

PREPARATION OF ORGANOSILICON HALIDES IN MOLTEN SALTS AS REACTION MEDIA

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INTRODUCTION

The use of fused salts as reaction media in the preparative chemistry has been carefully studied by us in recent years¹. The ionic liquid (as a fused salt may also be termed) is still an unexplored scientific field. The results obtained so far have, however, led to the conclusion that it will become an essential supplement to the non-polar and water-like solvents and, for specific preparative purposes, may even be the medium of choice.

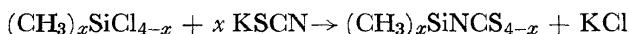
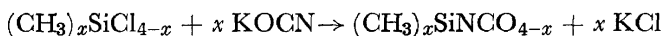
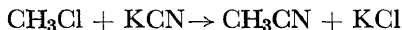
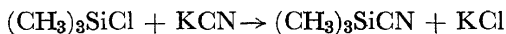
The majority of workers concerned with organosilicon chemistry are probably working with the conventional methods of organic chemistry. The use of molten salts as solvents will appear to them to be of purely academic interest. The fact that this is not quite so, and that the molten salts are of great value as media for the preparation of organometallic compounds, form the basis of the present lecture.

PROPERTIES OF FUSED SALTS

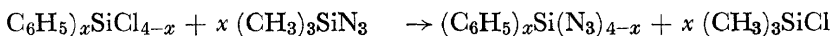
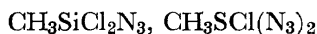
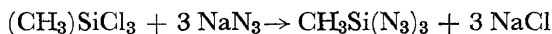
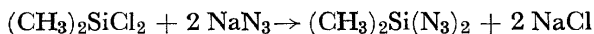
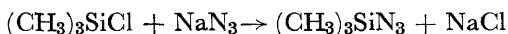
Fused salts are generally completely dissociated into ions, and they are good solvents for gases, salts, and metals. Good thermal stability, low vapour pressure, remarkably high electrical and thermal conductivities, partly low viscosity, and an extremely wide range of temperature between the melting and boiling points are the reasons for the growing technological importance of molten electrolytes. Owing to the good dissipation of heats of reaction, and to their property of dissolving otherwise volatile catalytically-active substances fused salts are highly suitable as media for catalytic processes. Compounds introduced into the melt are subject to strong polarizing forces through the ions, the reaction mechanism being mostly of ionic nature. Reactions in molten salts may further proceed involving the participation of the melt and consumption of one or more of its components, with no simple means of regenerating the latter. Other reactions of particular interest are those in which the melt acts only as a solvent for the reactants, or in which components of the melt are formed as by-products, or in which the by-products may be converted chemically or even electrochemically into the initial compounds (as these can be used for continuous cyclic processes). The outstanding phenomenon as regards the preparation of organosilicon halides in molten salts as reaction media is the fact that neither solvolysis with the reactants must be feared, nor are complicated operations required to separate the reaction products from the solvent.

APPLICATIONS OF FUSED SALTS

By using pseudo-halogen in place of halogen in molten alkali pseudo-halides we found² an interesting way for the preparation of cyanides, isocyanates, and isothiocyanates of silicon and carbon, e.g.

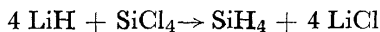


The use of alkali pseudo-halides is less expensive. Further, in contrast to the reaction with copper or silver cyanide we obtained acetonitrile from methyl chloride which led us to the assumption that alkali pseudo-halides in the melt also transfer their normal structure to silicon pseudo-halides regarded so far as *iso*-compounds. In the case of trimethyl cyanosilane this assumption was confirmed. In addition, the hitherto unknown methyl azidosilanes, $(\text{CH}_3)_x\text{Si}(\text{N}_3)_{4-x}$, and later on, the respective phenyl azidosilanes were prepared by us in solutions of sodium azide in molten salts³.

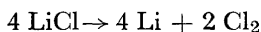


As shown in the above equations, in this group of substances also mixed halogen-pseudo-halogen substituted silanes, e.g. $\text{R}_x\text{Si}(\text{N}_3)_y\text{Cl}_z$ ($x + y + z = 4$; $x \geq 1$), have been prepared for the first time. The silicon pseudo-halides are particularly suitable for the transfer of pseudo-halogen groups to the halides of other elements³⁻⁵.

In recent years monosilane, SiH_4 , has become known on account of its conversion into high purity silicon for use in transistors. Both monosilane and trichlorosilane have also been used as starting materials for the preparation of hydrogen containing organosilicon halides. For the production of monosilane we have developed a process which makes use of molten salts as solvents⁶. Lithium hydride is dissolved in a lithium chloride-potassium chloride melt and reacted with silicon tetrachloride at 400°C , when monosilane is obtained in quantitative yield

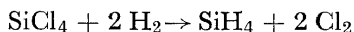


If the melt is electrolyzed and the lithium, formed besides chlorine, reacted with hydrogen, it is again lithium hydride that is obtained in a continuous procedure



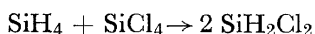
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The overall equation of the process would therefore be

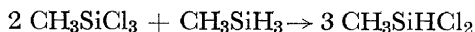


The chlorine obtained is again used for the preparation of silicon tetrachloride. Commercially, the process is now carried out in a three-branched apparatus⁶.

For the preparation of hydrogen containing organochlorosilanes various redistribution reactions in molten salts containing above all aluminium chloride have found vital application. Most people are still working with sealed tubes or autoclaves today. It is possible, however, to prepare the series of chlorosilanes, $\text{H}_x\text{SiCl}_{4-x}$, economically by means of catalysis in fused salts from monosilane and silicon tetrachloride, at normal pressure, e.g.



In addition, such products as dimethylsilane may also be obtained by the electrochemical hydrogenation process mentioned above. Redistribution reaction with dimethyldichlorosilane opens up the way to hitherto unknown (in its physical constants) dimethylchlorosilane⁷, $(\text{CH}_3)_2\text{SiHCl}$. This compound, however, is used as the starting compound for the synthesis of α, ω -hydridopolysiloxanes suitable for further reactions at the hydrogen atom. Numerous investigations have been made to modify the Rochow synthesis for increasing the yield of methyldichlorosilane, $\text{CH}_3\text{SiHCl}_2$, essential for certain silicone products. The results of these experiments were not satisfactory, because the yield of the side-products methyltrichlorosilane and silicon tetrachloride was quite high at the same time. By redistribution of methyltrichlorosilane with methylsilane from the hydrogenation process the methyldichlorosilane required may be obtained in fused salts as catalyst:



It would be a waste of time to discuss the advantages and the technical value of the Rochow synthesis in the organosilicon chemistry. The progress achieved by this synthesis is so evident that a chemistry of silicones would be hardly conceivable without it. Regardless of this already outstanding importance of the synthesis and an improved feasibility achieved after the initial discovery, the efforts focused either on the synthesis itself, or on an alternative access to organochlorosilanes have not lost impetus. Some of the reasons for the need for further work are as follows⁸. In the direct synthesis it is not only the valuable dimethyldichlorosilane which is produced, but also large amounts of the unwanted other methylchlorosilanes, in particular methyltrichlorosilane is an often disliked by-product. It is indeed very difficult to modify the process so that a specific methylchlorosilane is obtained without changing the yield of the other products, as shown in the above example of methyldichlorosilane. The commercial grades silicon react only very slowly and at high temperatures with methyl chloride. Requirements as to the purity and composition of the silicon are therefore high. The same applies to the copper or silver catalyst added in amounts up to 10 per cent. All these factors make the synthesis expensive and prevent spreading of silicones as it would be justified by their properties. Prior to the introduction of the fluid bed the temperature control of the highly exothermal reaction

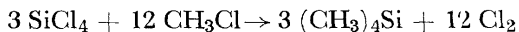
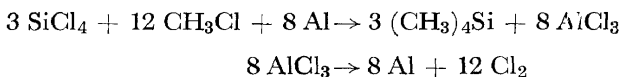
between methyl chloride and silicon presented difficulties. Local overheating resulted not only in products with a higher content of chlorine, but, above all, in a precipitation of carbon on the surface of the reactants and, consequently, in an obstruction to reaction and in increased pyrolytic decomposition of the products.

With this particular objective, investigations on the improvement of the temperature control were made with silicon suspended in molten salts^{9, 10}. The catalysts in question could be dissolved easily. In contrast to earlier stages a quantitative conversion of the silicon was achieved, but, here again, the desired modification in favour of a specific product was not possible and the expected higher yield of dimethyldichlorosilane was not obtained.

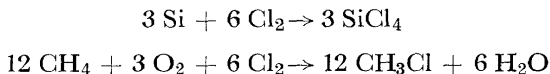
Very interesting, and from the technical angle entirely feasible, is the redistribution reaction between methyl and chlorine bonds in silanes, but the required higher-methylated compounds are not normally available. Intense studies have therefore been concentrated on a further alkylation of organochlorosilanes in which connection the experiments by Hurd¹¹ should be particularly mentioned. Methyltrichlorosilane and methyl chloride were allowed to pass over metallic aluminium at 450°C. However, the result was unsatisfactory with regard to preparative application and because of the high reaction temperature. Silicon tetrachloride did not react under these conditions at all. Good results were also expected from an alkylation via aluminium alkyls which, according to Ziegler *et al.*¹² are obtainable from aluminium, hydrogen, and olefins by simple techniques. Apart from the danger involved in handling aluminium trialkyls and alkylaluminium halides on a larger scale, however, this process, like the Grignard synthesis, had to be confined to special applications, since it were just the technically important methyl- and phenylchlorosilanes that could not be prepared by the "Mülheimer Verfahren". Experiments for synthesizing tetramethylsilane from methylaluminiumchloride and silicate materials and subsequently redistribution reaction to the methylchlorosilanes are of more recent date¹³. It is still too early to say whether this method has proved technically successful.

We have also dealt with the problem of further methylation and with the preparation of higher methylated products to be used in redistribution reactions, respectively. The following report refers to a new process by which metal-methyl compounds can be produced in a simple and continuous manner^{14, 15}. To explain the principle the preparation of tetramethylsilane has been chosen. If methyl chloride and silicon tetrachloride are passed through a fused salt in which a metal is suspended, tetramethylsilane and the respective metal halide are obtained in quantitative yield. Apart from the nature of the solvent used in this process, however, the reaction differs from the conventional Wurtz synthesis from the fact that in general no expensive alkali metal has to be used and that the resulting metal halide dissolves in the solvent used (in this case in the molten salt), whereby the metal surface is constantly kept free for further reaction. The main advantage of this process, provided melt and metal have been carefully chosen, is that the halogen-splitting metal may be regained by simple fused salt electrolysis from the metal halide formed. Among others, the system NaCl-AlCl₃-Al has proved particularly suitable. The reactions are presented by the following equations:

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The chlorine resulting from the electrolysis may be reused for the production of silicon tetrachloride from inexpensive ferrosilicon and from silicon waste from the Rochow synthesis or even for the oxychlorination of methane:



The advantage of the new process becomes obvious when one considers that tetramethylsilane is obtained from the direct synthesis in minor quantities only and, through the Grignard synthesis, only with a considerable excess of Grignard compound and a troublesome subsequent separation of ether. The same is true of the Wurtz synthesis. The "Mühlheimer Verfahren" as shown earlier cannot be used either. A suitable access to the tetramethylsilane, however, is provided by an extension of the preparation of other methylchlorosilanes via redistribution reactions. A particular advantage of the new process is that the methyltrichlorosilane resulting from the Rochow synthesis may be further methylated.

The method is not confined to the NaCl-AlCl₃-Al system. Almost all metals of groups I A to V A and partly those of the B groups of the Periodic System or of their alloys are suitable as acceptors for the halogen to be split off. In particular, we used the systems shown in *Table 1*.

Table 1. Molten salt-acceptor metal systems; reaction temperature

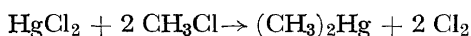
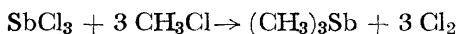
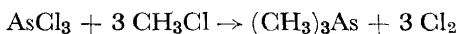
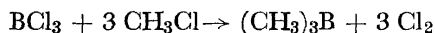
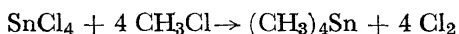
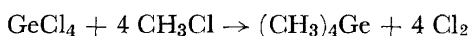
<i>System</i>	<i>Reaction temp.</i> °C
NaCl—AlCl ₃ —Al and Al—Hg	120–250
NaCl—AlCl ₃ —Mg	120–250
HgCl ₂ —KCl—Hg	200
ZnCl ₂ —KCl—Zn and Zn—Hg	230
SnCl ₂ —KCl—Sn	230
LiCl—KCl—Li—Sn and Li—Pb	360–400
MgCl ₂ —KCl—CaCl ₂ —Mg	425

Apart from keeping the reaction temperature as low as possible, which means a relatively low melting point of the salt or the eutectic mixture of salts respectively, it should be taken into account that each acceptor metal desired may again be deposited electrochemically. Therefore the acceptor metal must always have the lowest deposition potential in the system. It is of particular advantage if the acceptor metal is able to form with methyl chloride one or several stable intermediate compounds which act as carriers of the methyl group to the silicon tetrachloride. Known compounds of such nature involve aluminium (CH₃AlCl₂), and (CH₃)₂AlCl, and magnesium (CH₃MgCl). Zinc, mercury, tin, lead, antimony, etc., are also suitable. For the reaction of methyl chloride with silicon tetrachloride it is of course

advisable to use melts that likewise consist of chlorides. However, since the whole halogen is recovered in the electrolysis, there are, in principle, no objections to using the more expensive systems of bromides and iodides, *e.g.* of the system $\text{NaBr—AlBr}_3\text{—Al}$.

The following example is intended to briefly explain the experimental conditions chosen¹⁵. In a reaction vessel an equimolar melt from sodium chloride and aluminium chloride is submitted to electrolysis at 180°C until enough aluminium and the relevant amount of chlorine have deposited. The metal is deposited from the colourless melt in the form of fine silver coloured crystals, a fact that caused the failure of earlier experiments concentrated on the electro-metallurgical preparation of aluminium in this system. For our process, however, it is just this phenomenon which is especially advantageous, the metal is reacting almost three times as fast with the initially introduced methyl chloride to methyl aluminium dichloride and further to sodium methyltrichloroalunate as the commercial aluminium grit, at the end of the electrolysis. Finally, silicon tetrachloride is introduced into the melt containing the organoaluminium compound. Tetramethylsilane is obtained in quantitative yield (80 per cent). When using methyltrichlorosilane, a conversion of about 90–95 per cent is achieved due to the fact that this compound lends itself more easily to alkylation because of the asymmetric molecule¹⁶, here again with quantitative yield. After the consumption of the organoaluminium compound the melt is again submitted to electrolysis and the process started anew. Since the chlorosilanes do not react through reduction with the aluminium metal alone, they may also be introduced with the methyl chloride simultaneously. Moreover, this is always the case if an acceptor metal is used that does not form intermediate compounds. The semi-continuous process hitherto described may thus be changed to a continuous one, provided that the cathode chamber is separated from the anode¹⁵.

The process under consideration is not limited to the preparation of tetramethylsilane or methylchlorosilanes. Remarkable success has been achieved in the conversion of chlorobenzene and in making phenyltrimethylsilane from trimethylchlorosilane. Throughout, positive results were obtained with quantitative yields by using the method in question for the preparation of tetramethylgermanium tetramethyltin, trimethylboron, trimethylarsine trimethylantimony, and dimethylmercury.



As these compounds are partly used as valuable methylating agents—especially in the organosilicon chemistry—and as they are technically interesting raw materials themselves, they should not pass unmentioned.

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They may point to the more general applicability of the new process for the preparation of metal-methyl compounds.

We hope that the preparative methods for organosilicon halides described herein which constitute only a small section out of the methodically new field of chemical reactions in fused salts¹, will provide a better access to those simple and monomeric fundamental compounds upon which the modern chemistry of silicones is based.

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