INITIATION OF OLIGOMERISATIONS OF METHYLOXIRANE BY TRIPHENYLMETHYL SALTS CONTAINING PAIR ANIONS $SbCl_6^-$ AND AsF_6^-

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Received March 27th, 1980

Initiation of oligomerisations of methyloxirane (1,2-epoxypropane) by $Ph_3C^+SbCl_6^-$ and $Ph_3C^+AsF_6^-$ ($Ph = C_6H_5$) has been studied by spectral methods and by chemical analysis of the reaction mixtures and reaction products. The results obtained indicate that the triphenylmethyl salts react with methyloxirane simultaneously in two ways: *a*) by mechanism of the proton and electron pair transfer from methyloxirane molecule to the Ph_3C^+ cation to form triphenylmethane and active centers with the end groups —CHO; *b*) mechanism of the direct addition of the PhC^+ ion to the methyloxirane oxygen, resulting in formation of active centers with the end groups —O—CPh_3. The relative importance of both mechanisms in the overall initiation process is affected by temperature and by concentration conditions in the reaction mixture.

Until now the reactions of methyloxirane with triphenylmethyl salts were studied above all in connection with its co-initiation effect on cationic polymerisations of tetrahydrofurane[1]. It was found that at −30°C the initiation proceeds by the direct addition of triphenylmethyl ion to the methyloxirane molecule, followed by the reaction of the complex formed with another methyloxirane molecule. It was also observed that this process of the formation of active centers is much faster than the initiation by mechanism of formal transfer of hydride ion from tetrahydrofurane molecule to triphenylmethyl cation that is usual in the systems without methyloxirane[2,3]. When studying oligomerisations of methyloxirane initiated by $Ph_3C^+.SbCl_6^-$ and $Ph_3C^+AsF_6^-$ at 20°C, we have detected triphenylmethane among the reaction products by NMR spectroscopy, in contradistinction to the previous ideas about the course of this initiation. This finding initiated out study of the initiation of oligomerisations of methyloxirane by triphenylmethyl salts, the results of which are reported in the present work.

EXPERIMENTAL

Methyloxirane (Fluka, 99·5%) was refluxed over calcium hydride for 24 h and then distilled through a 65 TP column. The medium fraction was degassed and refluxed over CaH_2 for 48 h into the reservoir of the oligomerisation apparatus. Degassing was repeated several times, the monomer was transferred into another reservoir of the apparatus by vacuum distillation and stored there without contact with CaH_2. As found, the prolonged contact of methyloxirane with CaH_2 in the reservoir results in the formation of a polymer with $\overline{M}_w$ of about $1 . 10^6$ (measured by light scattering). It seems likely that we deal here with polymerisation initiated by traces of calcium hydroxide and calcium carbonate present in CaH_2.

1,2-*Dichloroethane* (Lachema, *p.a*) was shaken with distilled water several times, pre-dried with $CaCl_2$, refluxed over CaH_2 for 24 h and then distilled through a 65 TP column. The medium fraction was refluxed with CaH_2 for 48 h in the distillation apparatus equipped with a 30 TP column topped with a drying tube containing silica gel and phosphorus pentoxide. Dichloroethane was stored in this apparatus. The freshly distilled solvent was always introduced into an auxiliary flask of the vacuum apparatus in which it was dried with P_2O_5 and degassed. The dry and degassed dichloroethane was then vacuum distilled into the reaction flask.

Triphenylmethyl hexafluoroarsenate (Alfa Inorganics) was dissolved in 1,2-dichloroethane under an atmosphere of dry nitrogen, the insoluble components were removed by filtration with the use of G 4 and G 5 fritted glass and re-precipitated by heptane which was dried by refluxing over NaH. The precipitate was washed with heptane, vacuum dried at 40—60°C and stored in a dessicator placed in the dark.

Triphenylmethyl hexachloroantimonate (V) was prepared from triphenyl methyl chloride (Koch-Light) and antimony(V) chloride (Alfa Inorganics) in heptane under dry nitrogen. The precipitate of the salt was re-precipitated twice in 1,2-dichloroethane–heptane mixture and stored similarly as $Ph_3C^+AsF_6^-$.

Oligomerisations were carried out in a vacuum apparatus. The weighed amount of the initiator was introduced into the reaction flask against a stream of dry nitrogen, the flask was closed and the initiator was further dried at a temperature of up to 60°C under a vacuum of about 0·1 Pa. Then 1,2-dichloroethane was vacuum distilled into the flask. The reactions were started by adding the known volume of the monomer from the ampoule to the initiator solution pre-cooled to the temperature which was by 5°C lower than the reaction temperature (read from the vapour pressure of the solvent), the flask containing solution of the initiator being placed in a bath maintained at the reaction temperature. Blank experiments showed that the equilibrium between the gas and liquid phase of the reaction mixture is established in one to two minutes under these conditions (the time being dependent on concentration conditions). After the appropriate reaction time the oligomerisation mixture was poured into 85—90% ethanol. After 2 days standing, the precipitate of hydrolysis products of the initiator residues which were formed if initiation by $Ph_3C^+SbCl_6^-$ had been used was filtered-off with a G4 fritted glas. The precipitate was washed several times with benzene and dried in a vacuum oven. The solution of oligomers was freed from the solvent by distillation and also from the residual monomer on a vacuum line.

NMR spectra of reaction mixtures were recorded on Tesla BS 487 instrument equipped with proton stabilization at 80 MHz (temperatures 20—100°C). Hexamethyldisiloxane was used as an internal standard. With regard to the high concentration of the initiator in the reaction mixture which was required for NMR measurements by the given sensitivity of the instrument, the reaction mixtures were prepared by the block technique. The reaction of the monomer with the initiator was carried out in an evacuated reaction flask (the mole fraction of the initiator was 0·013) and NMR spectra were measured after 30 to 60 min the beginning of the reaction. IR spectra were recorded on a double beam UR 10, (Zeiss, Jena) spectrophotometer, using KBr pellets. UV spectra were measured with a double beam Specord (Zeiss, Jena) spectrometer at 20°C.

Qualitative chemical analysis of the reaction products was intended to prove the presence of the end groups —CHO, —$COCH_3$, OH and —Cl and was made by usual methods of qualitative organic analysis[4–6].

Kinetics of the initiation reaction was followed by UV spectrometry, using $Ph_3C^+AsF_6^-$ as the initiator. Blank experiments in the absence of monomer revealed that under given experimental conditions this salt does not undergo decomposition when exposed to the irradiation by the light source of the UV spectrometer while the absorbance of $Ph_3C^+SbCl_6^-$ solutions decreased, even though at a very slow rate. The initiation was followed with the use of a vacuum cell equipped with a mixing device. The whole device, which is represented schematically in Fig. 1, was connected to a vacuum line *via* ground glass joint 6 and after thorough evacuation, the gaseous monomer was introduced under given pressure. Then teflon valve 5 was closed, the whole device was turned into an appropriate position and methyloxirane was freezed quantitatively into reservoir 3 in which it was closed by valve 4. Then the mixing flask 2 was filled with dry nitrogen and against its stream the known volume of 1,2-dichloroethane solution of the initiator of the known concentration was introduced into the flask. After the apparatus had been closed, the solvent was quantitatively distilled-off and the initiator was dried directly in flask 2 *in vacuo* at a temperature of up to 60°C. After drying, the known volume of 1,2-dichloroethane was introduced into this flask by distillation, valve 5 was closed and the apparatus was disconnected from the vacuum line. Concentration of the initiator in the solution was checked by measuring the absorbance at 435 nm, *i.e.* at the absorption maximum of the band corresponding to triphenylmethyl cation, the molar absorption coefficient of which is $3{\cdot}96 \cdot 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ (ref.[7]). Valve 4 was then open, reservoir 3 was washed twice with the reaction mixture, the measuring cell was washed twice with the reaction mixture, filled with the solution and placed into the path of the measuring beam of the UV spectrometer. Time changes of the absorbance at 435 nm were recorded; the absorbance corresponds to that of Ph_3C^+ (neither Ph_3CO groups (ref.[7]) nor further products formed in the reaction mixture absorb at this wavelength).

RESULTS

The products of reactions of methyloxirane with $Ph_3C^+AsF_6^-$ and $Ph_3C^+SbCl_6^-$ are always mixtures of linear and cyclic methyloxirane oligomers with the average polymerisation degree varying from 4 to 10 (measured by vapour osmometer in benzene at 35°C). All the samples of oligomers showed positive reactions on the presence of hydroxyl and aldehyde groups. The reaction with *o*-nitrobenzaldehyde which is characteristic of the end groups —$COCH_3$ was not positive in any case investigated. The infrared spectra of oligomers show usual bands assignable to poly(methyloxirane) and they exhibit further: *a*) a weak band at 1650 cm^{-1}, indicating the presence of a small amount of the double bonds of vinyl or vinylidene type; *b*) a band at 1730 cm^{-1} which belongs to the C=O stretching frequency in aldehyde groups; *c*) bands at 3450 cm^{-1} and 3480 cm^{-1} which correspond to hydroxyl groups. In some cases also very weak bands at 1605 cm^{-1}, 1670 cm^{-1} and 1690 cm^{-1} have been detected. These can indicate the presence of other types of the double bonds, and can eventually be also the vibrations of the C=O group of ketones.

NMR spectra of the mixtures show always the signals characteristic for CH, CH_2 and CH_3 groups which are typical for poly(methyloxirane) and further the following signals: *a*) a signal at τ 2·85 corresponding to aromatic protons of the Ph_3C-group-

b) a signal at τ 2·58 which indicates the presence of Ph_3C—O end groups[3]; a signal at τ 4·60 corresponding to the aliphatic proton in triphenylmethane[1-3]. The dependence of the ratio of the intensities of the signals of aromatic to aliphatic protons at the temperature used for the preparation of the reaction mixture is shown in Fig. 2. As a rule, this ratio is greater than 15, which is the value for triphenylmethane. From this dependence it is further evident that this ratio decreases with the temperature used for the preparation of the reaction mixture, *i.e.* an increase in temperature leads to an increase in the relative amount of triphenylmethane formed from the triphenylmethyl salt. Quantitative evaluation of this dependence has not been attempted since the high initiator concentrations required for these measurements by the given sensitivity of the instrument did not allow to ensure a constant temperature throughout the whole volume of the reaction mixture after mixing the reactants.

The following way was used to prove that triphenylmethane present in the reaction mixture is not formed only by subsequent decomposition of the Ph_3C—O end group[1]. After 45 min after mixing the reaction components, NMR spectrum of the reaction mixture was measured at 100°C and during another one hour this measurement was repeated several times. It was found that the pattern of the spectrum does not change during this interval and the intensity of the signal at τ 4·60 does not increase. Only after 24 h maintaining the reaction mixture at 100°C we observed an increase in the intensity of this signal (by approx. 15 per cent).

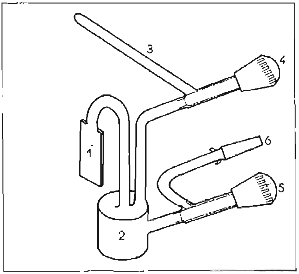


FIG. 1

Vacuum Apparatus for Spectrometric Study of Kinetics of Initiation

1 Cell, 2 mixing flask, 3 reservoir, 4, 5 valves, 6 ground glass joint for connection of the apparatus to the vaccum line.

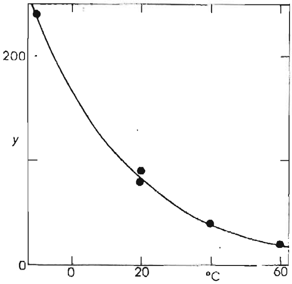
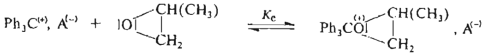


FIG. 2

Dependence of Ratio of Intensities of NMR Signals of Aromatic to Aliphatic Protons $y = (I_{2.58} + I_{2.85}/I_{4.60}$ on Temperature of the Reaction Mixture

Measurements of kinetics of the reaction of methyloxirane (M) with $Ph_3C^+AsF_6^-$ (I) were made with very diluted solutions of the reactants ($[I]_0 \approx 10^{-4}$ mol dm^{-3} and $[M]_0 \approx 10^{-3}$ to 10^{-2} mol dm^{-3}). Immediately after mixing the reaction components, the concentration of the initiator suddenly decreases and the rate of this process could not be measured by the experimental technique used. If concentrations of the reaction components are not too high, the extinction of the initiator proceeds in further stage of the reaction at a measurable rate. Kinetic curves (Fig. 3) obtained by the evaluation of time dependences of the absorbance at 435 nm in the ln [I] *vs t* coordinates are not linear, contrary to similar dependences obtained with the reaction mixture containing 1,3-dioxolane in place of methyloxirane[8].

In accordance with the present knowledge about the reactions of oxygen-containing heterocyclic compounds with triphenylmethyl[7] salts it seems very likely that the initial, sudden decrease in [I] is due to a very fast establishment of the equilibrium between carbonium and oxonium ions:



(*A*)

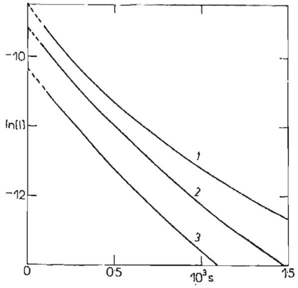


FIG. 3

Time Dependences of Initiator Concentration [I] (mol dm^{-3}) in Reactions with Methyloxirane for $Ph_3C^+AsF_6^-$

Initial concentration of methyloxirane $[M]_0$: *1* 14·01; *2* 13·23; *3* 13·01 mmol dm^{-3} and of the initiator $[I]_0$: *1* 0·129; *2* 0·097; *3* 0·055 mmol dm^{-3}.

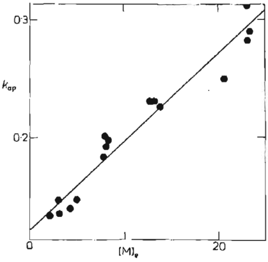


FIG. 4

Dependence of Apparent Rate Constant of Initation k_{ap} (s^{-1} mol^{-1} dm^3) on Equilibrium Initial Concentration of Methyloxirane $[M]_e$ (mmol dm^{-3})

This equilibrium preceds obviously further reactions that lead to the final transformation of Ph_3C^+ ions to active centers for oligomerisation. Initial equilibrium concentrations of the initiator $[I]_e$ (given by the equilibrium (*A*)) were determined by extrapolation of kinetic curves to the zero reaction time (Fig. 3). The equilibrium constant K_e was then calculated for each experiment according to the relation (*1*)

$$K_e = \frac{[I]_0 - [I]_e}{[I]_e\,[M]_e} \quad [M]_e = [M]_0 - ([I]_0 - [I]_e) \qquad (1)$$

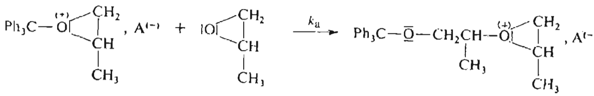
where $[I]_0$ and $[M]_0$ are the initial and $[I]_e$ and $[M]_e$ are the equilibrium concentrations of the initiator and the monomer (mol dm^{-3}), respectively. The average value of the constant K_e equals to 30 ± 5 at 20°C and for the given range of concentrations of the starting components.

Nonlinearity of the $\ln [I]$ *vs* t dependences (Fig. 3) in kinetically measurable region indicates that in contradiction to analogous systems with 1,3-dioxolane or tetrahydrofurane[7,8], in the case of the system containing methyloxirane, the active centers for oligomerisation are formed soon after the beginning of the reaction. Due to oligomerisation, the monomer concentration in the reaction mixture decreases at a faster rate than one can expect from its consumption solely *via* initiation reaction. This is demonstrated also by the rate retarding effect on the extinction of Ph_3C^+ ions. From the values of the slopes of tangents to the kinetic curves in the origin of the kinetically measured regions, we determined the values of the apparent rate constants for the extinction of Ph_3C^+ ions, k_{ap}, according to the equation: $k_{ap} = -\, d \ln [I]/M_e \, . \, dt$. Correlation of k_{ap}'s with $[M]_e$'s (which do not differ much from $[M]$ values) is shown in Fig. 4. It is evident that k_{ap} is not constant and increases monotonously with $[M]_e$.

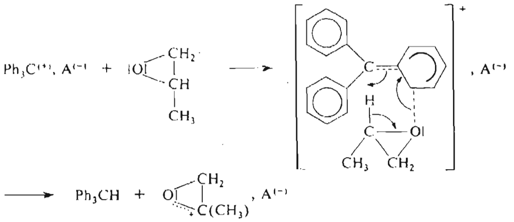
DISCUSSION

The results obtained enabled us to get a deeper insight into the mechanism of the reactions of triphenylmethyl salts with methyloxirane. Provided that the hydroxyl groups of oligomers are formed by transfer reactions, the proposed mechanism should explain: *a*) formation of the $-CHO$ and $Ph_3C—O—$ end groups; *b*) formaof triphenylmethane and the dependence of the yield of this compound on temperature of the reaction mixture; *c*) kinetic behaviour of the reaction system.

The first single reaction, which take place after mixing the reaction components is the equilibrium reaction (*A*). Compared to the rates of the reactions, the rate of the establishment of the equilibrium (*A*) can be regarded as infinitely fast. The equilibrium concentration of the spectroscopically detected Ph_3C^+ ions decreases in further stage of the reaction by reactions of both cations involved in the equilibrium (*A*) with methyloxirane:

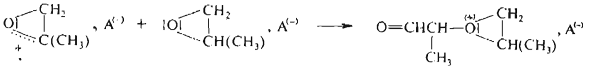


(*B*)



(*C*)

The reaction scheme (*B*) explains the formation of the end groups Ph_3C—O— and was suggested earlier[1] in connection with the study of the co-catalytic effect of methyloxirane on polymerisations of tetrahydrofuran. Reaction (*C*) is an analogy to the reaction of triphenylmethyl salts with tetrahydrofurane[9] and explains the formation of triphenylmethane. The consecutive reaction of the formed carbonium ion explains also the formation of the —CHO end groups:



(*D*)

With regard to the unproved presence of the end groups CH_3CO—, the hydrogen transfer from the CH_2 group of the oxirane ring can be practically excluded. It is therefore possible to assume that an intermediate product in the proton and electron pair transfer from methyoxirane to the Ph_3C^+ cation is the complex (Scheme *C*), the lifetime of which is long enough to direct the transfer toward formation of the thermodynamically more stable product, *i.e.* the higher branched cation. If the proton and electron pair transfer did not proceed within the framework of the metastable complex, the effect of the methyl group were not so distinguished. Among others, this assumption is justified by the formation of 2,6-dimethyl-1,4-dioxane evidenced by NMR spectroscopy[10] and by the head-to-head and tail-to-tail additions observed generally in cationic oligomerisations of methyloxirane[11-14].

The solution of kinetic equations corresponding to reactions (*A*) to (*C*) yields the following relation for the rate constant k_{ap}.

$$k_{ap} = -\frac{d \ln [I]}{[M]_e \, dt} = k_H + K_e k_a [M]_e \,, \tag{2}$$

which comports with the observed dependence of k_{ap} on $[M]_e$ (Fig. 4). By treatment of experimental data according to Eq. (*2*) for the pair anion AsF_6^- and a temperature of 20°C we obtained the following values of the rate constants: $k_H = 0{\cdot}122\ s^{-1}$ . . $mol^{-1}\ dm^3$; (k_H is the overall rate constant for reaction (*C*); $k_a = 0{\cdot}244\ s^{-1}\ mol^{-1}$ . . dm^3; the correlation coefficient of the dependence (*2*) equaled to 0·974.

According to mechanisms (*A*) to (*C*), the ratio of the rates of the consumption of the initiator in the reaction mixture by single reaction (*C*) and by single reaction (*A*) is given by expression: $k_H/k_a K_e [M]$. For $[M] = 10^{-2}\ mol\ dm^{-3}$ (the region of $[M]$ in which kinetic measurements were performed) the value of this ratio is 1·33. Of course, for $[M] = 1\ mol\ dm^{-3}$ (used in oligomerisation studies) the value of this ratio equals to 0·0133. This means that in the region of the higher methyloxirane concentrations, the production of triphenylmethane should be negligible, which contradicts the results obtained by NMR measurements (however, in these experiments also the initiator concentration was considerably higher, *c.* 10^{-2} to $10^{-1}\ mol\ dm^{-3}$).

The discrepancy just mentioned can be satisfactorily explained in terms of the proposed reaction mechanism, assuming that free Ph_3C^+ ions and Ph_3C^+, A^- ion pairs exhibit different reactivity in single reactions (*A*) to (*C*). One can expect that the free ions would be preferentially attacked on the central carbon by the oxygen of the monomer whereas the ion pairs would be preferentially attacked on the phenyls in *ortho* and *para* positions from steric reasons. As the first approximation, this idea can be expressed by the ratio of the rates of the initiator consumption by single reactions: $(1 - \alpha)\, k_H/\alpha k_a K_e [M]$.

The dissociation constants of triphenylmethyl salts in dichloroethane and dichloromethane vary at 25°C from $0{\cdot}7 \,.\, 10^{-4}$ to $2{\cdot}5 \,.\, 10^{-4}$ (for a number of pair anions)[15]. If *e.g.* for $Ph_3C^+SbCl_6^-$ we use the value[16] of $K_d = 1{\cdot}9 \,.\, 10^{-4}$, the calculation shows that the increase in $[I]$ from 10^{-4} to $10^{-1}\ mol\ dm^{-3}$ results in a decrease in the degree of dissociation of the salt (α) from 0·72 to 0·04. For $[I] = 0{\cdot}1\ mol\ dm^{-3}$ and $[M] = 1\ mol\ dm^{-3}$ the ratio of the rates expressed by the mentioned relation equals to 0·4, which agrees qualitatively with the results obtained by NMR measurements. Quantitative agreement can not be expected because of the effect of methyloxirane on the value of the dissociation constant of the triphenylmethyl salt and also due to experimental difficulties in preparation of the reaction mixtures for NMR measurements.

The effect of temperature of the reaction mixture on the yield of triphenylmethane is likely caused both by the different activation energies of single reactions and by the decreasing dissociation constant K_d with increasing temperature, which in the case of triphenylmethyl salts was generally observed[14,15].

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Translated by J. Hetflejš.