FORMATION OF SILENIUM DICATION FROM DIMETHYLDICHLOROSILANE

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Dedicated to honour the memory of Prof. Dr V. Veselý at the opportunity of the centenary of his birthday.

Hydrolysis of dimethyldichlorosilane with water in the presence of $HClO_4$ leads, under certain conditions, to the formation of a defined dication of high initiation efficiency. For the dication formation the initial mixture must contain the excess of hydrolysable Cl^- over H^+ from water and $HClO_4$. It is described the course of one-step and two-step hydrolysis and the efficiency of low-pressure removal of equilibrium volatiles. The dication formed is characterised by its molecular weight and by the content of ClO_4^- and Cl^-. Infrared and NMR spectra give the evidence that —Si—OH groups are present in the amount of less than 1% of the total $Si^+ClO_4^-$ groups. The initiation efficiency and the dication character of this initiator have been proved by polymerisation tests.

Most of cationic polymerisations known up to now are initiated by free cation or by ion pair which induces the growth of the chain on one of its ends. Because of study reasons and also for some technical applications, specially for block copolymers preparations, it was necessary to have an initiator which would allow the growth of both chain ends of cationically polymerisable monomer. Yamashita and coworkers[1] reported an intentional preparation of a dication (2,2'-octamethylene-bis(1,3-dioxolenium perchlorate)). Since then, several possibilities have appeared. Smith and Hubin[2] polymerised tetrahydrofurane (THF) with dications formed by the reaction of trifluoromethylsulfonic acid or its derivatives with THF. Another way for the preparation of a dication from THF and PF_5 have described Hoene and Reichert[3] (1,1'-tetramethylene-bis(tetrahydrofuranylium) bis-(hexafluorophosphate)). Burgess and coworkers[4] reported the formation of a dication by the reaction of $BrCH_2 . (C_6H_4)CH_2Br$ with $AgClO_4$.

Silenium initiator was used by us[5] more than ten years ago. Its properties have not so far been generally utilized. Only one paper reports the use of a similar cation[6]. In the present communication we give more detailed information about the preparation of our initiator and its dicationic character. The advantage of this initiator is in its relatively simple preparation, defined structure, solubility in nonpolar solvents, sufficient initiation activity and eventually its low tendency to split off H^+ or CH_3^+ at the reaction with carbanion.

EXPERIMENTAL

Chemicals

Dimethyldichlorosilane; the product of direct synthesis (made by VCHZ, Kolín) was rectified on a column having about 100 th. plates; according to GLC it contained less than 0·1% of other organosilicium derivatives and other impurities. Perchloric acid 70% was of analytical grade (Merck).

Methods

The content of Cl^- was determined by argentometric titration of hydrolysed samples. Concentrations of ClO_4^- were determined as the difference between the total sample acidity (determined by alkalimetry) and the content of Cl^-. The content of water was calculated from the volume of the water phase, the amount of $HClO_4$ and the density. Infrafed spectra were run on a UR 10 spectrometer, NMR spectra were measured on a JMR Tesla, BS 487A – 80 MHz apparatus; 2% toluene was used as an internal standard. Molecular weights were calculated from the ClO_4^- end group concentration and also determined by cryoscopy in benzene.

Procedure

The reactor consisted of a round bottommed graduated cylinder equipped with a side calibrated arm and a cock which made possible to remove the products of hydrolysis (HCl) and the sampling with a syringe. Perchloric acid and water were added to a measured amount of dimethyldichlorosilane in the reactor and the mixture was stirred at 24°C with a rod-shape stirrer rotating at 600 rpm; volatile products were freely leaving the reactor into a space where a slightly lower pressure was maintained ($\sim 9{\cdot}0 \cdot 10^4$ Pa; fume cupboard hood). The volumes of water and siloxane phases, respectively, were measured at selected intervals; simultaneously the samples from both phases were taken and the content of ClO_4^- and Cl^- determined.

After the one-step hydrolysis the reactors with selected mixtures were connected (through a ground joint) to a vacuum line, degassed and evacuated at 10^{-3} Pa. The samples were taken and analysed also from these selected mixtures. Some mixtures were hydrolysed in two steps. When the first hydrolysis was finished the calculated amount of water was then added, the contents were stirred for certain period of time and when the water phase disappeared the volatiles were removed on a vacuum line under the earlier described conditions.

The products of hydrolysis which should serve as initiators were preserved from contaminaiton; the reactor was sealed to a vacuum line, vacuum was interrupted by dry nitrogen (content of $H_2O < 2$ ppm), samples were taken under the cover of dry nitrogen, when the degassing was finished the initiator was diluted with benzene or hexane directly on the line.

RESULTS AND DISCUSSION

By mixing dimethyldichlorosilane with diluted perchloric acid the two-phase system is formed. The compositions of the used mixtures (1 – 6) are given in Table I. Hydrogen chloride released from dimethyldichlorosilane by hydrolysis saturates both phases and the excess leaves the reactor; it also takes out some dimethyldichlorosilane and water. The volume of water and organosilicon phases, respectively, gradually diminishes. The rate of phase volume reduction is influenced by a number of factors (temperature, diffusion, the way of removal of volatiles); the time dependences of volume changes under specified conditions are depicted in Fig. 1.

The initial rate of H_2O transfer from water to organosilicon phase is independent of the initial amount of water (Fig. 2). Simultaneously with the decrease of the total amount of water in the water phase occurs also the decrease if its concentration. Therefore, the transfer of water is faster than the transfer of $HClO_4$. In the presence of an excess of water (mixtures 4 – 6) certain amount of water phase, depending on $[Cl^-]/[H^+]$, remains preserved. If an excess of dimethyldichlorosilane is present (mixtures 1 – 3) the water phase disappears within several hours. The mixtures 1 and 6 behave quite differently. Perchloric acid concentration ($[H_2O]/[HClO_4]$) does not determine the character of the transfer.

The Fig. 3 depicts the time dependence of Cl^- content in each phase. The water phase becomes rich in Cl^- while they rapidly disappear from the siloxane one. The final content of Cl^- in the organosilicon phase is 1 – 6% from the initial hydrolysable Cl^-; this is so even in mixtures having an excess of H^+.

The way of $HClO_4$ transfer from the water into the organosilicon phase depends also on the $[Cl^-]/[H^+]$ ratio. In the mixtures 1 – 3 the transfer is practically quanti-

TABLE I

Composition of Charges Used for Preparation of Dications from Dimethyldichlorosilane (DDS)

Charge No	N_0, mmol			Cl^-/H^+	Initial Phase volume, ml	
	DDS	H_2O	$HClO_4$		water	DDS
1	146·4	87·4	38·3	1·37	3·45	18·8
2	148·7	97·0	39·9	1·27	3·70	18·8
3	146·6	114·9	36·6	1·10	3·5	18·8
4	155·0	139·0	38·8	0·98	4·4	19·7
5	148·0	199·0	38·0	0·68	5·4	18·8
6	155·0	176·1	77·5	0·72	7·0	19·9

tative (>90%, the rest goes with HCl); in the mixtures 4–6 only a partial transfer was observed. In any case, the $HClO_4$ concentration increases which is a further proof that water transfer is faster. These statements are substantitated by the evidence given in Fig. 4*a*.

The most important determination describes Fig. 4*b*. It shows the increase of ClO_4^- content in organosilicon phase. In the mixtures 1–3 more than 90% of $HClO_4$

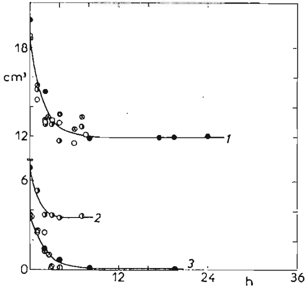


FIG. 1

Phase Volumes *vs* Time (24°C)

Phase: *1* organosilicon, *2* water, charge (No see Table I), *1* ○, *2* ●, *3* ⊗, *6* ◑.

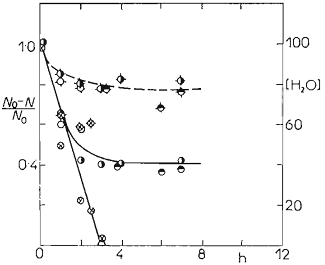


FIG. 2

Amount of Water in Water Phase *vs* Hydrolysis Duration

Overall amount of water in the charge (number): *1* ○, *3* ⊗, *5* ⊖, *6* ◑ (N_0 initial amount, mmol). Water concentration in the charge (number): *1* ○ (spiked points), *3* ⊗, *5* ⊖. *6* ◑.

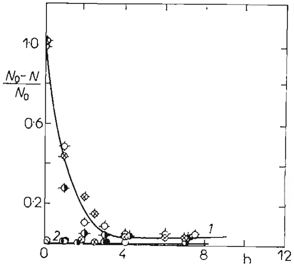


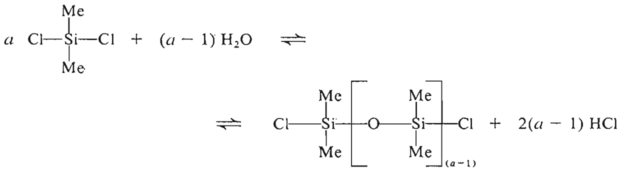
FIG. 3

Content of Cl^- in each of the Phases *vs* Time

Initial content — N_0 (mmol). Phase: *1* organosilicon; charge (number): *1* (spiked points) ○, *3* ⊗, *6* ◑; *2* water; charge (number): *1* ○, *3* ⊗, *6* ◑.

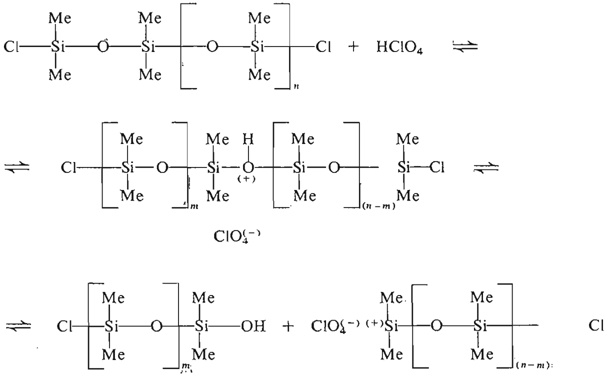
is found in the only one residual phase. If $[Cl^-]/[H^+] < 1$ than most of $HClO_4$ stays in a residual water phase; the amount depends on the initial $HClO_4$ concentration (compare the mixtures 5 and 6).

The results obtained indicate that hydrolysis of dimethyldichlorosilane comes first which is than followed by the transfer of $HClO_4$ by its reaction with siloxane bond:



$$a\ \mathrm{Cl{-}\underset{Me}{\overset{Me}{Si}}{-}Cl} + (a-1)\,\mathrm{H_2O} \rightleftharpoons \mathrm{Cl{-}\underset{Me}{\overset{Me}{Si}}\left[{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}\right]_{(a-1)}Cl} + 2(a-1)\,\mathrm{HCl}$$

(A)



$$\mathrm{Cl{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\underset{Me}{\overset{Me}{Si}}\left[{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}\right]_{n}Cl} + \mathrm{HClO_4} \rightleftharpoons \mathrm{Cl\left[{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\right]_{m}\underset{Me}{\overset{Me}{Si}}{-}\underset{(+)}{\overset{H}{O}}\left[{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\right]_{(n-m)}\underset{Me}{\overset{Me}{Si}}{-}Cl}\ \ \mathrm{ClO_4^{(-)}} \rightleftharpoons$$

$$\rightleftharpoons \mathrm{Cl\left[{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\right]_{m}\underset{Me}{\overset{Me}{Si}}{-}OH} + \mathrm{ClO_4^{(-)}\,{}^{(+)}\underset{Me}{\overset{Me}{Si}}\left[{-}O{-}\underset{Me}{\overset{Me}{Si}}{-}\right]_{(n-m)}Cl}$$

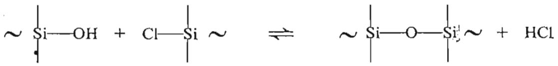
(B)

However, the direct reaction of $HClO_4$ with $-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{Cl}$ can not be ruled out:

$$\sim\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{HClO_4} \rightleftharpoons \sim\overset{|}{\underset{|}{\mathrm{Si}}}{}^{(+)}\mathrm{ClO_4^{(-)}} + \mathrm{HCl}$$

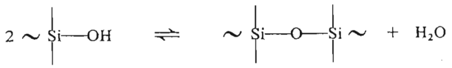
(C)

In the medium containing equivalent amount of Cl^- and H^+ the following reaction must take place:



$$\sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}OH} + \mathrm{Cl{-}}\overset{|}{\underset{|}{\mathrm{Si}}}\sim \;\rightleftharpoons\; \sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}O{-}}\overset{|}{\underset{|}{\mathrm{Si}}}\sim + \mathrm{HCl} \qquad (D)$$

and if H_2O is removed also the condensation of silanol groups:



$$2\sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}OH} \;\rightleftharpoons\; \sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}O{-}}\overset{|}{\underset{|}{\mathrm{Si}}}\sim + \mathrm{H_2O} \qquad (E)$$

The existence of a dication in "living" polymerisations is conditioned by the absence of free or bound Cl, $\sim\overset{|}{\underset{|}{\mathrm{Si}}}\mathrm{{-}OH}$ groups or of free water. As the reactions $(A)-(E)$ are the equilibrium ones and as $HClO_4$ is relatively little volatile we have a good chance to remove dangerous impurities under low pressure. The charge No 3 has been selected as the most suitable for measuring the efficiency of equilibrium shifts of the $(A)-(E)$ reactions brought about by the removal of volatile reaction products. After 7 hour's hydrolysis the charge mentioned contained 5% of the originally present

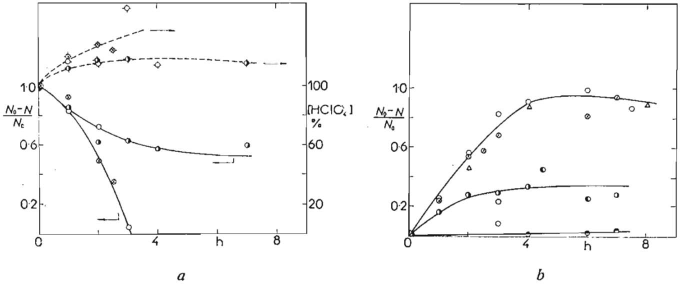


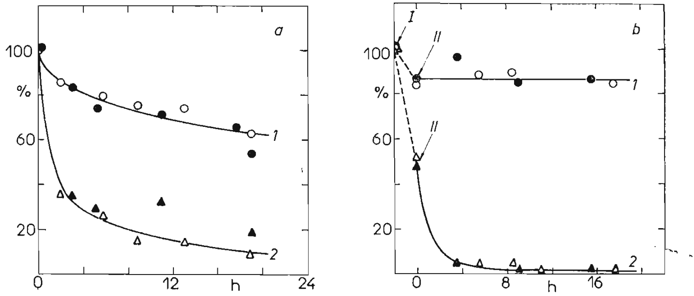
FIG. 4

Changes of ClO_4^- Content (initial $-N_0$, mmol)

a) Water phase (spiked points): *1* ○, *3* ⊗, *6* ○, ◑. *b*) organosilicon phase: *1* ○, *2* △, *3* ⊗, *4* ◐, *5* ◒, *6* ◑. (Curve from above: *1*, *2*, *3*).

Cl, no $\sim\overset{|}{\underset{|}{\mathrm{Si}}}\text{—OH}$ groups and no water detectable by IR spectroscopy. Fig. 5*a* depicts the decrease of Cl^- with time in a stirred sample at low pressure. The volume decreases during the operation (see curve *1* in Fig. 5*c*). The decrease of Cl^- is faster than that of ClO_4^-. After 20 hours only about 0·4% of the total Cl originally present in dimethyldichlorosilane is found. Nevertheless, this amount still makes more than 5% mol of the ClO_4^- content.

One-stage hydrolysis in the presence of small excess of Cl^- over H^+ leads to a one-phase system. The addition of water when the first stage is finished increases the number of phases only within the duration of the second stage (6 h). The excessive Cl^- can be removed by the two-stage hydrolysis without increasing the danger of



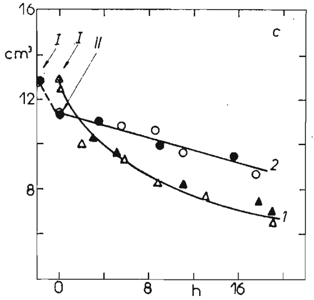


FIG. 5

Content of ClO_4^- and Cl^- *vs* Evacuation Time for Samples Hydrolysed in One (*a*) or in Two Stages (*b*) and Decrease of Sample Volume (*c*)

Blank and full points on the same curve denote the same charge of two parallel samples. *a*) Concentration (% in a charged sample) at end points of curves *1* in Fig. 3 and 4b were taken for 100%: *1* ClO_4^-, *2* Cl. *b*) *1* ClO_4, *2* Cl^-; *I* after first stage of hydrolysis, *II* after second hydrolysis and degassing. *c*) *1* one-stage hydrolysis, *2* two-stage hydrolysis: *I* after first stage of hydrolysis, *II* after second hydrolysis and degassing.

contamination with water. The course of the two-stage hydrolysis has been studied in three alternatives: water for the second stage was added so that $[Cl^-] = 2\,[H_2O]\,.$ $.\,[Cl^-] = [H_2O]$ and $5\,[Cl^-] = [H_2O]$. In the first alternative Cl^- content dropped to one half; *i.e.* to the amount found at the one-stage hydrolysis and evacuation. The course of concentration changes was qualitatively the same with the course observed at the second alternative.

Fig. 5*b* shows that the addition of water in the concentration equal to $[Cl^-]$ after the first stage of hydrolysis leads to the result required. The sample volume decreases (curve 2 in Fig. 5*c*) but not the ClO_4^- concentration. The amount of Cl^- decreases very rapidly. After about 10 hours of evacuation the amount of Cl^- is lower than 0·1% of the originally present Cl^- and lower than 1% of the present amount of ClO_4^-.

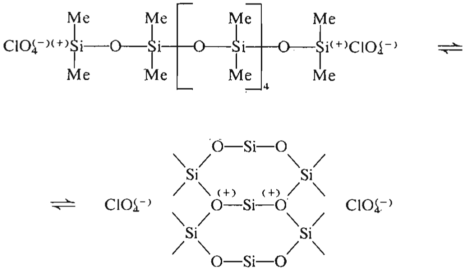
The shift of equilibrium of the reaction (*E*) executed by removing the condensation water at low pressure was tested by the addition of the excess of water ($[H_2O] = 5\,[Cl^-]$) for the second stage of the hydrolysis. After 17 hours of stirring the contents still consist of two phases. The water phase can be removed by a long-time stirring of the contents (30 h) at low pressure.

Molecular weights calculated from the ClO_4^- end-group concentration and determined by cryoscopy in benzene solution prove that *a*) in mixtures for which in the first stage of hydrolysis holds that $(n - 1) \leqq [H_2O] < n$ the number of Si atoms $2n$, in the initiator siloxane chain depends only on the Si/ClO_4^- ratio; *b*) the end-group method gives approximately twice as high molecular weight values (700) in comparison with cryoscopy (380). Probably a partial dissociation takes place

$$\sim\underset{|}{\overset{|}{\mathrm{Si}}}{}^{+}ClO_4^- \rightleftarrows \sim\underset{|}{\overset{|}{\mathrm{Si}}}{}^{+} + ClO_4^-;$$

c) condensation of silanol groups in vacuum proceeds so fast that they can be practically quantitatively removed. No substantial differences have been found in the content of $\sim\underset{|}{\overset{|}{\mathrm{Si}}}-OH$ bonds and in the molecular weight of the dication represented by the end point of the curve 2 (Fig. 5*b*) and of the dication prepared by evacuation of the sample whose hydrolysis in the second stage was performed with five-time excess of water. According to NMR spectra the content of $-\underset{|}{\overset{|}{\mathrm{Si}}}-OH$ is lower than 1% of the amount of $\sim\underset{|}{\overset{|}{\mathrm{Si}}}{}^{+}ClO_4^-$.

Infrared and NMR spectra, molecular weight and the ClO_4^- content confirm that under the given conditions the dication is formed:



(F)

The initiation efficiency of this compound has been tested at tetrahydrofurane and dioxolane polymerisations[5,7,8]. The dication character was proved in three ways: *a*) By comparison of polymerisation degrees of THF polymers polymerised with the same concentration either of $HClO_4$ or of the dication. Polymerisation initiated with silenium dication yielded polymers with approximately double chain length[9]. *b*) By comparison of polymerisation degrees of THF polymers polymerised with the same molar concentration either of $ClO_4^- \, {}^+CH_2 \, PhCH_2^+ClO_4^-$ or of the silenium initiator. Both products had the same molecular weight[9]. *c*) Mixing of the "living" poly-α-methylstyryl dianion with the silenium initiator leads to the recombination of ends and the degree of polymerisation of poly-α-methylstyrene increases by about an order of the magnitude.

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REFERENCES

1. Yamashita Y., Hirota M., Nobutoki K., Nakamura Y., Hirao A., Kozawa S., Chiba K., Matsui H., Hattori G., Okada M.: J. Polym. Sci. B, Polym. Lett. *8*, 481 (1970).
2. Smith S., Hubin A. J.: Polym. Preprints *13* (1), 66 (1972).
3. Hoene R., Reichert K.-H. W.: Makromol. Chem. *177*, 3545 (1976).
4. Burgess F. J., Cunliffe A. V., Richards D. H., Sherrington D. C.: J. Polym. Sci., Polym. Lett. Ed. *14* (8), 471 (1976).
5. Kučera M., Spousta E.: J. Chem. Soc. *1965*, 1478.
6. Minoura Y., Toshima H.: H. Polym. Sci. *A—1*, *10*, 1109 (1972).
7. Kučera M., Majerová K.: J. Polym. Sci., *A*—1, *6*, 527 (1968)
8. Kučera M., Hladký E., Majerová K.: J. Polym. Sci., *A—1*, *6*, 901 (1968).
9. Kučera M., Božek F., Majerová K.: Unpublished results.

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