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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Thermal Chlorination of Methyltrichlorosilane

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Abstract—The procedure for thermal chlorination of methyltrichlorosilane to chloromethyltrichlorosilane in a circulation flow system was developed. The yield of $ClCH_2SiCl_3$ was studied as influenced by the reaction temperature and the reactant ratio.

Chloromethyltrichlorosilane, $ClCH_2SiCl_3$ (CMTS), is a valuable reagent for preparing carbofunctional organosilicon monomers and polymers (surface-modifying and cross-linking agents, adhesion promoters, immobilized catalysts, etc. [1–6]) and is used in synthesis of sorbents, ion exchangers, and bioprotecting coatings. This compound is also a precursor of widely used biostimulant, 1-(chloromethyl)silatrane (Mival) [7, 8]. Chloromethyltrichlorosilane is usually prepared by free-radical chlorination of methyltrichlorosilane (MTS) with gaseous chlorine:

$$Cl_2 + CH_3SiCl_3 \rightarrow ClCH_2SiCl_3 + HCl.$$

The reaction is performed either in the vapor phase on exposure to UV [9, 10] or visible [11] radiation or in a solution in the dark in the presence of azobis(isobutyronitrile) as the initiator [9, 10]. It should be noted that, since chlorination of mono- and dichloromethyltrichlorosilanes ($ClCH_2SiCl_3$ and $Cl_2CHSiCl_3$) is considerably faster than that of the initial MTS, the monochloro derivative is prepared at its continuous removal form the reaction mixture or at a large excess of MTS. The first procedure is based on photochemical chlorination of $MeSiCl_3$ vapor with gaseous chlorine on exposure to UV [9, 10] or visible light [9].

Large-scale photochemical chlorination of MTS is complicated by the lack of industrial reactors containing parts made form optical quartz and by the need for intermittent removal of the polymeric film absorbing UV–Vis radiation from the surface of the transparent window or from the built-in light sources. It is difficult to construct powerful photochemical reactors since the light intensity decreases proportionally to the square of the distance form the light source. In some cases the photochemical reaction can be accompanied by spontaneous combustion or explosion of a mixture of gaseous reactants [10]. The industrial process of dark chlorination of MTS in the presence of asobis(isobutyronitrile) is performed in a distillation column under inversion conditions (the temperature in the reaction zone and in the still is 64 and 110°C, respectively) [12]. The CMTS yield based on the spent $MeSiCl_3$ is 75%. In this case the steady-state inversion conditions in the upper part of the column and the working temperature in the reaction zone are difficult to maintain, and large amount of the expensive initiator and large excess of $MeSiCl_3$ are required. In addition, $Cl_2CHSiCl_3$ and Cl_3CSiCl_3 are formed in considerable amounts, i.e., the selectivity of the process is low.

Another procedure for preparing CMTS is based on photochemical chlorination of $MeSiCl_3$ with sulfuryl chloride [13, 14]:

$$SO_2Cl_2 + CH_3SiCl_3 \xrightarrow{h\nu} SO_2 + ClCH_2SiCl_3 + HCl.$$

This reaction is catalyzed by yttrium chloride, lanthanum chloride, and manganese chloride [14]. Although this procedure does not require complex equipment, it is more expensive as compared to the chlorination with gaseous chlorine.

We developed a new procedure for preparing CMTS by chlorination of $MeSiCl_3$ with gaseous chlorine at 300–400°C in a circulation system.

This reaction occurs by the radical mechanism similar to that of thermal chlorination of alkanes [15]. The chain propagation involves formation of Cl and CH_2SiCl_3 radicals:

$$Cl_2 \xrightarrow{300\text{–}400°C} 2Cl^{\cdot},$$

$$Cl^{\cdot} + CH_3SiCl_3 \rightarrow CH_2SiCl_3 + HCl,$$

$$Cl_2 + {}^{\cdot}CH_2SiCl_3 \rightarrow ClCH_2SiCl_3 + Cl^{\cdot}.$$

Yield of $ClCH_2SiCl_3$ as influenced by the conditions of thermal chlorination of $MeSiCl_3$.

$T_{reactor}$, °C	Feed rate of $MeSiCl_3$, g h^{-1}	Flow rate of Cl_2, l h^{-1}	$MeSiCl_3 : Cl_2$, mol : mol	τ, h	CMTS yield, %	α,* %
350	829.4	1.18	105 : 1	12	82.2 (42)**	51.1
300	222.7	1.27	26 : 1	12	72.3 (35)	48.4
350	576.0	2.42	36 : 1	6	77.7 (38.5)	49.5
400	783.3	2.63	45 : 1	6	76.3 (40.6)	53.2
450	852.5	1.66	77 : 1	12	66.7 (40.2)	60.3
500	844.8	3.18	40 : 1	6	62.5 (35.2)	56.3
300	238.1	1.20	30 : 1	12	77.0 (37.8)	49.0
250	162.8	0.22	111 : 1	20	85.9 (7.7)	9

* α is the MTS conversion.

** Yield of CMTS based on reacted and initial (in parentheses) MTS.

It is known that the rate constants and activation energies of radical-chain consecutive chlorination reactions yielding mono-, di-, and trichloro derivatives are almost the same [15]. Hence, for CMTS to be selectively formed, large excess of MTS with respect to chlorine should be used and CMTS being formed should be removed from the reaction mixture.

The chlorination was performed at $MeSiCl_3 : Cl_2$ ~100 : 1 (see table). At 350°C the selectivity of the process (the CMTS yield based on consumed MTS) was higher than 82% and the MTS conversion in 12 h was 51%. With a larger MTS excess, the output of CMTS is lower. At $MeSiCl_3 : Cl_2$ = 25 : 1 49.5% of MTS is converted within 6 h; however the selectivity decreases to 77%. Thus, taking into account the output of the reactor and the process selectivity, the $MeSiCl_3 : Cl_2$ molar ratio can be varied from 25 : 1 to 100 : 1 depending on the technical and economical requirements.

The temperature influence on the MTS chlorination is similar to that of alkane chlorination. With increasing temperature the reaction is accelerated, and its selectivity decreases. In addition, at 500°C the reactor nozzle is strongly clogged with coke.

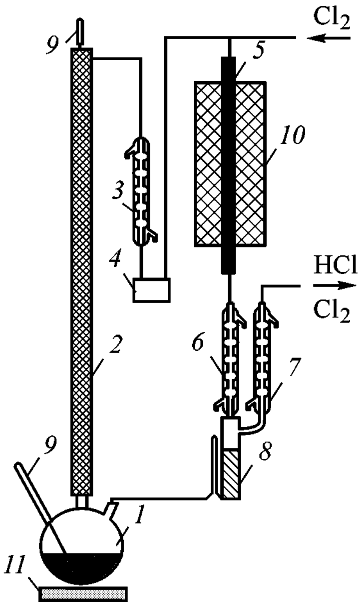
At the same time the process occurs even at 250°C. However, in this case, despite high selectivity (the CMTS yield based on consumed MTS is 86%), a 9% conversion of MTS is reached only in 20 h.

Thus, as seen from the table, the best reaction temperature is 350–400°C.

EXPERIMENTAL

Methyltrichlorosilane was chlorinated on a circulation unit (see figure). The unit consists of a 0.5-l heated flask (*1*), connected through a packed column (*2*) and a condenser with a dosing apparatus and then with an electrically heated flow reactor. The reactor is connected with two condensers (straight-run *6* and reflux *7*). The condensate formed in the first condenser goes in the accumulator with a siphon and then back in the flask. Gaseous HCl and unchanged Cl_2 pass to the absorbers through the reflux condenser. The reactor is a quartz tube 12.5 mm in diameter and 250 mm long, packed with quartz chips.

An MTS vapor formed in the flask passes through the packed column, is condensed in the condenser, and is fed into the dosing apparatus form which it is fed with a controlled rate to the reactor heated to



Scheme of the unit for gas-phase thermal chlorination of methyltrichlorosilane: (*1*) 0.5-l flask, (*2*) packed column, (*3, 6, 7*) condensers, (*4*) dosing pump, (*5*) reactor, (*8*) condensate accumulator, (*9*) thermometer, (*10*) tubular furnace, and (*11*) electric heater.

300 – 400°C. Chlorine is fed simultaneously form a cylinder. The flow rate of chlorine is measured with a rheometer. The flask temperature in the first and final steps of the process is 65 and 105°C, respectively. The temperature of the column head is about 65°C. The $MeSiCl_3 : Cl_2$ molar ratio at the outlet of the reactor was maintained constant.

An example of the CMTS synthesis is presented below. Methyltrichlorosilane (149.5 g, 1 mol) is placed in the still of the packed column and is heated to boil. When the temperature of the top of the column reaches 65°C, MTS condensate formed in the condenser is fed into the dosing apparatus and then with a 830 g h^{-1} (5.55 mol h^{-1}) flow rate into the reactor heated to 350°C. Simultaneously gaseous chlorine is fed with a 1.18 l h^{-1} (0.0526 mol h^{-1}) flow rate into the reactor. The $MeSiCl_3 : Cl_2$ molar ratio is 105 : 1. The process lasts for 12 h. In this period 14.2 l (0.63 mol) of chlorine is passed through the system. Fractionation of the bottoms on a 20-TP column yields the initial MTS (73.1, 0.49 mol) with bp 65– 66°C (720 mm Hg) and CMTS (77.3 g, 0.42 mol) with bp 117–119°C (720 mm Hg), n_D^{20} = 1.4530, d_4^{20} = 1.4420, and a 99.7% purity determined by GLC {published data [14]: bp 118–120°C (760 mm Hg), n_D^{20} = 1.4530}.

Found (%): C 6.56, H 1.03, Cl 77.00, Si 15.07,
6.25, 1.12, 76.91, 15.14.
CH_2Cl_4Si.
Calculated (%): C 6.53, H 1.10, Cl 77.10, Si 15.27.

The CMTS yield based on the initial $MeSiCl_3$ and spent MTS is 82.2 and 42%, respectively. The MTS conversion is 51.1%.

The weight of the remaining bottoms is 10.2 g. As determined by GLC, the bottoms contain 31% $Cl_2CHSiCl_3$ and 69% Cl_3CSiCl_3. $Cl_2CHSiCl_3$ (2.6 g, 0.012 mol) was isolated by fractionation of the bottoms; bp 141–142°C (720 mm Hg), 99.3% purity determined by GLC, n_D^{20} = 1.4715, d_4^{20} = 1.5503 {published data [14]: bp 144°C (760 mm Hg), n_D^{20} = 1.4715}.

Found (%): C 5.40, H 0.41, Cl 81.27, Si 12.32,
5.44, 0.53, 81.21, 13.05.
CH_2Cl_5Si.
Calculated (%): C 5.50, H 0.46, Cl 81.18. Si 12.86.

The purity of the chlorine-containing products was determined by GLC on an LKhM-80 chromatograph equipped with a catharometer. Helium was the carrier gas. A 3000 × 3 mm steel column was packed with 3% OV-17 on Inerton Super (0.160 – 0.200 mm). The column was heated form 40 to 180°C at a rate of 4 deg min^{-1}.

The ^1H NMR spectra were recorded at 25°C on a Tesla 480 C spectrometer operating at 80 MHz, with TMS as the internal reference. The spectra of $ClCH_2SiCl_3$ and $Cl_2CHSiCl_3$ contain only one singlet at 3.24 and 5.44 ppm, respectively. The chemical shifts agree with the published data [14].

The ^{35}Cl NQR spectrum of $ClCH_2SiCl_3$ recorded on an IS-3 spectrometer contains the following signals, ν^{77}, MHz : 36.77 ($ClCH_2$); 19.555, 19.470 ($SiCl_3$) (cf. [16]).

CONCLUSION

Thermal chlorination of methyltrichlorosilane with elemental chlorine in the gas phase at 300 – 400°C yields chloromethylchlorosilane in a 63–82% yield based on reacted $MeSiCl_3$.

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