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Reaction of Carboxylic Acids with Tetrachlorosilane

M. G. Voronkov, A. V. Vlasov, L. I. Belousova, O. Yu. Grigor'eva, and N. N. Vlasova

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences,
ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: natnicvlasova@irioch.irk.ru

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Abstract—Tetrachlorosilane reacted with carboxylic acids RCOOH (R = Me, Bu, *t*-Bu) to give the corresponding acid chlorides RCOCl in 75–95% yield. The reactions of $SiCl_4$ with trichloroacetic and 2-fluorobenzoic acids (R = Cl_3C, 2-FC_6H_4) occurred more difficultly, presumably for steric reasons, and the yields of the corresponding acid chlorides were 11 and 22%, respectively. Tetrachlorosilane failed to react with stearic acid under analogous conditions. Products of the reactions of $SiCl_4$ with chloroacetic and benzoic acids RCOOH (R = $ClCH_2$, Ph) were tetraacyloxysilanes $Si(OCOR)_4$, and tetrakis(chloroacetoxy)silane was formed in almost quantitative yield. The reaction of $SiCl_4$ with glutaric acid led to the formation of a rubber-like polymeric material with the composition $C_5H_6Cl_2O_4Si$. The effect of pK_a values of carboxylic acids on the direction and mechanism of the examined reaction is discussed.

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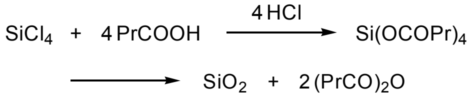
Carboxylic acid chlorides RCOCl constitute an important class of organic compounds which attract much interest as intermediate products in organic synthesis [1, 2]. The simplest procedure for the preparation of acyl chlorides is based on reaction of carboxylic acids with thionyl chloride ($SOCl_2$) or phosphorus chlorides (PCl_5, $POCl_3$, PCl_3) [3]. We set ourselves the task of replacing fairly expensive reagents for the transformation of carboxylic acid moiety into acid chloride by cheap tetrachlorosilane. In the recent time silicon tetrachloride has become a large-scale product in organosilicon industry and manufacture of semiconductor silicon.

The possibility for synthesizing carboxylic acid chlorides by reaction of carboxylic acids with $SiCl_4$ was noted in the first half of the XXth century [4–6]. Andreanov and Dolgopolov [7] proposed a procedure for large-scale preparation of benzoyl chloride from $SiCl_4$ and benzoic acid. Petrov et al. [8] reported that butyric acid reacted with excess tetrachlorosilane to produce up to 81% of butyryl chloride. If excess butyric acid was used, the major product was butyric anhydride (yield 80%). Later on, intermediate product in this reaction was isolated: it was tetrakis(butyryloxy)silane $Si(OCOPr)_4$ which underwent quantitative thermal decomposition into silicon dioxide and butyric anhydride [9] (Scheme 1). Labile tetrakis(formyloxy)silane was synthesized in a similar way [10].

Scheme 1.



$$SiCl_4 + 4PrCOOH \xrightarrow{4HCl} Si(OCOPr)_4 \longrightarrow SiO_2 + 2(PrCO)_2O$$

In the present work we examined reactions of tetrachlorosilane with acetic, chloroacetic, trichloroacetic, valeric, pivalic, benzoic, 2-fluorobenzoic, stearic, and glutaric acids. The goal of this study was not only to develop a simple and convenient procedure for the preparation of acyl chlorides (as precursors of acyl iodides that are the subjects of our systematic studies) but also to reveal how the reactant ratio and dissociation constants K_a of the acids affect their reaction with $SiCl_4$. The reactions were carried out under solvent-free conditions by heating the reactants, $SiCl_4$ and RCOOH, at a molar ratio of 2 : 1 at 50–70°C until hydrogen chloride no longer evolved (4–10 h). The reaction conditions and yields of the corresponding acyl chlorides are given in table.

For comparison, the reactions of $SiCl_4$ with carboxylic acids RCOOH (R = Et, Pr, *i*-Pr) in xylene were

Scheme 2.

$$SiCl_4 + 2RCOOH \longrightarrow 2RCOCl + SiO_2 + 2HCl$$

R = Me, Cl_3C, Bu, *t*-Bu, 2-FC_6H_4.

reported to produce 49–51% of the corresponding acid chlorides [5]. Our results (see table) indicated that the reactions followed Scheme 2.

The reaction of tetrachlorosilane with chloroacetic acid gave only stable tetra(chloroacetoxy)silane whose yield attained 98% at a $SiCl_4$–$ClCH_2COOH$ ratio of 1:4 (Scheme 3).

Scheme 3.

$$SiCl_4 + 4\,ClCH_2COOH \longrightarrow Si(OCOCH_2Cl)_4 + 4\,HCl$$

Benzoyl chloride was obtained in a high yield when the molar ratio $SiCl_4$–PhCOOH was 2:1 [7]. The reaction with excess benzoic acid (reactant ratio 1:2.5) gave tetrakis(benzoyloxy)silane as the major product (yield 65%). In addition, trichlorosilyl benzoate $PhCOOSiCl_3$ was formed as the first intermediate in the reaction of $SiCl_4$ with PhCOOH, which was not identified previously (Scheme 4).

Scheme 4.

$$SiCl_4 + 2.5\,PhCOOH \longrightarrow 0.5\,Si(OCOPh)_4 + 0.5\,PhCOOSiCl_3 + 2.5\,HCl$$

Neither acyloxy silanes $Si(OCOR)_4$ nor carboxylic acid anhydrides $(RCO)_2O$ were formed in the reactions of tetrachlorosilane with trichloroacetic and 2-fluorobenzoic acids. Here, the products were the corresponding acid chlorides, but their yields were poor (22 and 11%, respectively; see table; Scheme 5). Presumably, the reason is steric effect of bulky substituent in these acids. Likewise, no reaction occurred between $SiCl_4$ and stearic acid. On the whole, our experimental data suggest that the reaction of $SiCl_4$ with RCOOH can be regarded as a two-step process.

Scheme 5.

$$SiCl_4 + 4\,RCOOH \longrightarrow Si(OCOR)_4 + 4\,HCl$$
$$Si(OCOR)_4 + SiCl_4 \longrightarrow 4\,RCOCl + 2\,SiO_2$$

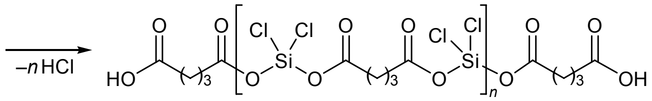
Reactions of carboxylic acids RCOOH with $SiCl_4$

R	Reaction time, h	pK_a	Yield of RCOCl, %
t-Bu	5	5.03	72
n-Bu	7	4.82	63
Me	10	4.75	95
Cl_3C	8	1.66	22
2-FC_6H_4	8	3.86	11

In the reaction of tetrachlorosilane with dibasic glutaric acid at a molar ratio of 2:1 we isolated only a rubber-like polymeric material with a composition of $C_5H_6Cl_2O_4Si$ (Scheme 6). The product was insoluble in water and organic solvents. In contrast, the reaction of $SiCl_4$ with sebacic acid was reported to afford monomeric dichloride $ClCO(CH_2)_8COCl$ in 37% yield [5]. According to the IR data, linear chains of the obtained polymer are terminated by carboxy groups: The IR spectrum contains a broad band in the region 3200–3400 cm^{-1} (OH) and a band at 1700 cm^{-1} (C=O).

Scheme 6.

$2n\,HOC(O)(CH_2)_3C(O)OH + n\,SiCl_4$



Presumably, the direction of the reactions of carboxylic acids with $SiCl_4$ is determined by their acidity. Such carboxylic acids RCOOH as acetic, valeric, pivalic, propionic, butyric, and isobutyric (R = Me, *n*-Bu, *t*-Bu, Et, Pr, *i*-Pr), whose pK_a values range from 4.75 to 5.03 log units may be regarded as weak acids, whereas chloroacetic acid is characterized by a pK_a value of 2.86. Therefore, chloroacetic acid more readily undergoes dissociation with formation of carboxylate ion, and its reaction with tetrachlorosilane stops at the stage of formation of tetrakis(chloroacetoxy)silane $Si(OCOCH_2Cl)_4$, The ionic Si–O bonds in the latter are fairly strong, and this compound does not decompose on heating into SiO_2 and $ClCH_2COCl$ according to Scheme 4. Increased strength of the Si–O bond is also intrinsic to tetrakis(benzoyloxy)silane generated from benzoic acid (pK_a 4.19), and benzoyl chloride is formed only in the presence of excess $SiCl_4$.

It is interesting that even stronger trichloroacetic acid (pK_a 1.66) and weaker 2-fluorobenzoic acid (pK_a 3.86) reacted with $SiCl_4$ fairly difficultly with formation of the corresponding acid chlorides. A probable reason is steric effect of bulky substituents in the acids. The same factor is likely to be responsible for the failure of tetrachlorosilane to react with stearic acid (pK_a 3.26) under analogous conditions. The formation of polymeric product in the reaction of $SiCl_4$ with glutaric acid (pK_a 4.34) may also be rationalized in terms of sterically hindered formation of primary mono- and bicyclic products.

Thus synthesis of carboxylic acid chlorides via reaction of the corresponding carboxylic acid with tetrachlorosilane may be recommended as preparative only for weak acids (pK_a < 4.7).

EXPERIMENTAL

The IR spectra were recorded from thin films on a UR-20 spectrometer.

Reaction of acetic acid with tetrachlorosilane. Tetrachlorosilane, 8.5 g (50 mmol), was slowly added to 6.0 g (100 mmol) of acetic acid, and the mixture was heated for 10 h at 50°C. The product was acetyl chloride, yield 7.4 g (95%), bp 50–51°C, n_D^{20} = 1.3890; published data [11]: bp 51.8°C, n_D^{20} = 1.3897. IR spectrum, ν, cm^{-1}: 1760 (C=O), 600 (C–Cl).

Reaction of chloroacetic acid with tetrachlorosilane. Tetrachlorosilane, 2.2 g (12.5 mmol), was added to 4.7 g (50 mmol) of chloroacetic acid, and the mixture was heated for 4 h at 50–55°C. We isolated 5.1 g (98%) of crystalline tetrakis(chloroacetoxy)silane, mp 153–154°C; published data [12]: mp 150°C. IR spectrum, ν, cm^{-1}: 1730 (C=O), 1190, 780 (Si–O–C), 630 (C–Cl).

Reaction of trichloroacetic acid with tetrachlorosilane. Tetrachlorosilane, 8.5 g (50 mmol), was added to a solution of 16.4 g (100 mmol) of trichloroacetic acid in 10 ml of hexane, and the mixture was stirred for 8 h at 50–55°C. We isolated 4.0 g (22%) of trichloroacetyl chloride, bp 118°C; published data [13]: bp 118–120°C. IR spectrum, ν, cm^{-1}: 1790 (C=O), 600 (C–Cl).

Reaction of valeric acid with tetrachlorosilane. Tetrachlorosilane, 17.0 g (100 mmol), was added to 20 g (200 mmol) of valeric acid, and the mixture was heated for 7 h at 50–55°C. We isolated 15.9 g (63%) of valeroyl chloride, bp 126–128°C, n_D^{20} = 1.4200; published data [11]: bp 128°C, n_D^{20} = 1.4207. IR spectrum, ν, cm^{-1}: 1790 (C=O), 600 (C–Cl).

Reaction of pivalic acid with tetrachlorosilane. Tetrachlorosilane, 12.8 g (75 mmol), was added to 15.3 g (150 mmol) of pivalic acid, and the mixture was heated for 5 h at 50–55°C. We isolated 13.0 g (72%) of pivaloyl chloride, bp 107°C, n_D^{20} = 1.4130; published data [14]: bp 108°C, n_D^{20} = 1.4139. IR spectrum, ν, cm^{-1}: 1820 (C=O), 600 (C–Cl).

Reaction of benzoic acid with tetrachlorosilane. Tetrachlorosilane, 6.8 g (40 mmol), was added to 12.2 g (100 mmol) of benzoic acid, and the mixture was heated for 7 h at 55–60°C. The mixture was cooled and distilled under reduced pressure to isolate 7.4 g (29%) of trichlorosilyl benzoate, bp 84°C (5 mm) [IR spectrum, ν, cm^{-1}: 1680 (C=O), 1280 (C–O), 920 (Si–O), 600 (Si–Cl). Found, %: C 32.42; H 2.06; Si 10.92. $C_7H_5Cl_3O_2Si$. Calculated, %: C 32.87; H 1.96; Si 10.95], and 8.3 g (65%) of amorphous tetrakis(benzoyloxy)silane, mp 125–126°C. IR spectrum, ν, cm^{-1}: 1680 (C=O), 1280 (C–O), 920 (Si–O). Found, %: C 65.47; H 5.20; Si 7.08. $C_{28}H_{20}O_8Si$. Calculated, %: C 65.62; H 5.20; Si 7.29.

Reaction of 2-fluorobenzoic acid with tetrachlorosilane. A mixture of 14 g (100 mmol) of 2-fluorobenzoic acid and 8.5 g (50 mmol) of tetrachlorosilane was heated for 8 h at 50–55°C. We isolated 1.8 g (11%) of 2-fluorobenzoyl chloride, bp 103°C (30 mm). IR spectrum, ν, cm^{-1}: 1800 (C=O), 610 (C–Cl). Found, %: C 52.59; H 3.12; Cl 22.24; F 11.97. C_7H_5ClFO. Calculated, %: C 52.66; H 3.13; Cl 22.25; F 11.91.

Reaction of glutaric acid with tetrachlorosilane. Tetrachlorosilane, 20.4 g (120 mmol), was slowly added to 8.0 g (60 mmol) of glutaric acid. Vigorous evolution of gaseous hydrogen chloride was observed (it was identified by qualitative test with $AgNO_3$). Unreacted tetrachlorosilane was removed from the reaction mixture by simple distillation. We isolated a polymeric product which decomposed at 300°C and was insoluble in water, diethyl ether, acetone, and chloroform. IR spectrum, ν, cm^{-1}: 1700 (C=O), 1050 (Si–O), 680 (Si–Cl). Found, %: C 28.10; H 3.01; Cl 28.93; Si 12.57. $C_5H_7Cl_2O_4Si$. Calculated, %: C 26.20; H 2.62; Cl 31.00; Si 12.22.

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