

Direct Formation of Element Chlorides from the Corresponding Element Oxides through Microwave-Assisted Carbohydrochlorination Reactions

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Abstract: A series of technically and economically important element chlorides—such as SiCl₄, BCl₃, AlCl₃, FeCl₂, PCl₃ and TiCl₄—was synthesized through reactions between hydrogen chloride and the corresponding element oxides in the presence of different carbon sources with microwave assistance. This process route was optimized for demonstration purposes for tetrachlorosilane formation and successfully demonstrates the broad applicability of various silicon oxide-containing minerals and materials for carbohydrochlorination. The chlorination

reaction occurs at lower temperatures than with conventional heating in a tubular oven, with substantially shorter reaction times and in better yields: quantitatively in the case of tetrachlorosilane, based on the silicon content of the starting material. The experimental procedure is very simple and provides basic information about the suitability of element compounds, especially ele-

ment oxides, for carbohydrochlorination. According to the general reaction sequence *element oxide* → *element* → *element chloride* used in today's technology, this one-step carbohydrochlorination with hydrogen chloride is considerably more efficient, particularly in terms of energy input and reaction times, avoiding the isolation of the pure elements required for chlorination to give the element chlorides with use of the more corrosive and toxic chlorine gas.

Keywords: carbon reduction · chlorine · halides · hydrogen chloride · oxides

Introduction

Most of the element chlorides—of, for example, phosphorus, titanium, aluminium, iron, boron and especially silicon—are of great technical and economical importance and are thus produced in well established large-scale processes in multiple tonnes per year.^[1] As starting materials they mainly serve for the direct synthesis of element-carbon and element-element bonded compounds by salt metathesis reactions with Grignard reagents or metal organyls and Wurtz couplings, the synthesis of highly reactive metals through reduction reactions (Rieke metals), or for distillable precursors for the formation of highly pure metals for, for example, electronic applications.^[1,2] As metal chlorides are mainly synthesized by direct oxidation reactions of metals with

chlorine ($E_m + nCl_2 \rightarrow E_mCl_{2n}$) and thus involve metal oxide reduction in a previous reaction step, direct element chloride formation from the corresponding oxides would be highly desirable, both to save the energy-consuming reduction step and to stay in the same formal element oxidation state. In general, one-step, high-temperature chlorination reactions both in the presence and in the absence of carbon are known for most of the element oxides EO_n ($E = Be, Mg, Ti, Zr, Hf, Nb, Ta, Cr, W, Mn, Fe, B, Al, Si$),^[1,3] but usually carbon is used for reduction and chlorine as the chlorinating agent [Eq. (1)]. Especially in the case of high-temperature carbochlorination reactions the starting materials have to meet very specific demands, and catalysts are often required for reasonable performance.



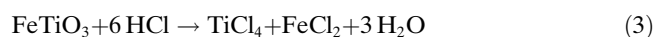
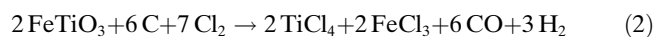
This causes quite a series of technical problems: i) phosgene, which is extremely poisonous,^[4] is formed as byproduct ($CO + Cl_2 \rightarrow COCl_2$) from the reaction between carbon monoxide and chlorine, ii) at high temperatures tetrachloromethane is formed from reactions between chlorine and carbon

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($T \approx 1600^\circ\text{C}$) or carbon monoxide ($T \approx 430^\circ\text{C}$),^[5] iii) because of its comparably high boiling point ($T = -34^\circ\text{C}$) excessive chlorine might be cocondensed with liquid or gaseous element chlorides upon product formation,^[6] and finally, iv) the gas itself is highly toxic^[6,7] and corrosive, and might run down the reactor and complicates the reaction process.

The replacement of gaseous chlorine by hydrogen chloride gas reduces these problems: i) reactions yielding phosgene or tetrachloromethane are avoided, ii) the lower boiling point ($T = -85^\circ\text{C}$) in relation to chlorine facilitates purification of the element chlorides, and iii) the hydrogen-containing gas HCl is far less corrosive and less toxic.

Carbochlorination and carbohydrochlorination reactions starting from ilmenite are exemplarily shown for the synthesis of titanium tetrachloride, the precursor for the large-scale production of titanium dioxide and of some hundred tons of titanium per year,^[7] while carbochlorination with chlorine [Eq. (2)] is a technically well established process,^[7] carbohydrochlorination [Eqs. (3) and (4)] is only described in the patent literature.^[8]



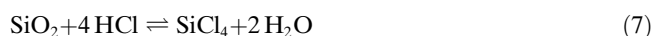
According to [Eq. (3)], hydrogen chloride oxidizes iron only to FeCl_2 instead of FeCl_3 , which results from chlorine oxidation [Eq. (2)],^[9] causing a reduction in chlorine consumption by 14 atomic percent. As HCl is supplied to the technical cycle instead of Cl_2 , subsequent controlled hydrolysis to give TiO_2 can technically be performed at far lower temperatures.^[10] As most of the element chlorides formed during carbohydrochlorinations are highly sensitive to moisture, the formation of water [Eq. (3)] has to be strictly avoided. According to the gas–water equilibrium [Eq. (4)], carbohydrochlorination reactions have to be carried out at temperatures higher than 800°C ^[11] to ensure complete formation of H_2 and CO , which both might be technically used as energy input to carry out the reduction process.^[12] Alternatively, the hydrogen formed can be used as a reducing agent for the production of highly pure elements: for example, photovoltaic grade silicon from silicon tetrachloride synthesized from sand, hydrogen chloride gas and carbon sources.^[13] To reach the high reaction temperatures required for carbohydrochlorinations very rapidly and efficiently, microwave irradiation of the reaction mixture is to be favoured over conventional heating: microwave transparent materials are not heated, the reactor is consequently thermally less stressed, and the energy input is minimized.^[14] Microwave heating is even more attractive because most of the element oxides do not absorb microwave energy, but carbon does so very well. The carbon sources needed for the reduction process are thus used both for heat transfer and for the chemical reaction. In this paper we report the carbohydrochlorination of a series of technically important element oxides, optimized

for demonstration purposes for silicon tetrachloride formation from different silicon-oxide-containing materials and different carbon sources. Experiments with zinc sulfide (ZnS) and barium sulfate (BaSO_4) demonstrate that the carbohydrochlorination reaction is not limited only to element oxides, but might be also attractive for element sulfides and sulfates.

Results and Discussion

Chlorosilanes are technically produced from silicon and chlorine or hydrogen chloride at temperatures above 300°C .^[15] As an alternative to conventional heating, these reactions can be efficiently performed with microwave assistance.^[16a] Starting from elemental silicon, the oxidation states $+IV \rightarrow \pm 0 \rightarrow +IV$ are passed through during the overall reaction sequence $\text{SiO}_2 \rightarrow \text{Si} \rightarrow \text{H}_n\text{SiCl}_{4-n}$ ($n = 0-3$). Economically it is more favourable to produce chlorosilanes directly from silicon-containing compounds or materials, even more so in view of the fact that large-scale silicon production allows only selected, highly pure and thus limited and expensive quartz materials as starting materials and requires a large molar excess of carbon both for heating and for reduction.^[17] In the process $\text{SiO}_2 \rightarrow \text{SiCl}_4$ the formal oxidation state of silicon remains $+IV$, and isolation and handling of elemental silicon is avoided.

From experimental observations, the following equilibria [Eqs. (5/6; 7/4)] can be discussed for the courses of the chlorination reactions:



i) Chlorination reactions occur even in the absence of carbon. Reactions with chlorine require temperatures higher than 1000°C (experimentally performed at 1200°C) and they are distinctively slower than those performed (at 1000°C) with hydrogen chloride.^[3e] ii) For chlorinations both with chlorine and with hydrogen chloride, consumption of silicon dioxide was significantly faster in the presence of carbon.^[3e] iii) If carbon would reduce the silicon dioxide to silicon first, with subsequent reaction of the latter with chlorine [Eq. (8), Eq. (9)], tetrachlorosilane formation should occur when the silicon dioxide/carbon mixture is first heated to reaction temperature ($750^\circ\text{C}/10\text{ h}$) and subsequently chlorinated with chlorine at 350°C .



However, this reaction sequence could not be verified.^[3f] It should be noted that no tetrachlorosilane was isolated either

in reaction (5) or in Reaction (7), only SiO_2 consumption being observed.^[3e,f]

In the carbohydrochlorination process, this route is formally carbon-free, because on shifting the water–gas equilibrium [Eq. (4)], carbon and water are formed from hydrogen and carbon monoxide; furthermore, as discussed in the Introduction, the disadvantages of gaseous chlorine usage are avoided.

Thanks to its microwave transparency, glass (SiO_2) cannot be heated by microwave irradiation, in contrast to carbon, which thus simultaneously acts as reducing agent and heat transfer element. Microwave irradiation of carbon and carbon-based materials causes white flashes—obviously electrical discharges or arcs—and it is assumed that carbochlorination occurs in these active reaction zones. That means that the actual reaction temperatures might be higher than the average temperatures measured by a pyrometer within the microwave cavity. Preliminary test experiments showed that carbon does not react with hydrogen chloride or water upon microwave irradiation; with chlorine some tetrachloromethane (CCl_4) is formed and detected by GC/MS. First runs of carbochlorination experiments for the synthesis of silicon tetrachloride were performed in a conventional household microwave reactor, which was modified according to the experimental requirements,^[19] despite all the problems concerning the reproducibility of such experiments reported in the literature.^[18] As can be seen from Table 1, which summarizes the carbohydrochlorination reactions performed with different starting materials, all the different kinds of silicon and silicon oxidic, carbidic and nitridic materials react with the different carbon sources investigated. Consuming both hydrogen chloride or chlorine gas, tetrachlorosilane is formed selectively and quantitatively, based on the silicon content of the starting materials, in all experiments. Tetrachloromethane and phosgene are formed as by-products only when chlorine is used for the carbochlorination reaction.

Table 2 reports SiO_2 consumption of quartz sand ($\text{SiO}_2 > 99.5\%$) within reaction intervals of two minutes [$(\Delta m \text{SiO}_2)$] and the additive mass consumption [$\Sigma \Delta m (\text{SiO}_2)$] for the whole reaction time, each as percentages. In Figure 1 the values of Table 2 are used to show the course of the carbohydrochlorination reaction graphically. It should be noted that independently of the reaction conditions (addition of hydrogen to HCl gas and/or variation of the microwave energy input) and the SiO_2 sources (Table 1), no trichlorosilane formation was ever observed. Obviously the reaction temperature is too high, because it is well known that the $\text{SiCl}_4/\text{HSiCl}_3$ ratios from silicon/HCl reactions are strongly temperature-dependent: the higher the reaction temperature, the more tetrachlorosilane is formed.^[20] As a result of the similarly temperature-dependent Boudouard equilibrium the oxygen from the silicon oxides reacts with carbon upon carbohydrochlorination to give carbon monoxide or dioxide. No BaCO_3 precipitated on exposure of the gas formed during the carbohydrochlorination to $\text{Ba}(\text{OH})_2$, so carbon monoxide and hydrogen had been formed completely. This points to reaction temperatures above 900°C .

In view of the poor reproducibility of experimental results obtained with conventional household microwave reactors with only roughly defined physical parameters, a second series of experiments was run with an industrial microwave reactor with very well defined parameters guaranteeing good reproducibility of experimental results.^[18] Formation of tetrachlorosilane is obviously based on a clean reaction of silicon dioxide with hydrogen chloride [Eq. (7)]. The formed reaction water subsequently reacts with carbon to give carbon monoxide and hydrogen directly [Eq. (4)], thus avoiding back-reaction by hydrolysis. Obviously the position of the water–gas equilibrium is strongly influential in the conversion of water and consequently in tetrachlorosilane formation. To study these effects in more detail, a series of experiments was performed at different reaction temperatures. Table 3 gives the reaction temperature (T), the average value, the median, the maximum and the standard deviation of the temperature, as well as the additive mass consumption of silicon dioxide [$\Sigma \Delta m (\text{SiO}_2)$] as a function of the reaction time. Figure 2 shows the course of the temperature in experiment 3 (Table 3), measured with a pyrometer, for demonstration purposes. Note that the heating rate achieved by microwave irradiation might be extremely high (Figure 2: $\Delta T \geq 1400^\circ\text{C s}^{-1}$). For a comparison of the suitability of hydrogen chloride vs. chlorine as chlorinating agent, experiments 4 (HCl) versus 7 (Cl_2) in Table 3 should be taken into consideration. For visualisation the experimental numbers of Table 3 are graphically shown in Figure 3.

Figure 3 shows that the carbochlorination reactions accelerate with increasing temperature and approach completion. Furthermore, from the graphs shown in Figure 3 and the numbers given in Table 3 it can be concluded that carbohydrochlorination shows remarkable product formation at temperatures above 800°C —the same temperature required to shift the water–gas equilibrium to carbon monoxide and hydrogen. For the performance of carbochlorination reactions hydrogen chloride seems to be more favourable than chlorine (experiment 4: HCl, 7: Cl_2 , Figure 3 and Table 3), because the additive mass consumption of silicon dioxide is bigger with hydrogen chloride than with chlorine.

It should be mentioned that all silicon dioxide sources and all carbon samples listed in Table 1 were successfully applied both in the industrial and in the household microwave reactors to give tetrachlorosilane.

Comparison with experiments under conventional heating

conditions: Carbochlorination reactions yielding tetrachlorosilane were performed with conventional oven heating^[16b] instead of microwave irradiation^[16c] for comparison. The results obtained from reduction of quartz sand with samples of activated carbon in the presence of hydrogen chloride or chlorine are listed in Table 4. At first sight carbochlorination with chlorine gas seems to be more favourable, because the silicon dioxide mass consumption is higher. However, obviously the reaction temperature has a decisive influence: at 1300°C the yield of silicon tetrachloride produced from the

Table 1. Chemical compositions and specifications of starting materials for microwave-assisted carbohydrochlorination reactions and analysis of products by EDX, PXRD and NMR spectroscopic investigations.^[8]

Material	Composition and specification of starting materials	Analyses of products		
		Reaction residue ^[a]	Sublimate ^[b]	Cooling trap ^[c]
Si	wafer; >99.999% Si	none	none	SiCl ₄
	technical grade; >98.5% Si; 70–400 μm	none	none	SiCl ₄
FeSi	98.5% Si	none	FeCl ₃ (traces, PXRD)	SiCl ₄
	75% Si	Fe (traces, PXRD)	FeCl ₃ (PXRD)	SiCl ₄
	50% Si	Fe (traces, PXRD)	FeCl ₃ (PXRD)	SiCl ₄
SiC	37 μm	C _{amorphous} (traces, PXRD)	none	SiCl ₄
	Si ₃ N ₄ 44 μm	none	none	SiCl ₄
mica	EDX: ^[d] O 66, Al 14, Si 16, K 4, Fe 1	K, Al, Fe oxides (traces, PXRD)	AlCl ₃ , FeCl ₂ (PXRD)	SiCl ₄
fumed silica	380 m ² g ⁻¹	none	none	SiCl ₄
quartz sand	> 99.5% SiO ₂	none	none	SiCl ₄
quartz dust	> 98.5% SiO ₂ ; 4.4 m ² g ⁻¹	none	none	SiCl ₄
desert sand ^[e]	Fe ₂ O ₃ 0.317 (1.213), TiO ₂ 0.0453 (0.0608), CaO 11.6 (9.8), K ₂ O 0.911 (1.118), MgO 1.080 (3.400), Na ₂ O 0.585 (0.508), P ₂ O ₅ 0.051 (0.0243), Al ₂ O ₃ 1.62 (2.12), SiO ₂ 83.8 (81.8)	traces of (Fe, Ca, K, Mg, Na, Al) oxides/chlorides	Fe/Al-chloride mixture (EDX); PXRD: amorphous	SiCl ₄
quartz glass	> 96% SiO ₂	none	none	SiCl ₄
brown bottle glass	≈ 80% SiO ₂	traces of Na, Mg, Ca-oxides (EDX); PXRD: amorphous	none	SiCl ₄
soda-lime glass	> 73% SiO ₂	traces of Na, Mg, Ca-oxides (EDX); PXRD: amorphous	none	SiCl ₄
rice ash (Japan)	EDX: ^[d] C 10, O 61, Na 1, Al 3, Si 20, K 2, Ca 3	traces of metal oxides/chlorides (EDX, PXRD)	PXRD: amorphous	SiCl ₄
zeolite	EDX: ^[d] Al 14, Na 12, O 61, Si 13	traces of Na, Al-oxides/chlorides (EDX)	none	SiCl ₄
SiO	< 44 μm	none	none	SiCl ₄
Al ₂ O ₃	99%; < 150 μm; EDX: ^[d] Al 38, O 62 ≈ Al ₂ O _{3,3} ; PXRD: Al ₂ O ₃	EDX: ^[d] Al 18, O 54, Cl 21; PXRD: amorphous	AlCl ₃ (PXRD)	AlCl ₃ (EDX) PXRD: amorphous
bauxite	EDX: ^[d] O 65, Al 19, Si 3, Ca 2, Ti 1, Fe 11 ≈ 10 Al ₂ O ₃ ·TiO ₂ ·2 CaCO ₃ ·3 SiO ₂ ·6 Fe ₂ O ₃ + O 16 ^[d]	traces; EDX: ^[d] O 53, Al 34, Si 4, Ti 1, Fe 7	FeCl ₂ (EDX, PXRD)	EDX: ^[d] O 27, Al 6, Si 1, Cl 51, Ti 1, Fe 14; PXRD: amorphous
B ₂ O ₃	≥ 99.98%; PXRD: amorphous	none	none	BCl ₃ ·Et ₂ O ¹¹ B NMR: 12 ppm
borax	Na ₂ B ₄ O ₇ ·10H ₂ O; 99–103%; PXRD: amorphous	none	none	BCl ₃ ·Et ₂ O ¹¹ B NMR: 12 ppm
Fe ₂ O ₃	≥ 99%; 5 μm; EDX: ^[d] Fe 44, O 56 ≈ Fe ₂ O _{2,5} ; PXRD: Fe ₂ O ₃	none	EDX: ^[d] Fe 25, O 34, Cl 42, ≈ FeO _{1,4} Cl _{1,7} ; PXRD: FeCl ₂	none
HfO ₂	98%; EDX: ^[d] Hf 50, O 50 ≈ HfO; PXRD: HfO ₂	none	EDX: ^[d] Hf 17, O 38, Cl 45 ≈ HfO _{2,2} Cl _{2,6} ^[g] ; PXRD: HfCl ₄	none
Ca ₃ (PO ₄) ₂	34–50% Ca; PXRD: amorphous	none	none	PCl ₃ ³¹ P NMR: 221 ppm
TiO ₂	≥ 99.8%; EDX: ^[d] Ti 33, O 66 ≈ TiO ₂ ; PXRD: TiO ₂	EDX: ^[d] Ti 26, O 71, Cl 3	none	TiCl ₄ ·2D ^[h]

Table 1. (Continued)

Material	Composition and specification of starting materials	Analyses of products		
		Reaction residue ^[a]	Sublimate ^[b]	Cooling trap ^[c]
ilmenite	EDX: ^[d] O 65, Al 1, Si 2, Ca 1, Ti 10, Fe 21, ≈10 Ti-FeO ₃ ·5.5Fe ₂ O ₃ ·CaCO ₃ ·SiO ₂ ·0.5Al ₂ O ₃ , +O 9; ^[f] PXRD: FeTiO ₃	EDX: ^[d] O 69, Si 14, Cl 1, Ti 16	EDX: ^[d] O 32, Si 2, Cl 41, Fe 25	TiCl ₄ ·2D ^[h]
residue of titanium break up	EDX: ^[d] O 67, Na 1, Mg 1, Al 2, Si 10, Ca 1, Ti 18, Fe 1 ≈TiFeO ₃ ·17TiO ₂ ·CaCO ₃ ·10SiO ₂ ·Al ₂ O ₃ ·MgCO ₃ ; PXRD: TiO ₂	PXRD ^[i] : FeCl ₂ ·2H ₂ O; FeCl ₃ ·6H ₂ O	PXRD ^[i] : FeCl ₂ ·2H ₂ O	TiCl ₄ ·2D ^[h]
BaSO ₄	99%; EDX: ^[d] O 67, S 13, Ba 18, Na 1, Si 1 ≈BaS _{0.7} O _{3.7} ; PXRD: BaSO ₄	PXRD ^[i] : BaCl ₂ ·H ₂ O; EDX: ^[d] Ba 33, O 15, Cl 49, Si 3 ≈25BaCl ₂ ·3SiO ₂ ·9BaO	PXRD: BaCl ₂ ; EDX: ^[d] Ba 2, Cl 2, S 71, Si 1, O 24 ≈2BaCl ₂ ·SiO ₂ ·21S _{3.4} O	none
ZnS	>99.9%; EDX: ^[d] S 38, Zn 62 ≈ZnS _{0.7} ; PXRD: ZnS	none	PXRD: ZnCl ₂ /ZnS; EDX: ^[d] Zn 37, O 9, Cl 51, S 4 ≈26 ZnCl ₂ ·3ZnS·8ZnO	none
petro coke	98% C; < 0.1% H ₂ O			
hard coal	86% C; 9% H ₂ O			
brown coal	89% C; 0.5% H ₂ O			
activated carbon powder	>90% C; <10% H ₂ O			
activated carbon granules,	>95% C; <6% H ₂ O			
Ø ≈ 2 mm				
graphite	>95% C; <1% H ₂ O			

*³) The use of chlorine as chlorinating agent leads to the same products as reported for hydrogen chloride, so those experiments are not listed in this table. While experiments to give silicon tetrachloride were run both in a conventional household reactor and in an industrial microwave reactor, all other experiments were performed exclusively in an industrial microwave reactor. [a] Residue remaining from the mixture of starting materials after carbohydrochlorination. [b] Yellow greenish solids, deposited in the cooler parts of the reaction chamber. [c] Volatile reaction products collected in a cooling trap (-196 °C); SiCl₄: characterized by δ²⁹Si NMR (19.3 ppm), yield of SiCl₄ quantitative according to the silicon content of the starting material. [d] Element in atom %. [e] Sand from the White and Red Desert, Abu Dhabi; composition in weight %. [f] Excess of oxygen might result from presence of hydroxides. [g] Commercial standard: EDX:^[d] HfO_{0.9}Cl_{1.4}. [h] Addition of pyridine or THF (=D) yielded an amorphous yellow solid; subsequent hydrolysis gives TiO₂ (EDX:^[d] O 69, Si 14, Ti 16; PXRD: amorphous). [i] Origin of water from the atmosphere or from starting material, which contains up to 20% water.

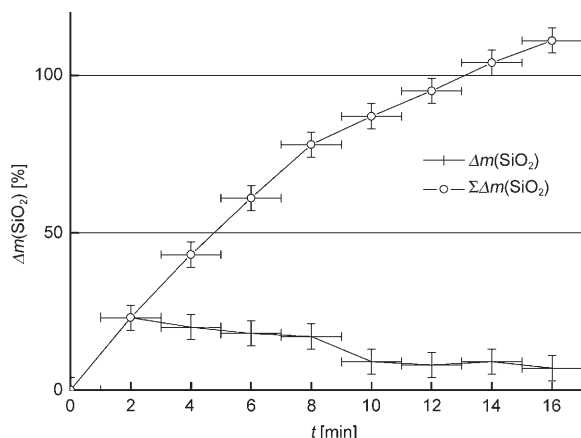


Figure 1. Course of carbohydrochlorination reactions of quartz sand in a conventional household microwave reactor.

hydrogen chloride reaction is higher than 80% and at 1400 °C it is quantitative.^[21]

Comparison of reactions carried out with microwave assistance (Table 3 and Figure 3) with those experiments performed under conventional heating conditions (Table 4)

Table 2. Carbohydrochlorination of SiO₂ in a household microwave reactor

t [min]	Δm (SiO ₂) [%]	ΣΔm (SiO ₂) [%] ^[a]
2	23	23
4	20	43
6	18	61
8	17	78
10	9	87
12	8	95
14	9	104
16	7	111

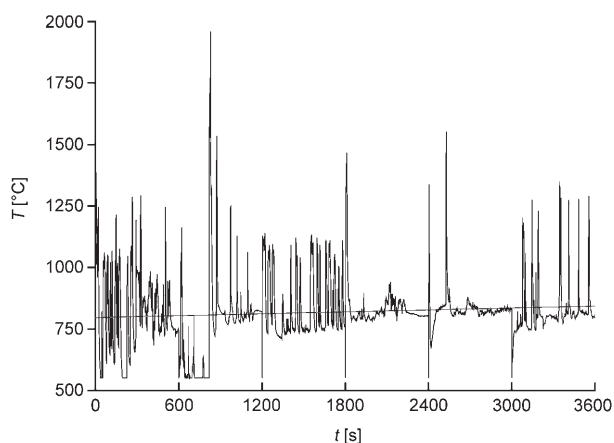
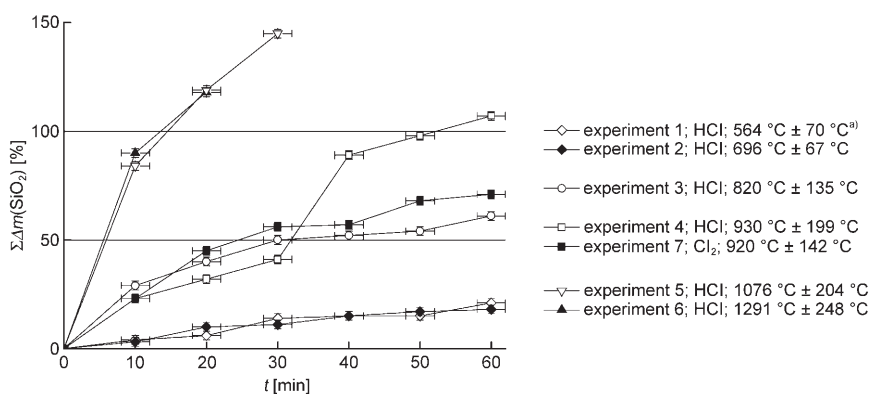
[a] Mass consumptions above 100% relate to reactions with reactor material.

shows that at comparable temperatures the conversion rate of SiO₂ is much higher with microwave irradiation (Figure 4). Moreover, it should be mentioned that the reaction time in microwave-assisted reactions was 30 min, while that in a conventional oven was 12 hrs—24 times longer! In addition, the mixture of starting materials had to be prepared according to the experimental requirements (see Experimental Section). Linear extrapolation in Figure 4 gives minimum carbohydrochlorination reaction temperatures of 600 °C (microwave reactor) and 750 °C (oven heating). Ex-

Table 3. Carbochlorination reactions of quartz sand in a technical microwave device.

Experiment no.	1	2	3	4	5	6	7
Chlorination agent	HCl						Cl ₂
	T [°C]						
average	564	696	820	930	1076	1291	920
median	550	692	810	892	1024	132	902
maximum	1548	1519	196	1846	1868	1769	1885
standard deviation ^[a]	70	67	135	199	204	248	142
	ΣΔm (SiO ₂) [%]*						
reaction time [min]							
10	4	3	29	23	84	90	23
20	6	10	40	32	119	118	45
30	14	11	50	41	145		56
40	15	15	52	89			57
50	15	17	54	98			68
60	21	18	61	107			71

[*] Yield greater than 100% is due to conversion of reactor material.
 [a] The microwave reactor is operated by preadjusting the power input by hand before starting the experiment. The manual control and the extremely rapid changes in temperature (Figure 2) result in the standard deviations listed in the table.

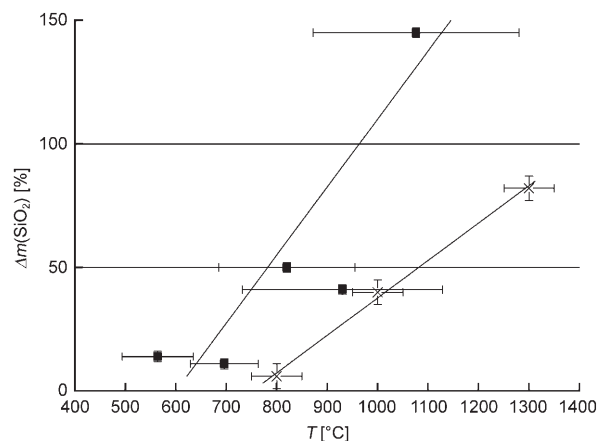
Figure 2. Microwave-induced course of temperature upon carbohydrochlorination of SiO₂; T measurements performed with a pyrometer.Figure 3. Carbochlorination of SiO₂ with HCl or Cl₂ at different temperatures; mass losses of more than 100% are the result of reactions with the reactor material. [a] For the standard deviations see footnote of Table 3.

perimentally observable product formation starts at approximately 560 versus 800 °C.

Table 4. Carbochlorination reactions of SiO₂ in a tubular oven.

m (SiO ₂) [g]	m (C)+m (starch) [g] ^[a]	T [°C]	t [h]	Δm (SiO ₂) [%]	Chlorination agent
4	4.3+2	1300	12	82	HCl
4	4.3+2	1300	12	90	Cl ₂
4	4.3+2	1000	12	40	HCl
4	4.3+2	1000	12	51	Cl ₂
4	4.3+2	800	12	6	HCl
4	4.3+2	800	12	7	Cl ₂

[a] For performance the materials have to be ground and granulated using starch.

Figure 4. Mass losses of SiO₂ in carbohydrochlorination reactions at different temperatures: T input by microwave irradiation (■, t=0.5 h) and conventional oven heating (×, t=12 h); mass losses greater than 100% are the result of reactions with the reactor material.

Microwave-assisted carbohydrochlorination of other selected compounds: From the experience and results obtained from the (hydro)carbochlorination of silicon oxygen-containing materials, the synthetic method used was transferred

to other selected compounds to demonstrate its general character. As representative elements, titanium,^[8] boron,^[8] aluminium, iron and phosphorus were chosen (see Table 1), because on one hand these elements form thermodynamically very stable oxides,^[1a,3a] and on the other, these element oxides and their corresponding chlorides are of great technical and economical importance. For demonstration purposes, zinc sulfide and barium sulfate were investigated as non-oxidic compounds, demonstrating the general applicability of the carbohydrochlorination reaction.

All compounds tested were treated with hydrogen chloride and carbon sources as reported in

Table 1. Borax and the breaking up residues for TiO_2 generation were dried prior to carbohydrochlorination. On completion of the reactions, the inner surface of the industrial microwave reactor was usually covered with a greenish-yellow solid, denoted as "sublimate" in Table 1. Generally, all products formed were analysed and characterized by powder X-ray diffraction (PXRD) measurements and, in part, by energy dispersive X-ray analysis (EDX) (aluminium and titanium; see Table 1). Iron(III) oxide, bauxite and ilmenite absorb microwave energy and thus are, at least in part, chlorinated even in the absence of carbon as reductant. Boron trichloride was characterized as its Lewis base–acid adduct with diethyl ether by ^{11}B NMR spectroscopy and phosphorous trichloride by ^{31}P NMR spectroscopic investigation. Hafnium dioxide was transformed into its tetrachloro derivative, zinc sulfide reacted to afford zinc dichloride, and barium sulfate yielded barium dichloride monohydrate.

Titanium tetrachloride could not be characterized by GC/MS analysis because of its very high moisture sensitivity, which prevented direct identification. For indirect detection the chlorinated product was collected in pentane and treated with pyridine or THF, giving yellow, amorphous precipitates of the bis-donor adducts $\text{TiCl}_4 \cdot 2\text{D}$ (D = pyridine, THF). Addition of water to these or to the pentane solutions yielded an amorphous white solid, which was dried and identified as titanium dioxide by EDX analysis (Table 1).

After carbohydrochlorination of aluminium-containing compounds, no reflections could be detected within the sublimate or the reaction residue by PXRD. Additional EDX analysis, however, showed that both the sublimate and the condensates of bauxite and ilmenite contained aluminium and titanium, respectively. The presence of aluminium in the sublimation product hints that a sublimable aluminium compound, obviously AlCl_3 , was at least temporarily formed in the chlorination reaction.

Conclusion

To demonstrate their general suitability, carbohydrochlorination reactions were performed with a series of technically and economically important element oxides, with special emphasis being placed on silicon dioxide-containing materials, to give tetrachlorosilane in a one-step reaction. A similar procedure has already been described, but only using the very corrosive and toxic elemental chlorine instead of hydrogen chloride for chlorination and with use of catalysts and other additives^[1,3] to the solid/gas reaction mixture. Iron(III) oxide, bauxite and ilmenite, which can be heated by microwave irradiation even in the absence of carbon, react, at least in part, with hydrogen chloride to give the corresponding chlorides. Ilmenite, bauxite and coal have to be dried prior to use. Carbon samples that are contaminated by hydrocarbons yield aromatic compounds—for example, benzene, toluene and styrene—as byproducts upon carbohydrochlorination. In that case small amounts of methyltrichloro-

silane are formed from silicon oxide-containing precursors. This silicon methylation reaction could not be improved further—for the direct one-step synthesis of dimethyldichlorosilane, the main product of the Rochow–Müller Direct Process,^[1a,3a] for example—by addition of methane and/or chloromethane to the chlorinating gases hydrogen chloride and/or chlorine. With regard to the reaction temperatures given in Table 3 and Figure 2, it should be noted that electric arcs resulting from carbon irradiation might warrant consideration as active reaction zones for the carbohydrochlorination reaction, as indicated by formation of tetrachloromethane in low yields as a trace product from chlorine and carbon and/or carbon monoxide. This reaction is normally observed at temperatures higher than 1600°C . Reacting chlorine always entails phosgene formation, which is an indication of the presence of carbon monoxide during the carbohydrochlorination; moreover, carbon dioxide cannot be trapped by $\text{Ba}(\text{OH})_2$. This shows both i) that the water–gas equilibrium is completely shifted to carbon monoxide and hydrogen, and ii) that the Boudouard equilibrium lies completely on the carbon monoxide side. As can be seen from Figure 3 and Table 3, the carbochlorination reactions accelerate and go to completion with increasing temperature. From the experiments performed it is obvious that carbohydrochlorination with hydrogen chloride is at least comparable to chlorine-based processes; it even seems to run better.

Thanks to silicon tetrachloride formation at temperatures significantly lower (Figures 3 and 4, Tables 3 and 4) than are required for the technical silicon dioxide reduction by coal ($T > 1550^\circ\text{C}$), the carbohydrochlorination process proceeds in two steps, starting with silicon dioxide chlorination [Eqs. (5,7)]. In the presence of carbon, oxygen or water are transformed into carbon monoxide and in the latter case into additional hydrogen [Eqs. (4,6)].

In early papers on carbochlorinations of silicon dioxide it had already been mentioned that the use of hydrogen chloride should be more favourable than that of chlorine, because the equilibrium between silicon dioxide and hydrogen chloride should be reached more rapidly than that between silicon dioxide and chlorine.^[3c] From the experimental work described in this paper, it can be concluded that carbochlorination reactions carried out with microwave assistance are technically much simpler to perform and can be run more rapidly than those under conventional heating conditions. In the latter experiments it was rather difficult to fix the mixture of carbon and the corresponding element compounds to be chlorinated. For good performance the mixture had to be hardened and granulated by use of starch, and the water–gas equilibrium was not completely shifted towards carbon monoxide and hydrogen; this can only be overcome by working at temperatures higher than 1300°C .^[21] In the colder oven parts product water condensed and partially hydrolysed the moisture-sensitive element chlorides. On the other hand, it should be noted that for large-scale production of element chlorides with microwave assistance the penetration depth of microwaves into the carbon-containing mixtures is rather limited, thus requiring a more specific re-

actor design. Nevertheless, carbohydrochlorination under microwave irradiation conditions provides basic information about the applicability of an element compound, especially of its oxides, to production of element chlorides within a few minutes.

Experimental Section

Materials: First experiments were run in a reconstructed Panasonic microwave reactor, which is described elsewhere.^[19] For more controlled reaction conditions, the second series of experiments was performed in an industrial microwave device (MX 4000, $P_{\max} L^{-1} \approx 5000$ W, Firma Muegge Electronics GmbH, Germany) fitted with a pyrometer (KT 18.03, 550–1800 °C, Heitronics Infrarot Messtechnik GmbH, Germany). The reactor consisted of quartz glass (tube, inner diameter 2 cm, length 60 cm, fitted with NS 29 ground joints) to reduce thermal stress on the reactor material. The reaction mixture was placed on a quartz glass carrier (quartz glass tube cut in half and equipped with feet made of quartz glass). For comparison, corresponding experiments were conducted in a tubular oven (ROF 5/25, Heraeus Holding GmbH, Germany $T_{\max} = 1300$ °C). The same quartz glass tube as applied in the microwave assisted reactions was used. Chlorine and hydrogen chloride (2.8, dry, Messer Griesheim GmbH, Germany) was used without further purification. Different kinds of carbon sources (petro coke, pit coal, brown coal, powdered and granulated activated carbon and graphite), as well as silicon-containing materials (see Table 1) were tested. Other materials containing non-silicon elements are listed in Table 1. Solvents (diethyl ether, pentane, toluene, pyridine and THF, Sigma–Aldrich Chemie GmbH, Germany) were of chromatographic quality or were dried by standard techniques.

Analyses were carried out by X-ray powder diffraction (PXRD; SG-9R RIGAKU), energy dispersive X-ray analysis (EDX) on an OxFord 6446 detector integrated into a scanning electron microscope (Atomika/AMRAY 1920 ECO Environment Controlled SEM), gas chromatography coupled with a mass spectrometer (GCMS; Trace GC 2000 Series and Trace MS; ThermoQuest Corp.) and NMR spectra were obtained with a Bruker Avance 400 spectrometer (^{29}Si NMR, 50 MHz; ^{11}B NMR, 128 MHz; ^{31}P NMR, 162 MHz) in C_6D_6 (Sigma–Aldrich Chemie GmbH, Germany) as solvent. Chemical shifts are reported in δ (ppm) relative to $\text{Me}_2(\text{H})\text{SiCl}$ for ^{29}Si , $\text{BCl}_3 \cdot 2\text{THF}$ for ^{11}B and PCl_3 for ^{31}P .

Methods: Because of the sensitivity of most of the element chlorides investigated toward moisture, the complete setup was evacuated for at least 30 min before experiments were run. Gas flows were varied from 20 L h^{-1} to 300 L h^{-1} (± 20 L h^{-1}) and controlled with a flow meter. In microwave-accelerated reactions, the educts were used as received and oven-dried (180 °C, ≥ 8 h); 2–10 g of each reaction mixture was used for reaction. The temperature was manually controlled by continuously changing the applied power. Reactions were paused every 10 min to isolate products and to measure the loss of the educt mass. Formation of products was quantitatively followed only by mass losses. Products were isolated by standard Schlenk techniques. Gaseous or liquid products were frozen in a cooling trap containing pentane (2–5 mL) by liquid nitrogen or ethanol freezing mixtures. During warming to room temperature, the traps were fitted with balloons to compensate the increasing pressure. PXRD measurements of moisture-sensitive compounds were performed in Vaseline.

To rule out reactions between chlorine, hydrogen chloride or water and carbon, blank reactions were made. In all cases no mass loss was detectable.

In contrast with the microwave experiments, it was necessary to dry the starting materials for the oven experiments (800 °C, ≥ 8 h) and to fix the samples with quartz glass wool (VWR International GmbH, Germany) as binder. Powders were granulated with starch (a few percent, Merck K-GaA, Germany). Gas flows were varied from 1–10 L h^{-1} and reactions were performed for 2–12 h; 8–20 g of each reaction mixture was used.

Acknowledgements

Investigations into carbohydrochlorination reactions were supported by Wacker-Chemie AG, Dow–Corning Corp. and City Solar Technology. We express our thanks to: F. Maysamy Tmar (for performing reactions in tubular oven and PXRD analysis) and D. Ceglarek (EDX analysis). We thank the following companies for gifts of material: RWE AG (brown coal), OMV Deutschland GmbH (petro coke), Deutsche Steinkohle AG (pit coal), Quarzwerke GmbH (different kinds of quartz sand), Possehl Erzkontor GmbH (bauxite), Sachtleben Chemie GmbH (ilmenite), Wacker-Chemie AG (silicon and ferrosilicon) and New Energy GmbH (zeolith). We thank Elkem for the performance of sand analyses.

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Received: October 23, 2007
Published online: March 5, 2008