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Promising Catalyst for Chlorosilane Dismutation

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Abstract: Currently, the most common method of silane synthesis for electronics and photovoltaics is trichlorosilane dismutation. Therefore, an experimental study of the kinetics of the dismutation reaction of chlorosilanes is of scientific and practical interest. A catalyst has been proposed that allows the dismutation reaction to be carried out in a wide range of temperatures and pressures. Both kinetic and thermodynamic data on the dependence of the rate of the dismutation reactions of trichlorosilane, dichlorosilane, and monochlorosilane on pressure were experimentally obtained. In addition, the dependence of saturated vapor pressure on temperature for monochlorosilane and dichlorosilane were also experimentally determined. Using the example of TCS, it was experimentally established that increasing the pressure to six atmospheres makes it possible to increase the specific productivity of the reactor by at least an order of magnitude due to the acceleration of the chemical reaction and the increase in the molar concentration of chlorosilanes in the vapor mixture. Consequently, it becomes possible to multiply the reactor's load on the substance and, accordingly, the performance of the chlorosilane dismutation apparatus in general.

Keywords: trichlorosilane; dichlorosilane; catalytic dismutation reaction; monochlorosilane; thermodynamics; saturated vapor pressure; kinetics

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1. Introduction

Modern opto-, micro-, and nanoelectronics are closely related to the widespread use of volatile compounds of elements that make up simple and complex semiconductor materials. Among semiconductor elements, silicon is the undisputed leader in terms of the scale of application, and among its volatile compounds, silane (MS), dichlorosilane (DCS), trichlorosilane (TCS), and silicon tetrachloride (STC) are most widely used. These compounds are used in the production of silicon for helioenergetics, high-resistance semiconductor silicons used in microcircuit bases, and epitaxial silicon patterns. Nowadays, there are several methods for producing silicon. For example, the Siemens process [1–4], based on TCS synthesis, includes deep purification and thermal decomposition in the presence of hydrogen, which leads to the formation of silicon, various chlorosilanes, and hydrogen chloride. This method has a number of disadvantages, such as the high cost of equipment, high energy consumption, as well as the environmental hazard of volatile reaction products.

Currently, the method of obtaining silicon by the thermal decomposition of silane is the most widespread [5,6].

Recently, great progress has been made in the use of metal-containing nanocatalysts. These catalysts have been successfully used for both the decomposition [7] and synthesis [8] of various compounds. However, no publications in the field of silane production using metal-containing nanocatalysts have been found in the literature.

Among the various methods of silane synthesis, the method of synthesis by the catalytic dismutation of trichlorosilane has become the most widespread [9–15].

To expand the production of silane, it is attractive to increase the productivity of the synthesis process. Performance improvements can be achieved by increasing the rate of the dismutation reaction. To increase the reaction rate, it is possible to use a more active catalyst, increase the synthesis temperature, and, for steam and gas phase reactions, increase the pressure in the reactor. Therefore, considering the influence of these factors on the rate of chlorosilane dismutation is an urgent task.

The dismutation process consists of three reversible reactions involving five components: TCS, DCS, MHS, STC, and MS [10].

$$2SiHCl_3 \rightarrow SiCl_4 + SiH_2Cl_2, \quad (1)$$

$$2SiH_2Cl_2 \rightarrow SiHCl_3 + SiH_3Cl, \quad (2)$$

$$2SiH_3Cl \rightarrow SiH_2Cl_2 + SiH_4. \quad (3)$$

It is known from the literature [11,12] that Lewis bases, for example, aluminum trichloride, heterocyclic arenes, and acyclic nitriles, can be used as catalysts for TCS dismutation. However, these catalysts have not found practical application since they are all a source of difficult-to-remove impurities in reaction products.

In this regard, only anion exchange resins with a large selection of chemically inert polymer matrices with various functional groups and a large specific surface area, which are practically non-volatile and do not enter the reaction products and which matrices are chemically inert to chlorosilanes, have become practically widespread.

The first in the process of the catalytic dismutation of chlorosilanes to find practical application were anion exchange resins based on a polystyrene-co-divinyl benzene containing weakly basic tertiary amino -N+H(CH_3)$_2$ or strongly basic quaternary ammonium –$N^+(CH_3)_3$ as functional groups. These include Amberlyst A-21, Amberlyst A-26, and IRA-400 anionites produced on an industrial scale by foreign companies [13–16].

Amberlyst A21 is a neutral ion-exchange resin and a solid base, which, in addition to chlorosilane dismutation, is also used as a catalyst in the three-component reaction of aldehyde and malonitrile with various active methylene compounds for the synthesis of a number of pyran annulated heterocycles. AN18-12P anionites (analog of Amberlyst A-21) are industrially produced in Russia. Amberlyst A26 is a highly basic anion exchange resin used to remove transition metal complexes and mercaptans from hydrocarbons, remove acids from non-polar solvents, and degrease phenol-acetone solutions. Amberlyst A26 is also used as an adsorbent in gas chromatography columns. The porous structure of the resin makes it a good polymer catalyst in non-aqueous and aqueous media; it has no pH restrictions. AB17-12P (analog of Amberlyst A-26) are industrially produced in Russia.

Amberlite IRA-400 is a highly basic anion exchange resin for water purification. The resin practically does not emit organic substances. Therefore, it is used for the deionization of water, production of high-purity silicon dioxide by STC hydrolysis, deoxidation, removal of amino acids at high pH, and separation of kanamycin A and B. Amberlite IRA-400 in the form of chloride is used as a separation medium for thin-layer, paper, and LPL chromatography.

A feature of all anionites based on a polystyrene-co-divinyl benzene, to which amino groups are grafted, is relatively low temperature resistance. In our previous papers, we investigated the catalytic activity of a number of anionites in the trichlorosilane dismutation reaction [17,18]. It was experimentally established that at temperatures above 80 °C, the anionites began to lose their catalytic activity, and at 120 °C, they decomposed with the release of organic amines [16]. Since careful dehydration is required to prepare anionite for the role of a catalyst for the chlorosilane dismutation reaction, and heating to a temperature above 100 °C is impossible, azeotropic distillation from anionite was used for dehydration when boiling with toluene.

It was also found in Ref. [17] that the anionite called the "VNIIHT pilot sample", which is currently called VP-1AP or AN-251, showed high temperature resistance and did not lose its catalytic activity up to 230 °C. In this regard, the dehydration of this anionite is possible by heating up to 200 °C in an inert gas stream to a water concentration in the exhaust gas below 1 ppm.VP-1AP (AN-251) resin is a strongly basic quaternary ammonium macroporous anionite, a copolymer of 2-methyl-5-vinylpyridine and divinylbenzene, and is methylated by pyridine nitrogen (Figure 1).

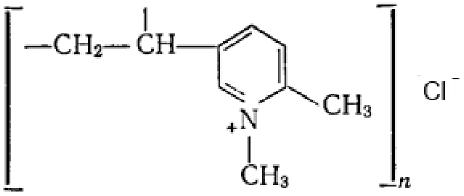

Figure 1. Structure of the active link of the VP-1AP anionite.

VP-1AP resin is supplied in a sulfate form, so its preparation was required before this study. To carry this out, the samples were treated with a 10% solution of sodium hydroxide for conversion to the OH form and then with a 10% solution of hydrochloric acid for conversion to the Cl form. After these operations, the resin was washed with distilled water to a neutral reaction and dehydrated by weekly calcination in a helium stream at 200 °C.

The catalytic effect of the AN-251 anion exchange resin is probably associated with the ability of a silicon atom to exhibit acceptor properties in compounds [19] with respect to donor atoms having undivided electron pairs (N, Cl, O, etc.). The acceptor properties allow the silicon atom in chlorosilane to receive an electron pair from the chlorine atom in the outer sphere of the anion exchange resin. As a result of the transition of the electron pair to the silicon atom, the covalent bonds in the chlorosilane molecule are weakened and the atoms in it acquire mobility. The scheme of the ionization of the silicon atom in the chlorosilane molecule on the example of trichlorosilane (TCS) is shown in Figure 2.

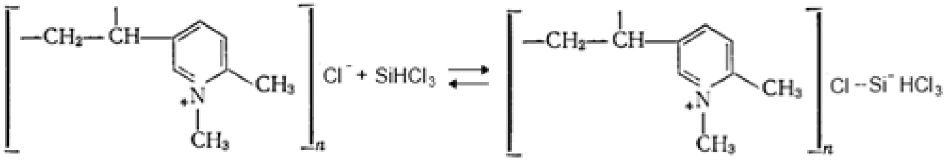

Figure 2. Scheme of electron pair transition from donor atom (Cl) to acceptor atom (Si).

The ionized silicon atom can transfer an electron pair to the hydrogen atom in the chlorosilane molecule with the likely appearance of a hydride anion, which can take the place of the chlorine anion in the outer sphere of the anion exchange resin. The scheme of the metabolic reaction is shown in Figure 3.

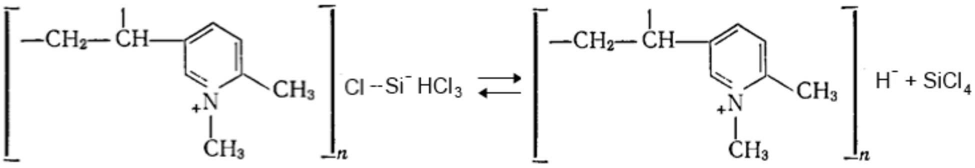

Figure 3. The scheme of the exchange reaction of the chlorine anion to the hydride anion in the outer sphere of the anion exchange resin.

Then, the anion exchange resin with the hydride anion in the outer sphere interacts with the chlorosilane molecule according to a similar ion exchange scheme. As a result, the anion exchange resin returns to its original form with the chlorine anion in the outer sphere, and the chlorosilane passes into a more hydrogenated form. The general scheme of the process on the example of dichlorosilane (DCS) synthesis is presented in Figure 4.

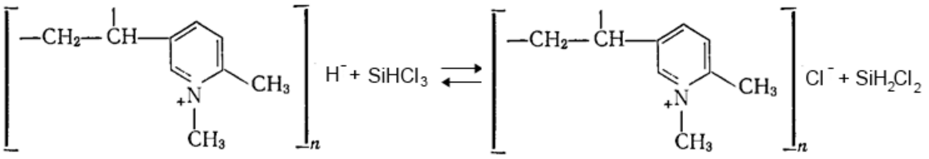

Figure 4. General scheme of the synthesis of DCS when the anion exchange resin interacts with the hydride anion in the outer sphere with TCS.

Similar schemes for the catalytic action of Amberlyst A21 and A-26 anion exchange resins are presented in [20].

It should be noted that the catalytic activity of AN-251 is practically independent of the total exchange capacity of the anion exchange resin but is significantly associated with the pore structure. Thus, in [16], it was found that the highest catalytic activity is observed in anion exchange resins with a macroporous structure.

The kinetics of the chlorosilane dismutation reaction on this anionite over a wide temperature range was investigated in our previous study [18]. It has been established that anionite is not inferior to catalysts known from the literature in terms of activity in chlorosilane dismutation reactions. It is also shown that an increase in the reaction temperature does not significantly affect the kinetics of catalytic dismutation since the activation energy is low and probably associated with adsorption–desorption processes.

It remains that researchers should consider the effect of increased pressure on the kinetics of catalytic dismutation of chlorosilanes in the vapor phase. In addition, a dependence of the saturated vapor pressure of DCS and MCS on the temperature, which is necessary for conducting and processing the results of experiments to study the kinetics of chlorosilane dismutation at elevated pressure, has not been found in the literature. These dependencies have also been determined experimentally.

2. Experimental Procedure

The installation diagram for determining the dependence of saturated steam pressure on temperature is shown in Figure 5.

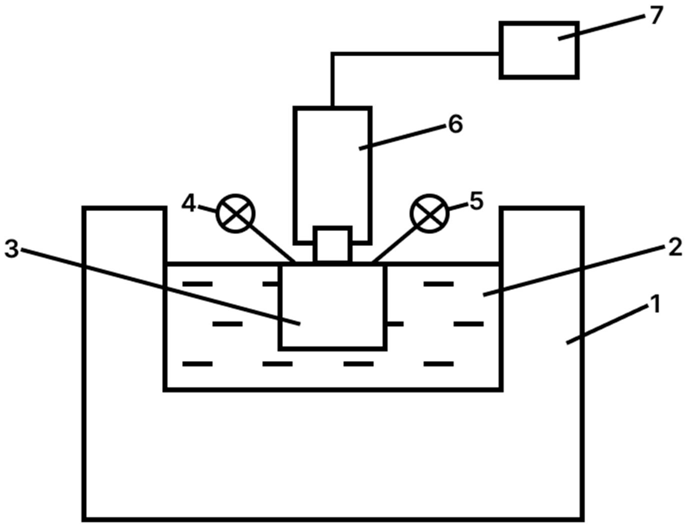

Figure 5. Installation for determining the dependence of the saturated vapor pressure of chlorosilanes on temperature. 1—liquid thermostat; 2—coolant; 3—stainless-steel measuring cell of original design; 4, 5—needle-shaped valves made of stainless steel; 6—diaphragm pressure sensor; 7—pressure sensor electronic control unit.

A thermostat HLM-2005W (HuXi) (Shanghai Huxi Industry Co., Shanghai, China) with an operating temperature range from minus 20 up to 100 °C and an absolute error of temperature control of ±0.1° was used.

A coolant Termolan D based on ethylene glycol manufactured by research and production company "POLYESTER" (RF) with an operating temperature range from minus 65 up to 195 °C was used.

A diaphragm pressure sensor with an electronic control unit PD-I-45 manufactured by PJSC Steklopribor (Ufa, Russia) had an operating measurement range from minus 0.1 up to 60 MPa with a relative error of the measurement result of 0.005.

To conduct the experiment, cell 3 was vacuumized to a residual pressure of 1.3×10^{-5} bar through a tap 5, and a chlorosilane subsample was loaded through a tap 4. After that, thermostat 1 was turned on, and the cell temperature was stabilized using a thermostat. Equilibrium was considered to be established when the pressure sensor readings did not exceed the measurement error of the device.

Studies were carried out for DCS in the temperature range from 0 to 100 °C and for MCS from minus 20 to 50 °C.

In the experiments, DCS (4N) and MCS (3N) manufactured by LLC "HORST" were used.

As established earlier, the most rational operating temperature of the catalyst (VP-1AP resin) is 100 °C. Therefore, the influence of pressure in the range of 1–6 bar on the rate of chlorosilane dismutation was studied at this temperature. The pressure range was chosen to exclude TCS condensation on the catalyst at 100 °C.

This study was carried out on the installation, the scheme of which is shown in Figure 6.

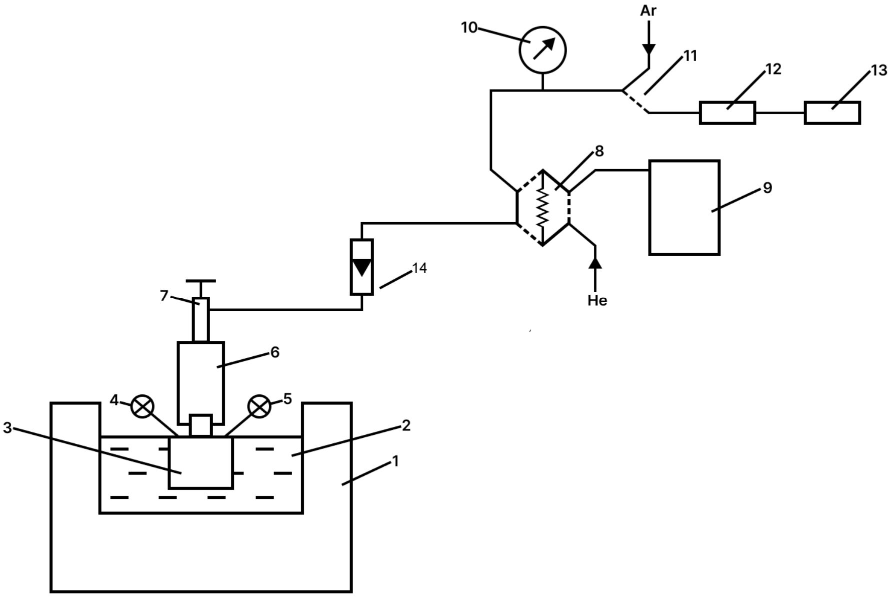

Figure 6. Installation for carrying out the dismutation reaction of chlorosilanes at elevated pressure. 1—liquid thermostat; 2—coolant; 3—measuring cell; 4, 5—taps; 6—reactor thermostat with a catalyst; 7—fine adjustment valve; 8—six-port sampling valve; 9—gas chromatograph; 10—vacuum gauge; 11—three-port valve; 12—pressure stabilizer "up to itself" 44-2300 TESCOM™ (Moscow, Russia); 13—vacuum pump; 14—rotameter.

The installation used a fine adjustment valve, a six- and three-port valve, as well as a Chromos GC-1000 gas chromatograph manufactured by Chromos Engineering (Dzerzhinsk, Russia); a 2NVR-5DG plate-rotor vacuum pump manufactured by JSC Vacuummash (Kazan, Russia); a vacuum meter VP4A-Uf "Phystech" (Tomsk, Russia); RMF production rotameter "Teplopribor" (Chelyabinsk, Russia); and the VP-1AP catalyst manufactured by JSC VNIIHT (Moscow, Russia).

The kinetics of the dismutation reaction at an elevated pressure was studied in the flow. To carry this out, chlorosilane was loaded into the cell, the temperature of the reactor thermostat was set to 100 °C, and the temperature of the liquid thermostat was set to ensure a set pressure in the cell. The rest of the installation, including the metering valve in the "sampling" mode, was pumped to a pressure of 0.2 bar before the fine adjustment valve 7 by using a pressure stabilizer 12. The pressure was chosen to exclude condensation at room temperature of the products of the dismutation reaction in the system after valve 7. Then, by opening valve 7, the required flow rate of chlorosilanes was set using rotameter 14 to ensure a predetermined time of the contact of chlorosilanes with the catalyst. The method for calculating the contact time of chlorosilane with the catalyst was described in [19], and the relative error in calculating the contact time was 10%. After the stabilization of the chlorosilane flow rate through the catalyst, the mixture was sampled after dismutation for chromatographic analysis by transferring the dispenser tap from the "sampling" position to the "analysis" position. The result was considered reliable when the deviation of the three concentration measurement results did not exceed the relative error of the analysis, which was 5%. The conditions of gas chromatographic analysis are described in [16,21].

3. Results and Discussion

Table 1 shows the results of the experimental measurement of saturated DCS and MCS steam pressure from temperature.

Table 1. The pressure of DCS and MCS saturated steam at different temperatures.

DCS		MCS	
T, K	**P, bar**	**T, K**	**P, bar**
273	0.81	253	1.43
283	1.15	263	1.99
293	1.60	273	2.71
303	2.18	283	3.61
313	2.90	293	4.71
323	3.80	303	6.03
333	4.90	313	7.62
343	6.22	323	9.47
353	7.79	---	---
363	9.64	---	---
373	11.79	---	---

The data in Table 1 are given with a relative error of 0.5%.

The obtained results were processed by linear regression in the Arrhenius plot. As a result, the following dependencies of saturated steam pressure on temperature were obtained:

$$\ln(P) = 9.783 - 2728.7/T \quad (4)$$

for DCS and

$$\ln(P) = 9.077 - 2205.6/T \quad (5)$$

for MCS, where P—saturated vapor pressure, bar; T—temperature, K.

Using the presented equations, the enthalpy of DCS and MCS evaporation was calculated, which turned out to be 22.68 ± 0.11 kJ/mol and 18.33 ± 0.08 kJ/mol, respectively.

It should be noted that the obtained data are in good agreement with the NIST data on the normal boiling point and enthalpy of DCS vaporization (281.3 K and 22.2 ± 0.7 kJ/mol, respectively), and similar data for MCS are in good agreement with the data of the handbook [22] (242.95 K and 15.899–20.083 kJ/mol, respectively).

To work with TCS, the equation of the dependence of the saturated vapor pressure on temperature, presented in NIST, was used:

$$\log10(P) = 4.21609 - (1170/(T - 27)), \quad (6)$$

where P—the vapor pressure (bar); T—the temperature (K).

To study the effect of pressure on the kinetics of the chlorosilane dismutation reaction, experiments were conducted to determine the dependence of the composition of the reaction mixture on the contact time of chlorosilane with the catalyst τ at different pressure levels. The experimental results are presented in Table 2.

Table 2. The concentrations of the components in the reaction mixture at different contact times of TCS, DCS, and MCS with the catalyst at a reactor pressure from 1 to 6 bar and a catalyst temperature of 100 °C.

TCS dismutation kinetics 1 bar total pressure					
τ (s)	**Mole Fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.00000	0.000347	0.0459	0.878	0.0466
1	0.000027	0.00110	0.0729	0.822	0.0752
1.75	0.000089	0.00190	0.0900	0.785	0.0941
2.5	0.000126	0.00223	0.0955	0.773	0.100
3	0.000136	0.00231	0.0968	0.770	0.102
4	0.000135	0.00230	0.0968	0.768	0.104
TCS dismutation kinetics 2 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.000025	0.00108	0.0717	0.809	0.0740
0.8	0.000076	0.00176	0.0866	0.777	0.0904
1	0.000110	0.00201	0.0911	0.767	0.0954
1.3	0.000126	0.00221	0.0942	0.760	0.0990
1.5	0.000134	0.00227	0.0952	0.758	0.100
2	0.000134	0.00227	0.0952	0.758	0.100
2.5	0.000145	0.00238	0.0977	0.768	0.103
3.5	0.000144	0.00239	0.0978	0.767	0.103
TCS dismutation kinetics 3 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.000067	0.00165	0.0836	0.768	0.0871
0.7	0.000089	0.00188	0.0878	0.759	0.0919
0.8	0.000113	0.00209	0.0913	0.751	0.0958
1	0.000126	0.00219	0.0930	0.747	0.0978
2	0.000128	0.00220	0.0928	0.746	0.0980
TCS dismutation kinetics 4 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.000110	0.00196	0.0882	0.742	0.0924
0.7	0.000116	0.00210	0.0905	0.737	0.0950
0.9	0.000126	0.00218	0.0917	0.734	0.0965
2	0.000125	0.00216	0.0918	0.735	0.0964
TCS dismutation kinetics 5 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.000134	0.00220	0.0905	0.710	0.0954
1	0.000135	0.00221	0.0904	0.711	0.0953
TCS dismutation kinetics 6 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.000132	0.00216	0.0890	0.700	0.0938
1	0.000130	0.00217	0.0891	0.699	0.0937

Table 2. *Cont.*

DCS dismutation kinetics 1 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0840	0.126	0.468	0.291	0.00184
0.6	0.0866	0.127	0.460	0.295	0.00219
0.7	0.0882	0.127	0.455	0.298	0.00251
2	0.0881	0.128	0.456	0.298	0.00252

DCS dismutation kinetics 2 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0891	0.125	0.441	0.296	0.00340
1	0.0890	0.125	0.440	0.297	0.00341

DCS dismutation kinetics 3 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0894	0.125	0.442	0.298	0.00342
1	0.0893	0.126	0.442	0.298	0.00341

DCS dismutation kinetics 4 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0866	0.122	0.429	0.289	0.00331
1	0.0866	0.122	0.429	0.288	0.00332

DCS dismutation kinetics 5 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0867	0.121	0.429	0.289	0.00332
1	0.0867	0.122	0.430	0.289	0.00332

DCS dismutation kinetics 6 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.0853	0.121	0.422	0.284	0.00327
1	0.0854	0.120	0.423	0.284	0.00326

MCS dismutation kinetics 1 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.413	0.213	0.275	0.0682	0.000290
1	0.413	0.214	0.276	0.0682	0.000288

MCS dismutation kinetics 2 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.413	0.213	0.276	0.0682	0.000288
1	0.413	0.214	0.276	0.0682	0.000290

MCS dismutation kinetics 3 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.408	0.211	0.272	0.0673	0.000284
1	0.407	0.211	0.273	0.0673	0.000285

Table 2. *Cont.*

MCS dismutation kinetics 4 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.409	0.211	0.273	0.0674	0.000285
1	0.408	0.211	0.273	0.0674	0.000286
MCS dismutation kinetics 5 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.402	0.208	0.268	0.0664	0.000280
1	0.402	0.208	0.269	0.0664	0.000281
MCS dismutation kinetics 6 bar total pressure					
τ (s)	**Mole fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
0.5	0.396	0.204	0.264	0.0653	0.000277
1	0.396	0.205	0.265	0.0654	0.000276

From the data presented in Table 2, it can be seen that the molar fractions of the components in the reaction mixture, which is in a close to equilibrium state, within the measurement error, are weakly dependent on pressure. It indicates a weak dependence of equilibrium concentrations on pressure, which is typical for reactions that proceed without changing the number of moles. On the other hand, the pressure increase significantly reduces the contact time with the catalyst required to achieve equilibrium. It indicates the beneficial effect of pressure on the kinetics of chlorosilane dismutation reactions.

Also, using the data of Table 2, the kinetic curves of the TCS dismutation reaction at a pressure in the reactor in the range of 1–4 bar were determined.

The kinetic curves are presented in Figures 7–10.

The reaction rates at different pressures in the reactor were calculated from the initial section of the kinetic curve. The reaction rate vs. pressure plot shown in Figure 11 was then plotted.

It can be seen from the figure that the reaction rate increases by almost an order of magnitude with a fourfold increase in pressure.

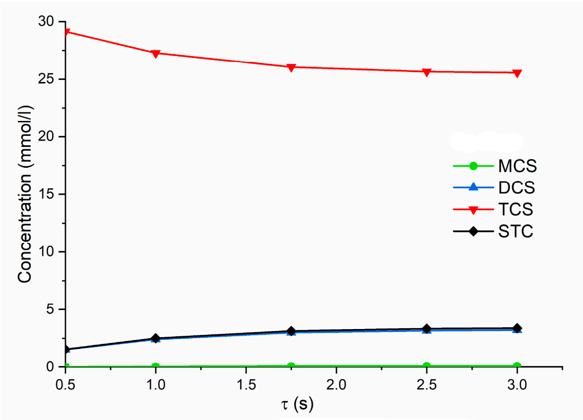

Figure 7. Kinetic curves of the TCS dismutation reaction at a pressure of 1 bar in the reactor.

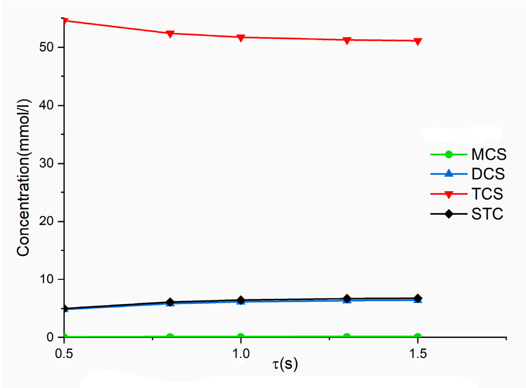

Figure 8. Kinetic curves of the TCS dismutation reaction at a pressure of 2 bar in the reactor.

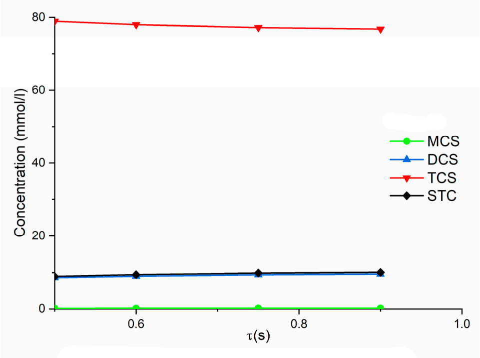

Figure 9. Kinetic curves of the TCS dismutation reaction at a pressure of 3 bar in the reactor.

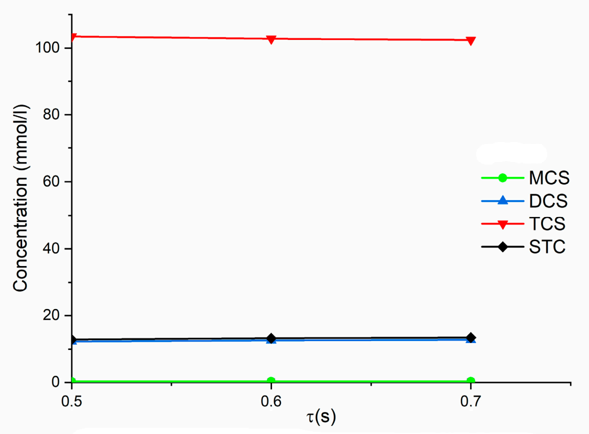

Figure 10. Kinetic curves of the TCS dismutation reaction at a pressure of 4 bar in the reactor.

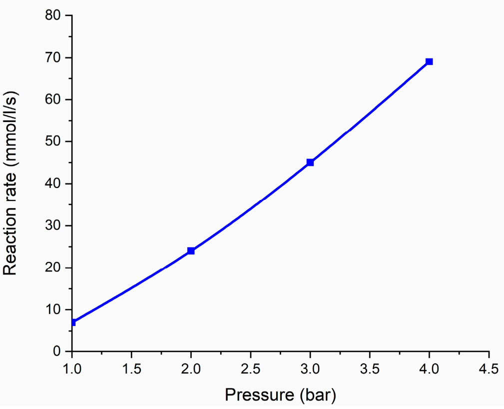

Figure 11. The dependence of the rate of the TCS dismutation reaction on the pressure in the reactor.

To estimate the specific productivity per unit volume of the reactor for the catalytic dismutation of chlorosilanes, it is advisable to switch from molar fractions to molar concentration. Since the dismutation process was experimentally investigated at an increased pressure, the effect of steam imperfection on the molar volume of the reaction mixture was taken into account when recalculating the concentration. In [21], it was found that the deviation from the ideal vapor of chlorosilanes at elevated pressure is well described by the Redlich–Kwong equation.

To estimate vapor nonideality, the original Redlich–Kwong equation was used, and the critical properties of DCS and MCS were calculated using the Lidersen group component method. It was established that with an increase in pressure above 3 bar, the deviation from the ideal vapor of chlorosilanes becomes comparable to the error of gas chromatographic analysis. Therefore, neglecting this effect in the calculation of molar concentrations introduces a significant error in the calculation result.

The results of calculating the molar concentration in a reaction mixture close to equilibrium, within the measurement error, during the dismutation of TCS, DCS, and MCS are presented in Tables 3–5.

Table 3. The equilibrium molar concentrations of the products of the TCS dismutation reaction at various pressures and the contact time with the catalyst sufficient to achieve an equilibrium state.

Molar Concentration (mmol/L)						
Total Pressure, bar	**Mole Fraction**					
	S	**MCS**	**DCS**	**TCS**	**STC**	**τ (s)**
1	0.00481	0.0791	3.25	25.5	3.42	3
2	0.00963	0.158	6.49	51.0	6.84	2.5
3	0.0145	0.238	9.77	76.7	10.3	1
4	0.0194	0.318	13.1	103	13.7	0.9
5	0.0242	0.398	16.3	128	17.2	0.5
6	0.0291	0.478	19.6	154	20.6	-

Table 4. The equilibrium molar concentrations of the products of DCS dismutation reaction at different pressures.

Total Pressure, bar	**Mole Fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
1	3.01	4.23	14.9	10.0	0.115
2	6.01	8.46	29.8	20.0	0.230
3	9.05	12.7	44.8	30.1	0.346
4	12.1	17.0	59.8	40.2	0.462
5	15.1	21.3	74.8	50.4	0.579
6	18.2	25.6	89.9	60.5	0.695

Table 5. Equilibrium molar concentrations of the products of the MCS dismutation reaction at different pressures.

Total Pressure, bar	**Mole Fraction**				
	S	**MCS**	**DCS**	**TCS**	**STC**
1	13.7	7.10	9.16	2.26	0.00955
2	27.4	14.2	18.3	4.53	0.0191
3	41.3	21.3	27.6	6.81	0.0288
4	55.1	28.5	36.8	9.10	0.0384
5	69.0	35.7	46.1	11.4	0.0481
6	82.8	42.8	55.3	13.7	0.0577

It was possible to evaluate the effect of pressure on the contact time of chlorosilanes with the catalyst during the experiment only for TCS. It can be assumed that for DCS and

MCS, the tendency will persist, and the contact time required to achieve an equilibrium state will decrease with increasing pressure.

From the data presented in Tables 3–5, it can be seen that the concentration of all components in the reaction mixture increases almost proportionally to the pressure, which indicates the immutability of the mechanism of the dismutation reaction in chlorosilanes with increasing pressure. The combination of an almost multiple pressure increase in the concentration of components in the reaction mixture with a decrease in contact time, as can be seen from Table 3 at six atmospheres, makes it possible to increase the specific productivity of the reactor [mol/(L·s)] with the dismutation of trichlorosilane by at least an order of magnitude.

4. Conclusions

As a result of this study on the kinetics of the chlorosilane dismutation reaction on the heat-resistant AN-251 catalyst, it was found that, despite the insignificant effect of temperature on the reaction rate, an increase in temperature provided an opportunity to increase the pressure in the reaction zone without the condensation of chlorosilane vapors. Thus, increasing the temperature of the catalyst to 100 °C allows for the increase in the pressure of chlorosilanes in the reactor to six atmospheres.

Using the example of TCS, it was experimentally established that increasing the pressure to six atmospheres makes it possible to increase the specific productivity of the reactor by at least an order of magnitude due to the acceleration of the chemical reaction and the increase in the molar concentration of chlorosilanes in the vapor mixture. Consequently, it becomes possible to multiply the reactor's load on the substance and, accordingly, the performance of the chlorosilane dismutation apparatus in general.

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Informed Consent Statement: Informed consent was obtained from all subjects involved in the study. Written informed consent has been obtained from the patients to publish this paper.

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