and precipitated by  $\text{CCl}_4$  checked to have  $\epsilon_{\text{max}} = 4 \times 10^4 \pm 0.4 \times 10^4$  in  $\text{CH}_2\text{Cl}_2$  solution

( $\lambda_{\text{max}} = 427 \text{ nm}$ ), was transferred quickly into tube 1 (Fig. 9). The whole apparatus shown in Fig. 9 was then attached through joint 2 to the vacuum line and pumped until the gaseous products were removed. Then, 40 ml of  $\text{CH}_2\text{Cl}_2$  was distilled from the black-painted vacuum container in which  $\text{CH}_2\text{Cl}_2$  was stored over  $\text{CaH}_2$ . A 1.5-g portion ( $2 \times 10^{-2}$  mole) of I, stored in the vacuum reservoir over a liquid Na/K alloy, was vacuum-distilled into the solution prepared in this way, giving a 0.15 mole/liter solution of I in  $\text{CH}_2\text{Cl}_2$ . After a few minutes at  $0^\circ\text{C}$ , III  $\text{SbF}_6^-$  started to precipitate; in 30 min at room temperature the yellow color of II cation had disappeared, and the reaction was assumed to be completed after a further 30 min. After closing a Teflon-glass stopcock (3), the whole apparatus I was removed from the line and attached through cone 4, in the inclined

position, to socket 5 of the adapter II. This adapter was attached to the vacuum line through the cone 6. By using this adapter the solution was removed through the sintered glass (7) and the solid III  $\text{SbF}_6^-$  was left in the apparatus I. This procedure was repeated many times, using fresh portions of  $\text{CH}_2\text{Cl}_2$  until III  $\text{SbF}_6^-$  became white (usually 4-5 times).

After drying, III  $\text{SbF}_6^-$  was distributed under vacuum into vials 8 connected with I through cone 2 and weighed after sealing off at 9. The vials were evacuated before distribution through stopcock 10.

VII was purified by fractional distillation (Perkin-Elmer 151 spinning band column) and stored over liquid Na/K alloy.

IX was prepared according to Baganz and Domaschke [17], and VIII according to Olah and Svoboda [18].

The  $^1\text{H-NMR}$  spectra were obtained with a 60 MHz Jeol  $^1\text{H-NMR}$  spectrometer. All the NMR data are given as  $\delta$  in ppm from TMS (internal standard).

Mass spectra were obtained with a LKB 9000 F mass spectrometer at 70 eV. The spectrometer was coupled with a PDP 8e computer.

The GLC Cvet Model 2-65 with a dual column and flame ionization detection was used at  $130^\circ\text{C}$  with a 2 m column, 10% OV-17 on Gaschrom Q 100/120 mesh support.

The kinetics of cationation was studied in evacuated, sealed NMR tubes with the Jeol apparatus.

#### REFERENCES

- [1] S. Słomkowski and S. Penczek, *Chem. Commun.* 1970, 1347.
- [2] P. Kubisa and S. Penczek, *Makromol. Chem.*, **144**, 169 (1971).
- [3] S. Penczek, *Makromol. Chem.*, **175**, 1217 (1974).
- [4] H. Meerwein, V. Hederick, H. Morschel, and K. Wunderlich, *Liebigs Ann. Chem.*, **635**, 1 (1960).
- [5] C. U. Pittman, Jr., S. P. McManus, and J. W. Larsen, *Chem. Rev.*, **72**, 357 (1972).
- [6] H. Perst, *Oxonium Ions in Organic Chemistry*, Verlag Chemie and Academic Press, New York, 1971.
- [7] M. P. Dreyfuss, J. C. Westfahl and P. Dreyfuss, paper presented to Division of Polymer Chemistry, American Chemical Society, 1966; *Polym. Preprints*, **7**(2), 413 (1966); *Macromolecules*, **1**, 437 (1969).
- [8] K. Ito, T. Inoue, and Y. Yamashita, *Makromol. Chem.*, **117**, 279 (1968).
- [9] K. Matyjaszewski and S. Penczek, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1905 (1974).
- [10] G. Łapienis and S. Penczek, *Macromolecules*, **7**, 166 (1974).

- [ 11 ] P. Kubisa, Ph. D. Thesis, Lódź, 1969.
- [ 12 ] P. Kubisa, Bull. Acad. Polon. Sci., Ser. Sci. Chem., **25**, 627 (1977).
- [ 13 ] F. R. Jones and P. H. Plesch, Chem. Commun. 1969, 1231.
- [ 14 ] O. A. Plechova, V. V. Ivanov, T. I. Prokofieva, E. F. Olejnik, and N. S. Enikolopian, Vysokomol. Soedin., **15A**, 14 (1973).
- [ 15 ] M. Szwarc, Makromol. Chem., **35A**, 123 (1960).
- [ 16 ] R. Szymański and S. Penczek, to be published.
- [ 17 ] H. Baganz and L. Domaschke, Chem. Ber., **91**, 650 (1958).
- [ 18 ] G. Olah and J. A. Svoboda, Synthesis, 1973, 490.

Accepted by editor May 15, 1977

Received for publication June 24, 1977